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**Semi-Continuous Emulsion Copolymerization of Styrene-Butyl Acrylate with Methacrylic Acid:
Structure-Property Relationship**

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**SEMI-CONTINUOUS EMULSION COPOLYMERIZATION
OF STYRENE –BUTYL ACRYLATE WITH
METHACRYLIC ACID: STRUCTURE-PROPERTY
RELATIONSHIP**

Hong Hua

A thesis submitted to the
Faculty of Graduate and Postdoctoral Studies
in fulfillment of the requirements
for the degree of Doctor of Philosophy
in
Chemical Engineering

**DEPARTMENT OF CHEMICAL AND BIOLOGICAL ENGINEERING
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Statement of Contributions of Collaborators

I hereby declare that I am the sole author of this thesis. The polymerization experiments, polymer characterizations and data analysis were performed by myself except for the acquisition of ^1H -NMR results which were contracted out to the Department of chemistry at the University of Ottawa.

My thesis supervisor, Professor Marc A. Dubé provided the scientific guidance, continuous input and day-to-day supervision throughout the tenure of this project, as well as editorial comments to all my written work.

Hong Hua

ABSTRACT

Styrene-acrylic emulsion polymers are widely used for exterior coatings because of their good exterior durability. Different monomer combinations can produce a variety of copolymer products for coating applications. A broad range of functional chemical groups can also be incorporated into the polymer chain to improve coating adhesion to the substrate, sites for crosslinking, as well as compatibility with other polymer materials. The versatility of styrene-acrylic latex chemistry, from the point of view of polymer chain microstructure, polymerization process manipulation, and molecular weight and particle size control, leaves much to be exploited to meet the challenges of producing products with desired structures and application-related material properties and minimizing cost and waste. Systematic studies, as well as newer and more sophisticated chemical, physical, colloidal and computer-oriented analytical and modelling tools will allow the correlation of synthesis, microstructure and performance properties.

This study looks at the semi-continuous emulsion polymerization of styrene (St) – butyl acrylate (BA) with methacrylic acid (MAA) to produce latex for coating applications. The objectives were to investigate the factors influencing the polymerization process, latex polymer and coating adhesion properties. Statistical experimental design techniques were used to study their relations in order to improve coating adhesion.

An experimental screening design was first used to investigate the effects of five variables, i.e., St/BA ratio, MAA contents, pH, emulsifier content, and chain transfer agent (CTA) content on various product properties. The impact of these variables on the carboxylic acid distribution in the latex, the average latex particle diameter, the molecular

weight and distribution of the polymer products, and the glass transition temperature of the polymer were studied using a 2^{5-1}_{IV} fractional factorial experimental design. The results from the screening design also showed that inside the chosen experimental region, the pull-off adhesion between the latex coating and a polycarbonate substrate was influenced by the pH of the emulsion polymerization. Reactions under increased pH produced latexes with higher adhesion forces to the polycarbonate substrate.

Following the screening design of experiments, three variables, i.e., St/BA ratio, MAA content, and pH, were further investigated through a Box-Behnken design over a wider experimental region. Their influence on the latex polymer properties when the CTA and the emulsifier contents were held constant was studied. Copolymers with a broader range of T_g were produced. Experimental results also showed how the pH affected the distribution of carboxylic acid in the polymer particles. An empirical model was obtained through the regression analysis to correlate pull-off adhesion to the three variables.

The viscoelastic behaviour of the polymer products was studied by dynamic mechanic analysis (DMA). This was a step to correlate the polymer structural properties, which were affected by variables in the emulsion polymerization with their performance properties such as the adhesion to polycarbonate substrate. It was found that ionic and hydrogen bonding interactions which led to the interfacial crosslinking of particles improved the cohesive strength of the latex film and hence the coating adhesion performance. This was also affected by the carboxylic group distribution in different St/BA/MAA emulsion polymerization systems.

This work shows that a combination of techniques offers the opportunity to investigate the influence of different variables to improve the coating adhesion properties of St/BA/MAA based latexes. The empirical model based on the extensive experimental program has led to an improved understanding of the St/BA/MAA emulsion polymerization and its latex polymer product properties.

RÉSUMÉ

Les polymères styrène-acryliques en émulsion sont présentement employés pour les enduits extérieurs en raison de leur bonne longévité extérieure. Les différentes combinaisons de monomères peuvent créer une variété de produits de copolymère pour des applications d'enduit. Une large gamme de groupes chimiques fonctionnels peuvent également être incorporés dans la chaîne de polymère pour améliorer l'adhérence d'enduit au substrat, les emplacements pour réticuler et la compatibilité avec d'autres matériaux de polymère. La polyvalence de la chimie du latex styrène-acrylique, du point de vue de la microstructure de chaîne de polymère, la manipulation du processus de polymérisation, le contrôle du poids moléculaire et de la dimension particulaire, offrent beaucoup à exploiter envers relever les défis de fabrication de produits avec des structures désirées et des propriétés matérielles application-connexes en plus de réduire les coûts et les pertes. Les études systématiques, ainsi que les nouveaux outils analytiques et de modélisation permettront la corrélation des propriétés de synthèse, de microstructure et de performance.

Cette étude observe la polymérisation en émulsion semi-continue du styrène (St) - acrylate de butyle (BA) avec de l'acide méthacrylique (MAA) comme bût de produire du latex pour l'application d'enduits. Les objectifs étaient d'étudier les facteurs influençant le procédé de polymérisation, les propriétés du polymère de latex et d'adhérence de l'enduit. Des techniques de plan d'expérience statistiques ont été employées pour étudier leurs relations afin d'améliorer l'adhérence d'enduit.

Un plan d'expérience préliminaire a été employé pour étudier les effets de cinq variables, c.-à-d., le ratio entre St/BA, le contenu de MAA, le pH, le contenu d'émulsifiant et le contenu de l'agent de transfert de chaîne (CTA) sur de diverses propriétés. L'impact de ces variables sur la distribution d'acide carboxylique dans le latex, le diamètre moyen des particules de latex, le poids et la distribution moléculaire des produits de polymère, et la température de transition vitreuse du polymère ont été étudiés utilisant un plan d'expérience factorielle partiel 2^{5-1}_{IV} . Les résultats du plan d'expérience préliminaire ont également prouvé qu'à l'intérieur de la région expérimentale choisie, l'adhérence établi par une force d'arrachage entre l'enduit de latex et un substrat de polycarbonate a été influencée par le pH de la polymérisation par émulsion. Les réactions avec un pH accru ont augmenté les forces d'adhérence du latex au substrat de polycarbonate.

Après les expériences préliminaires, trois variables, c.-à-d., le rapport de St/BA, le contenu de MAA, et le pH ont été étudiées par conception d'un plan de Box-Behnken auprès d'une région d'influence expérimentale plus large sur les propriétés de polymère de latex quand les CTA et le contenu d'émulsifiant ont été jugés constants. Des copolymères avec une température de transition vitreuse plus large ont été produits. Les résultats expérimentaux ont également montré la façon donc le pH a affecté la distribution de l'acide carboxylique dans les particules de polymère. Un modèle empirique a été obtenu par l'analyse de régression pour corrélérer l'adhérence d'arrachage du latex au substrat de PC avec les trois variables.

Le comportement de visco-élasticité des produits de polymère a été étudié par analyseur mécanique dynamique (AMD). Cet étape a corréler les propriétés structurales

du polymère qui ont été affectées par des variables dans la polymérisation d'émulsion avec leurs propriétés de performance d'adhérence au substrat de polycarbonate. Il a été constaté que les interactions de liaison ioniques et d'hydrogène qui ont mené à la réticulation interfaciale des particules ont amélioré la force cohésive du film de latex et par conséquent la performance d'adhérence d'enduit. Ceci a aussi été affecté par la distribution du groupe carboxylique dans les systèmes différents de polymérisation d'émulsion de St/BA/MAA.

Ce travail montre que les combinaisons de techniques offrent l'occasion de rechercher l'influence de différentes variables pour améliorer les propriétés d'adhérence d'enduit du latex à base de St/BA/MAA. Le développement du modèle empirique basé sur le programme expérimental a mené à une compréhension améliorée de la polymérisation d'émulsion de St/BA/MAA et des propriétés de son latex.

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List of Abbreviations

AA = Acrylic Acid

APS = Ammonium Persulfate

ASTM = American Society for Testing and Materials

BA = Butyl Acrylate

CMC = Critical Micelle Concentration

CTA = Chain Transfer Agents

DMA = Dynamic Mechanical Analysis

DSC = Differential Scanning Calorimetry

2-EHA = 2-Ethylhexyl Acrylate

GPC = Gel Permeation Chromatography

KPS = Potassium Persulfate

MA = Methyl Acrylate

MAA = Methacrylic Acid

MW = Molecular Weight

MWD = Molecular Weight Distribution

PBA = Poly(butyl acrylate)

PMMA = Poly(methyl methacrylate)

PS = Polystyrene

PVAc = Poly(vinyl acetate)

PVOH = Poly(vinyl alcohol)

PSA = Pressure-Sensitive Adhesives

SDS = Sodium Dodecyl Sulphate

SLS = Sodium Lauryl Sulphate

St = Styrene

VAc = Vinyl Acetate

¹H-NMR = Proton Nuclear Magnetic Resonance

THF = Tetrahydrofuran

Nomenclature

Symbols

G' = storage modulus

G'' = loss modulus

f = initiator efficiency

I = initiator

K = Mark-Houwink parameter

k_d = initiator decomposition rate constant

k_p = propagation rate constant

k_{pij} = propagation rate for the addition of monomer j to an initiator fragment

k_{pij} = rate constant of addition of monomer j to the radical ending with monomer unit i

k_t = termination rate constant

k_{tc} = termination by combination rate constant

k_{td} = termination by disproportionation rate constant

M^* = total concentration of all chain radicals

M_j = monomer j

m_i = mass of monomer i

M_n = number average molecular weight

$[M]_p$ = monomer concentration inside a particle

M_w = weight average molecular weight

MW_m = molecular weight of the repeat unit

N = number of latex particles

$\bar{n}$ = average number of radicals per particle

N_a = Avogadro's number

n_i = mole of monomer i

P = polymer

R^* = primary radical

R_I = rate of initiation

$R_m^\bullet$ = growing polymer chains size of m

$R_{r,j}^\bullet$ = radical of chain length r ending in monomer unit j

$R_{r+1,j}^\bullet$ = radical of chain length $r + 1$ ending with monomer unit j

R_p = rate of polymerization

r_i = reactivity ratio of monomer i

R_t = rate of termination

t = time

T_g = glass transition temperature

X = overall conversion

x_i = conversion of monomer i

Greek Letters

α = Mark-Houwink parameter

β = molecular weight contribution due to termination by combination

γ = shear rate

η = viscosity

Chapter 1 Introduction

1.1 Emulsion polymerization and polymer latex

Emulsion polymerization is a unique heterogeneous process that can be employed for free radical chain polymerizations. It involves the polymerization of monomers in a colloidal dispersion. The main ingredients of a typical emulsion polymerization recipe include water, emulsifier, monomer, and water-soluble initiator. This heterogeneous system is composed of three phases at the beginning of the reaction: the monomer droplet phase, which acts as a monomer reservoir; the continuous aqueous phase, which acts as a species transport medium and provides a proper heat transfer; and the polymer particle phase, the main locus of polymerization.

When the emulsifiers dissolve in water at a concentration above the critical micelle concentration (CMC), they will cluster into micelles with their hydrophilic ends directed towards the aqueous phase. Hence, monomers can either exist inside the micelles' highly hydrophobic core or form large monomer droplets stabilized by the emulsifier molecules absorbed on the droplets' surfaces. Free radical oligomers, generated from a water-soluble initiator reacting with monomers, can propagate with dissolved monomers in the water phase, recombine with initiator fragments, react with monomer droplets, be captured by emulsifier micelles and by polymer particles. Once a free radical oligomer is captured by a particle, a micelle or a droplet, it may: propagate, mutually terminate, react with monomer soluble impurities, undergo chain transfer reactions, and participate in internal- and terminal double bond polymerizations. Within each particle the reaction takes on the characteristic of a bulk polymerization. The

process is characterized by the production of high molecular weight polymers at a higher reaction rate compared to homogeneous systems.

As a result, the latex product is a dispersion of polymer particles in water. Nowadays, synthetic polymer latexes prepared by the emulsion polymerization process can be used as commodity polymers in a wide variety of applications such as synthetic rubber, paints, paper coatings, adhesives, sealants and biomedical products. Used as coatings and adhesives, latex polymers have the advantage of reducing volatile organic content (VOC) during the production and application processes compared to their organic solvent-based counterparts. The use of water-borne emulsion polymerization can be expected to increase further as restrictions on VOCs become more stringent.

A better understanding of emulsion polymerization processes and polymer latex product properties is needed because of more stringent polymer quality requirements and increasing pressure for production cost reduction. For instance, the development of polymerization reaction process monitoring and control techniques is key to the efficient production of tailored, high quality polymers. Also, there is a need for reducing the levels of residual monomer in the product to meet the environmental standards of VOCs. These objectives cannot be achieved without the knowledge obtained from comprehensive studies on emulsion polymerization processes and latex product properties.

1.2 Aims of the project

Nearly 30% of commercial emulsion polymers are derived from acrylic and styrene-acrylic monomers, a compositionally diverse and versatile family of commercially important monomers.¹ These monomers can copolymerize well with each

other, which leads to an enormous range of accessible copolymer compositions and physical properties.

Acrylic and styrene-acrylic emulsion polymers are widely used for exterior coatings because of their good exterior durability. Their use as coatings accounts for over one-third of the consumption of acrylic and styrene-acrylic latexes.¹ An important consideration is to select a monomer combination that produces a copolymer with the appropriate glass transition temperature (T_g) for application, namely, a low T_g for adhesives, and a T_g near room temperature for latex paint binders. The T_g of poly(butyl acrylate) is -54°C , and the T_g of polystyrene is 100°C , thus styrene/butyl acrylate (St/BA) emulsion copolymers have a wide T_g range suitable to a variety of end-use application. They also find use in adhesive markets including pressure-sensitive adhesives for tape and labels, contact adhesives for product assembly, and construction adhesives.

Another valuable consideration of styrene-acrylic monomers is their ability to incorporate a broad range of functional chemical groups into the polymer chain. These functional groups can provide good adhesion with substrates, compatibility with other polymers, sites for crosslinking, etc. Some auxiliary and specialty monomers are used in styrene-acrylic latexes, usually in amounts less than 10% by weight, to impart special properties to the latex copolymers. One example is the addition of carboxylic acid monomers (acrylic acid [AA] or methacrylic acid [MAA]) in the preparation of acrylic latexes. The incorporated carboxyl functional groups can enhance the mechanical properties of films formed from the latex as well as the adhesion of the polymer towards the substrate and provide good adhesion and sites for crosslinking reactions.

Because synthetic latexes are colloidal dispersions of polymer particles, they have a dual character where colloidal properties are superimposed upon those of the polymer. Their final application performance requires specific properties of the synthetic latex in the colloid state as well as of the polymer in the “dry” state.

The versatility of styrene-acrylic latex chemistry, from the point of view of polymer chain microstructure, polymerization process manipulation, and molecular weight and particle size control, leaves much to be exploited to meet the challenges of producing products with desired structures and application-related material properties and minimizing cost and waste. Systematic studies, as well as newer and more sophisticated chemical, physical, colloidal and computer-oriented analytical and modelling tools will allow the correlation of synthesis, microstructure and performance properties.

Figure 1.1 shows the relationships of polymerization process conditions, polymer and latex properties and their end-use performance properties represented in three blocks.

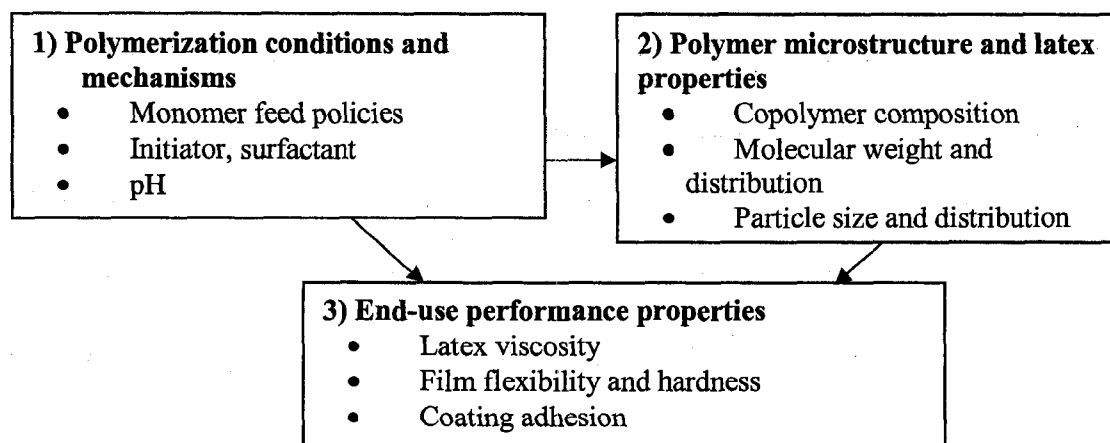


Figure 1.1 Synthesis/Structure/Property relations

Block 1 in Figure 1.1 shows some of the many variables that can affect emulsion polymerization reaction rates and product characteristics. Changes in polymerization reaction conditions and mechanisms that reactions undergo can greatly alter the polymer microstructure and latex polymer properties listed in Block 2. Meanwhile, the final

product performance shown in Block 3, such as latex viscosity, film flexibility and hardness, coating adhesion are all dependent on the latex polymer microstructure and properties.

So far, academia has concentrated mainly on issues related to the mechanism and kinetics of emulsion polymerization including the polymerization rate profile, the development of molecular weight and molecular weight distribution (MWD), the evolution of particle size and particle size distribution (PSD), particle morphology and how these are influenced by polymerization process parameters such as ingredient types and concentrations, temperature, and the monomer feed policies. Efforts have been focused on trying to model the process and predict the polymer microstructure properties by linking Block 1 and Block 2 together. On the other hand, industrial interest has been focused on the properties of polymer product performance including the latex polymer processability, coating and adhesive properties, and durability to the applied environment. Thus, there is a clear need to seek mathematical correlations between process conditions (Block 1), polymer microstructure (Block 2) and polymer end use performance (Block 3). This would allow one to optimize the process to produce polymers with tailor-made properties.

The primary objective of this project was to study the relations between St/BA latex polymer properties and emulsion polymerization process conditions. Previous work was done to determine the relation between latex polymer microstructure (Block 2) and emulsion polymerization conditions (Block 1). Thus, the main goal is to correlate the performance properties of latex polymer products (Block 3) with emulsion polymerization process conditions (Block 1) based on more knowledge about the latex

polymer microstructure (Block 2). This will be fulfilled via an extensive data collection and sample characterization of St/BA/MAA emulsion polymerization reactions guided by rigorous statistical experimental design techniques. It will help to find optimal conditions for improved final latex polymer product properties such as adhesion and film flexibility without using conventional trial and error methods. The data generated from these runs will be of help to ongoing kinetics studies of this emulsion polymerization system.

1.3 Thesis outline

This thesis is composed of several manuscripts that will be submitted for publication in refereed journals

Chapter 2 is a literature review on the St/BA/MAA emulsion polymerization mechanism and kinetics as well as latex polymer structure property relationship.

Chapter 3 (paper 1) presents a 2^{5-1}_{III} fractional factorial screening design of experiments conducted to identify the effects of St/BA ratio, MAA content, pH, emulsifier content, and chain transfer agent content on various product properties in the semi continuous emulsion copolymerization of St/BA/MAA. It will be submitted to *Journal of Polymer Science*.

Following the screening design of experiments, Chapter 4 (paper 2) describes a Box-Behnken design used to determine the regression expression of the three factors: the St/BA ratio, the MAA content and the pH and their interactions affecting the latex polymer properties. It will be submitted to *Industrial and Engineering Chemistry Research*.

Chapter 5 (paper 3) presents a study of the viscoelastic properties of the latex polymers produced from the experiments shown in Chapters 3 and 4 and their correlation

to the coating adhesion of these latex products to a polycarbonate substrate. It will be submitted to *Polymer*.

The final section comprises a general discussion of the entire thesis and lists conclusions and recommendations based upon the results. The appendix includes sample calculations for a representative polymerization recipe as well as an example of latex polymer characterization results.

Chapter 2 Literature Review

2.1 Emulsion polymerization mechanism and kinetics

It is convenient to divide conventional batch emulsion polymerizations into three intervals according to the Smith-Ewart scheme summarized in Table 2.1.² The emulsion polymerization mechanism and its kinetics can then be interpreted from the evolution of the different phases in the process.

Table 2.1 Different intervals of an emulsion polymerization reaction

Interval	Typical conversion range (%)	Micelles	Monomer droplets	Particle number	Particle size
I	0-10	present	present	increases	increases
II	10-40	absent	present	constant	increases
III	40-100	absent	absent	constant	roughly constant

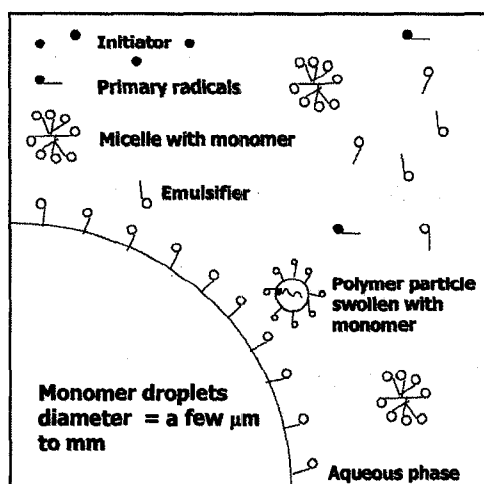


Figure 2.1 Simplified schematic representation of a batch emulsion polymerization: Interval I

Interval I. This step is called nucleation step. In this stage as shown in Figure 2.1, when the emulsifier is dissolved in water at a concentration above a critical micelle concentration (CMC), the emulsifier molecules will aggregate to form micelles.

Monomers are dispersed in the water phase as droplets that serve as monomer reservoirs. Monomer then diffuses from the droplets through the water phase into the micelles according to a thermodynamic equilibrium. Monomer can also be dissolved in the water phase.

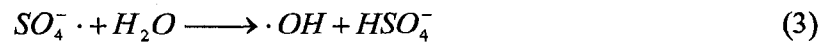
Particle formation and growth, by far the most important phenomenon in conventional emulsion polymerizations³, starts from the initiation reaction in the aqueous phase. In the presence of heat, water-soluble initiator such as potassium persulfate (KPS) will decompose into two highly reactive primary free radicals $SO_4^{\cdot -}$.



The rate of initiation R_I is expressed as:

$$R_I = 2fk_d[I] \quad (2)$$

where k_d is the rate constant for initiator decomposition, f is the initiator efficiency, and $[I]$ is the molar concentration of the initiator. The reaction of water with persulfate radicals may result in the production of acidic by-products as shown in equation (3). Here an $\cdot OH$ radical is formed which is able to initiate polymerization. Because the HSO_4^- can alter the pH, the reactivity may change as a result of changing pH though the concentration of radicals does not change.



Free radicals generated in the water phase can undergo several distinctive reactions as follows:

(1) The initiator radicals can react with monomer molecules 1 or 2 (i.e. in the case of copolymerization) to form monomeric radicals:



where M_j denotes monomer 1 or 2. $R_{r,j} \cdot$ denotes a radical of chain length r ending in monomer j , and k_{p1j} denotes the propagation rate constant for the addition of monomer j to an initiator primary radical. The monomeric radicals so-formed can undergo all reactions related to a free radical polymerization scheme to form oligomeric radicals: propagation with dissolved monomer units, cross-propagation in case of a copolymerization system, as well as termination and transfer reaction.

(2) The oligomeric radical may enter emulsifier micelles or already existing polymer particles. The first event forms a monomer-swollen polymer particle that grows by propagation reactions known as heterogeneous or micellar nucleation. The entry of radicals in the particle phase is one of the key issues in latex particle growth and emulsion polymerization kinetics.

(3) Particles can also be generated through a homogeneous nucleation mechanism. This occurs when significant amounts of monomer are dissolved in the water phase. Radicals generated in the aqueous phase continue to propagate by adding monomer units to form water-soluble oligomeric radicals. The propagation will stop when these radicals reach their solubility limit in the aqueous phase and precipitate. The precipitated oligomeric radicals form primary particles that absorb surfactant molecules for stabilization and absorb monomer for further propagation. The homogeneous nucleation is statistically negligible under conventional emulsion polymerization conditions.⁴

(4) Radicals can react with water-soluble impurities (WSI) to form a dead polymer molecule $P(WSI)$:



where k_{zj} is the water-soluble impurity reaction rate constant. This reaction may cause some induction time in the polymerization process if large amounts of radicals are consumed by the impurities instead of adding monomers.

(5) Small radicals can desorb from the polymer particles into the water phase due to chain transfer reactions. Desorbed radicals may also reabsorb into the polymer particles.

The rate of polymerization R_p in emulsions can be written as the product of radical concentration $[R\cdot]$, and the monomer concentration inside particles $[M]_p$:

$$R_p = k_p [R\cdot] [M]_p \quad (6)$$

where k_p is the propagation rate constant. Here inside an active particle the radical concentration is higher than radical concentration in most homogeneous polymerization systems and the radical lifetime here is only a few thousandths of a second.⁵ Entry of a second radical into the active particle immediately terminates the chain reaction. The particle is then dormant until another (the third) radical arrives to activate the particle and resume the propagation step. The cycle of alternate growth and inactivity of the polymer chain continues until the monomer conversion is essentially complete. Thus the radical concentration $[R\cdot]$ can be expressed as:

$$[R\cdot] = \frac{N_p \bar{n}}{N_A} \quad (7)$$

where N_p is the total number of particles in the system, $\bar{n}$ is the average number of radicals per particle, and N_A is Avogadro's number. Combining equations (6) and (7) gives the rate of polymerization R_p as:

$$R_p = \frac{k_p [M]_p N_p \bar{n}}{N_A} \quad (8)$$

Equation (8) has been applied successfully to monomers with very low water solubility such as styrene. For polymerization reactions of water-soluble or partially soluble monomers, additional water phase polymerization reactions can cause deviations from the model.

The average number of radicals per particle, $\bar{n}$, is of critical importance when used in equation (8) to determine the rate of emulsion polymerization. For example, $\bar{n} = 0.5$ is usually the case described in texts as applicable to most emulsion polymerizations. It occurs when desorption of radicals is negligible compared to the rate of radicals entering particles and when the particle can accommodate no more than one radical. It also requires the initiation rate not be excessively low and negligible termination of radicals in the aqueous phase. When there is significant radical desorption from particles and termination in the aqueous phase is not negligible, $\bar{n}$ will be less than 0.5. $\bar{n}$ will be even lower for small particle sizes and low initiation rates.³⁻⁵ If some portion of the polymer particles are large enough to contain two or more radicals, $\bar{n}$ will be more than 0.5 when radical desorption from particles and termination in the aqueous phase are not important. The number of polymer particles can also affect the rate of polymerization. During *Interval I*, R_p increases due to the increasing number of particles in the particle formation stage according to the Smith-Ewart scheme (see Table 2.1).

In a way similar to that in homogeneous polymerizations, the number-average degree of polymerization for emulsion polymerization, $\bar{X}_n$, is given by the following equation:

$$\bar{X}_n = k_p [M]_p \frac{N_p \bar{n}}{R_t} \quad (9)$$

assuming the absence of any chain transfer reaction as well as negligible radical desorption and termination in aqueous phase. Combining equations (8) and (9) indicates one of the characteristics of the emulsion polymerization that one can increase the rate of polymerization without lowering the molecular weight of the polymer, which is not possible in bulk or solution polymerizations.

Interval II. Figure 2.2 shows that after approximately 15% conversion of the initially charged monomer, micelles are exhausted and no new particles will be generated. Monomer diffuses from the monomer droplets into the latex particles through the aqueous phase. The monomer concentration inside the particles, $[M]_p$, remains constant based on a thermodynamic equilibrium. Thus, R_p will remain constant during this stage according to equation (8).

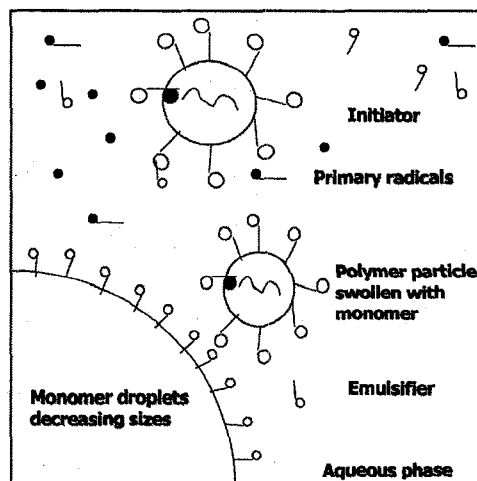


Figure 2.2 Schematic representation of a batch emulsion polymerization: Internal II

Interval III. After approximately 40-60% of the monomer is polymerized, the monomer droplets disappear (see Figure 2.3) and the polymerization rate may decrease when the concentration of monomer inside the particles decreases. However, at high conversion levels, there may be several radicals co-existing in a large particle and $\bar{n}$ may be well above 0.5, which can cause a higher rate of polymerization than in interval II. During this stage, the particle number remains the same in Interval III as in Interval II.

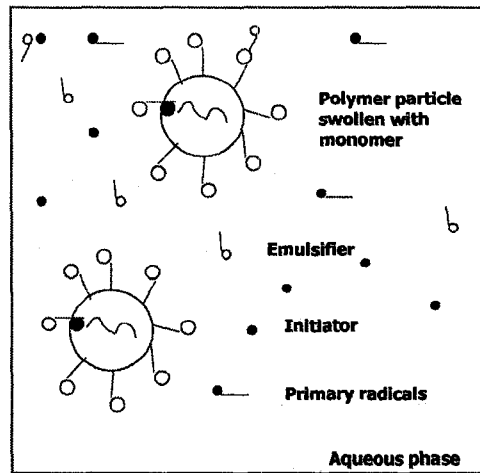
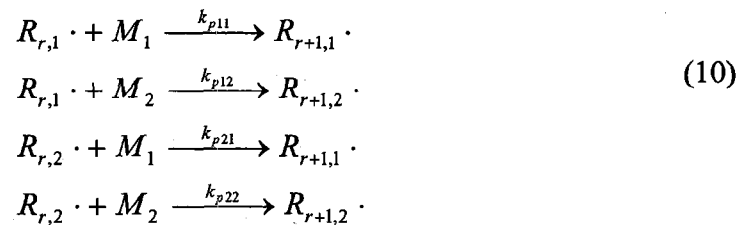


Figure 2.3 Simplified diagram representation of a batch emulsion polymerization: Interval III

As shown in Interval I scheme, inside polymer particles the free radical polymerization proceeds with the addition of monomers. For copolymerization processes, the propagation reactions can be expressed as follows according to the terminal model ^{6,7}:



where $R_{r,j} \cdot$ denotes a free radical of chain length r ending in monomer unit M_j and k_{pij} denotes the rate constant for a propagating chain ending in monomer unit M_i adding to a monomer unit M_j . According to the *terminal model*, the reactivity of each radical is determined by the monomer unit at the active centre of the chain end. Reactivity ratios are defined in equation (11). They indicate the preference of a radical to react with each monomer type. For example, when $r_1 > 1$, it describes the preference for the radical to homo-propagate while when $r_1 < 1$, it means cross-propagation is preferred.

$$r_1 = \frac{k_{p11}}{k_{p12}} \quad , \quad r_2 = \frac{k_{p21}}{k_{p22}} \quad (11)$$

In the event of greatly differing reactivity ratios, the chemical composition of the polymer formed will drift throughout a batch reaction. In this case, semi-batch composition control policies are necessary to ensure a homogeneous polymer composition.⁸ Due to their direct influence on composition and polymerization reaction rate, the reactivity ratios are the most important parameters used in the modelling of copolymerization.

Radicals may terminate to form polymer chain upon encountering one another through combination or disproportionation reactions as shown in reaction (12)



The rate of termination R_t , is then given as:

$$R_t = k_t [R \cdot]^2 \quad (13)$$

where k_t is the overall termination rate constant.

Chain transfer reactions to small molecules such as initiator, monomer, and solvent or chain transfer agent can also take place and are shown as:



where XA can be the initiator, monomer, solvent or chain transfer agent and $k_{tr, XA}$ is the chain transfer rate constant. This reaction is due to the premature termination of a polymeric radical by transferring hydrogen or other atom to it from the small molecule XA present in the system. The new radical $A \cdot$ may then reinitiate the polymerization:



Chain transfer reactions are chain-breaking reactions. It results in a decrease in the size of the propagating polymer chain though they may not usually have an effect on the overall rate of polymerization.

There is also the possibility of radical chain transfer to polymeric molecules. Transfer to polymer results in the formation of a radical site on a polymer chain, which can lead to the production of branched polymer. This reaction cannot be neglected when the polymerization reaction reaches high conversion or the polymer concentration is very high at the site of polymerization (i.e. as is the case in an emulsion polymerization). Transfer to polymer does not necessarily reduce the overall degree of polymerization because each act of transfer can produce a branched polymer molecule of larger size than the initially terminated polymer chain. For example, the generally accepted mechanism for the formation of short chain branching involves a backbiting intramolecular transfer reaction in which the propagation radical abstracts hydrogen from the methylene groups before the radical chain end. Then, the resultant radicals can propagate with monomers to form short branches.⁵ Polymers with reactive propagating radicals can have a great extent of branching.

2.2 Batch and semi-batch emulsion polymerization processes

Using the same ingredients, different procedures and conditions can be carried out to produce latexes and polymers with quite different properties and performance characteristics. Generally, there are three modes of ingredient addition policies that can be used: *batch*, *semi-batch* (also referred to as *semi-continuous batch*), and *continuous* processes.⁹ In *batch* processes, all reactants are added into the reactor vessel at the start of polymerization. In *semi-batch* processes, only part of the total reaction mixture is introduced at the beginning of the reaction, the remainder is added during the course of the polymerization according to a determined feed profile.

In an emulsion copolymerization batch process, the composition of the produced copolymer may drift with conversion due to differences in the monomer reactivity ratios. For example, as shown in Table 2.2, monomer reactivity ratios for St and BA are quite different.¹⁰ Thus, in a batch St/BA copolymerization, the more reactive monomer, St, is depleted more quickly in the process, leading to a decreasing fraction of St in the monomer mixture and a corresponding decrease in the fraction of St units in the produced copolymer.

Table 2.2 Reactivity ratios in St/BA/MAA copolymerizations¹⁰

System	r_1	r_2
St/BA	0.956	0.183
MAA/BA	1.25	0.31
MAA/St	0.6	0.124

The partitioning of different monomers in the aqueous phase, monomer droplets and latex particles can also affect the copolymer composition. Worthy of special mention are copolymerizations involving carboxylic acid systems, where acid monomers such as

acrylic acid (AA) and methacrylic acid (MAA) are added to improve the colloidal stability of latexes and to enhance the performance of emulsion copolymer applications.

As shown in Table 2.3, the three monomers St, BA, and MAA have very different water solubility.

Table 2.3 Water solubility of St, BA, MAA monomers

Monomer	Water solubility (at 25°C)
St	0.027%
BA	0.16%
MAA	100%

Because MAA is completely soluble in water, the carboxylic acid group in the monomer, polymer, or free radical formed in the water phase can dissociate or ionize according to the following equilibrium between the acid and base conjugate pairs:



This equilibrium can be described by the dissociation constant K_a :

$$K_a = \frac{[R - COO^-][H^+]}{[R - COOH]} \quad (17)$$

where $[-COOH]$ and $[-COO^-]$ are the concentrations of the carboxylic acid group and the ionized carboxylic acid group, respectively. The degree of acid dissociation, α , can be defined as the ratio of the ionized acid group concentration to the initial concentration of carboxylic acid, where $0 < \alpha < 1$:

$$\alpha = \frac{[R - COO^-]}{[R - COOH] + [R - COO^-]} \quad (18)$$

Combining equations 16 and 17 gives a relation between pH, pK_a , and α ¹¹:

$$pH = pK_a - \log_{10} \left(\frac{1 - \alpha}{\alpha} \right) \quad (19)$$

Equation 18 predicts that the pH value of the reaction mixture has a strong effect on the distribution of carboxylic acid monomer in different phases, which can subsequently affect the copolymerization mechanism, kinetics and latex properties. It follows that when the pH is greater than pK_a , the degree of acid dissociation α will be closer to 1, i.e. more acid will be ionized. The acid groups will then be distributed throughout the latex: in the polymer forming the particles, in the polymer absorbed at the particle surfaces, or in the water-soluble polymer in the aqueous phase.¹²

In a batch emulsion copolymerization reaction, the differences in monomer reactivity ratios and partitioning will lead to the formation of heterogeneous copolymers. Although the limited control that can be exerted over polymer and latex properties restricts the industrial application of batch processes, they still find important use in mechanistic investigations and the evaluation of formulations. For example, Yang and Yang¹³ studied St/BA emulsion polymerization batch processes using fractional factorial experimental design strategies. The influence on particle size and molecular weight distribution from factors such as initial monomer mixture composition, reaction temperature, agitation speed, and initiator and emulsifier concentration were investigated. A detailed regression and variance estimate analysis was carried out to identify important process conditions and their interactions affecting the latex polymer properties.

Araujo et al.¹⁴ performed experimental studies on styrenic and acrylic binary and ternary copolymerization systems to obtain extensive experimental data and validate their model predictions.¹⁵ Monomers with a wide range of solubilities in water were selected. Mixed experimental designs starting with fractional factorial designs were used to find the effects of process variables on latex polymer properties such as polymer composition,

particle size, and gel fraction. The five factors included reaction temperature, initial monomer feed composition, monomer concentration, and initiator and emulsifier concentration.

Compared to batch emulsion polymerizations, where all ingredients are added at the outset of a process and only limited variables can be manipulated for the manufacture of latexes, the semi-batch process is more versatile. Keeping in mind such limitations as heat removal, a proportion of a reaction component can be added over a period of time during a semi-batch process. Usually, the most important feature of semi-batch processes is the controlled introduction of monomer to the reaction vessel either as neat monomer or as an emulsion containing monomers, emulsifier, and water.⁹

In a semi-batch process, the rate of monomer addition to the reaction vessel, R_m , is of crucial importance because, at low addition rates, it controls the monomer concentration inside the particle, $[M]_p$, during the course of polymerization and hence, controls the polymerization rate.

One possible monomer addition policy is the monomer-starved condition. In this policy, a heel of monomers 1 and 2 at the desired concentration levels is added to the reactor at time 0. Then, monomers 1 and 2 are fed to the reactor with a time-varying feed rate to maintain constant monomer concentrations, $[M_1]_p$ and $[M_2]_p$. The R_m is kept low enough that $[M_1]_p$ and $[M_2]_p$ fall below saturation values and the monomer addition rate is the limiting factor in controlling the polymerization rate. Although the use of monomer-starved conditions can produce copolymers with a desired chemical composition, the low monomer concentration will lead to a low polymerization rate, i.e. a low production rate. The low monomer concentration inside the particles may also give

rise to copolymers with broader molecular weight distributions and high degrees of branching due to increased chain transfer to polymer reactions taking place.

Another policy is an optimal monomer addition rate profile.⁷ In this approach, all of the slower monomer and sufficient of the faster monomer are added to the reactor to give the desired composition at time 0. The faster monomer is then fed to the reactor according to a time-varying feed rate profile to maintain a constant monomer composition with reaction time.

Garcia-Rejon et al.¹⁶ used semi-batch processes under monomer starved-feed conditions to produce homogeneous St/BA copolymers. Their results showed a linear relationship between the copolymerization rate and the monomer feed rate. To develop the optimal monomer feed profile for St/methyl acrylate (MA) emulsion polymerizations, Schoonbrood et al.¹⁷ used an iterative procedure applying empirical correlations to account for model mismatch and unknown parameters. This iterative process took a long time to converge to the optimal policy but the polymerization process was more efficient compared to the monomer-starved process. Gugliotta et al.¹⁸ used on-line calorimetric measurements for conversion and copolymer composition estimation to develop an optimal monomer addition policy in a semi-batch St/BA emulsion copolymerization process to produce homogeneous copolymer within a minimum time according to a theoretical calculation of the polymerization rate evolution. It required monomer reactivity ratios, partition coefficients, homopolymerization enthalpies, and propagation rate constants as model parameters. Galimberti et al.¹⁹ developed a monomer feed policy for St/BA semi-batch emulsion copolymerization combining a composition-conversion model with on-line monitoring of conversion through both densimetry and through

measuring the ultrasound velocity in the latex. The evolution of the reacting system was modelled as a function of conversion instead of time. It followed the methods derived for other systems such as St/MA and MA/vinyl acetate (VAc).^{20, 21}

From the literature, we can see that considerable experimental effort is required to establish optimum values of parameters for each system when developing the optimum addition rate profiles for a particular emulsion copolymerization reaction, i.e. its specific formulation and reaction conditions. Because there are large numbers of variables and many of them depend upon the reaction conversion, it is necessary to compare experiments with predictions and to iterate to values of the parameters that give a best-fit correlation with experimental data.

2.3 Styrene/Butyl Acrylate (St/BA) emulsion copolymerization

Emulsion copolymerizations of St/BA allow for the preparation of copolymers for latex paints and coatings with a wide range of properties such as colloidal stability, impact and solvent resistances, elasticity and compatibility. These final latex properties are determined by factors such as the copolymer composition, MWD, frequency of branches or cross-link points, particle morphology and PSD. To control these properties, different process variables can be manipulated (e.g. temperature, comonomer ratio (St/BA), initiator, emulsifier, and chain transfer agent (CTA) concentrations) and different reaction processes (batch and semi-batch) can be used under different control strategies.²² Various research groups have studied the St/BA emulsion copolymerization from a variety of angles. A review of that work will allow us to acquire direct knowledge on how process conditions affect the performance properties of latex polymer products.

Due to the lack of studies on St/BA/MAA emulsion copolymerization, this review can also help us determine the parameters for our study of the effect of adding MAA into St/BA emulsion systems.

Table 2.5 lists several key references to work performed on the St/BA emulsion copolymerization system. As shown in the second column of Table 2.5, a wide range of comonomer ratios (St/BA) was used (from 10/90 to 90/10 weight ratio) by various research groups. This variable can greatly affect the rate of polymerization and the MWD due to the BA chain transfer to polymer reaction. Cruz-Rivera et al.²³ performed emulsion copolymerizations with three different comonomer ratios and obtained homogeneous copolymers using semi-batch processes. Their focus was on how the comonomer ratios and the reaction pathway affect the particle morphology, the molecular weight and colloidal properties. Models were developed to explain the evolution of copolymer composition and glass transition behaviour. The latexes displayed a particle size decrease with increasing St content. Higher molecular weights were also observed when the BA content was increased, probably due to its decreasing cross-termination rate constant. Yang and Yang¹³ found the same trends under batch conditions. Saldivar et al.²⁷ also observed that the parameters for the gel effect of BA and micelle surface area covered by an emulsifier molecule increased with the increase of BA content in the monomer mixture. The kinetic studies in Cruz-Rivera et al.²³ showed that the reactivity ratios determined in batch emulsion polymerization at low conversion were close to those obtained in bulk or solution polymerization.

Table 2.5 Key references on St/BA/carboxylic acid emulsion copolymerizations

References	St/BA	^b Solids content	Carboxylic acid	[^c KPS]	[^c SDS]	[^c CTA]	T (°C)	Process
Barudio et al. ²⁴	69/31	20%	N/A	0.15	0.15	0, 0.1, 0.2, 0.5, 1.0	60	Batch, semi-batch
Charnot et al. ²⁵	47.5/47.5	51%	AA: 5	0.39	0.2	N/A	80	Semi-batch
Cruz-Rivera et al. ²³	23/77, 45/55, 69/31	N/A	N/A	0.6	^f MA80: 3.6 22N: 0.7	N/A	70	Semi-batch
Galimberti et al. ¹⁹	20/80, 23/77, 74/26	10%, 13%	N/A	1.5	5.0, 8.0	N/A	50	Batch, semi-batch
Garcia-Rejon et al. ¹⁶	20/80, 40/60, 50/50, 60/40, 80/20	29%	N/A	0.33	1.5	0.37	70	Semi-batch
Garcia-Rejon et al. ²⁶	50/50, 90/10	15%	N/A	0.08, 0.09, 0.11, 0.12	2, 4, 6, 8	0.5, 0.7, 1.1	60	Batch
Saldivar et al. ²⁷	30/70, 70/30	26%, 36%	N/A	^d APS: 0.08, 0.13, 0.27	0.7, 1.2, 2.4	N/A	60	Batch
Santos et al. ¹²	50.3/46.3	20%	AA or MAA: 3.4	0.30	^e HBV: 0.6	N/A	60	Semi-batch
Yang and Yang ¹³	10/90, 90/10	10%	N/A	2.4, 7.3	0, 2.0	N/A	60, 70	Batch
Zubitur et al. ²⁸	54/45	55%	1	^d APS: 2	^h 1.5 & CO630: 1.0	0.5	70	Semi-batch

^a All amounts in phm, parts per hundred parts monomer unless otherwise indicated.

^b Weight percentage.

^c KPS, potassium persulfate used as the initiator unless otherwise indicated.

^d APS, ammonium persulfate used instead of KPS.

^e SDS, sodium dodecyl sulfate used as the emulsifier unless otherwise indicated; ^f Aerosol MA80 and 22N used instead of SDS.

^g HBV, Hostapal BV used instead of SDS; ^h SDS used together with Antarox CO630.

ⁱ *n*-dodecanethiol used as the CTA unless otherwise indicated.

In seeded semi-batch emulsion copolymerizations of St and BA at 75°C, Plessis et al.²⁹ varied the St contents in the monomer feed by a small amount (less than 10 wt.%). They found that the change in the St/BA ratio had a significant impact on both the reaction kinetics and the copolymer microstructure. The higher the St content was in the monomer feed, the lower the gel fraction and the branching level and the higher the weight-average molecular weight of the sol polymer were found in the copolymers. These, in turn, influenced the properties of adhesives derived from the latexes.

The third column in Table 2.5 reveals that typically, the solids contents used were rather low (below 30%). Only Charmot et al.²⁵ and Zubitur et al.²⁸ worked at solids contents higher than 50%. Industry is interested in high solids content systems from a process economics point of view but there are concerns about maintaining the colloidal stability of the latex when the frequency of collisions between particles is high. Another concern is that the latex viscosity increases associated with a high solids content may affect the heat transfer and mixing characteristics of the reaction. For the case of St/BA emulsion copolymerizations, gel formed during high solids content reactions can make matters worse because chain transfer to polymer reactions take place very often in BA-rich copolymerization processes.²⁵ In Yang and Yang¹³, for compositions in the range St/BA = 90/10-10/90 and at reaction temperatures between 60 and 70°C, no gel was reported though the solids content was as low as 10%. In another study at a high solids content level, Zubitur et al.²⁸ studied the agitation effect on semi-batch St/BA emulsion copolymerizations. Agitation was found to play an important role in monomer emulsification, mass transfer between droplets and particles, nucleation and coagulation

processes, and heat transfer. No effect of the agitation rate on the particle size distribution was observed. In the presence of CTA, the polymer molecular weights decreased with increasing agitation rate, whereas they increased in the absence of CTA. It is possibly due to the fact that there are diffusion limits on the CTA that affect the copolymer molecular weights during the reaction.

Carboxylic acid monomers such as AA and MAA are typically included in emulsion polymerizations to improve overall latex properties.¹ For example, they are commonly used in latex preparations for paints. The introduction of these monomers can improve the shear and freeze-thaw stability of latexes used as binding agents in paints, improve the mechanical properties of films formed from the polymer latex, bring desirable viscosity profiles vs. pH, and have a positive effect on polymer adhesion towards substrates such as metals and clays.³⁰

For the St/BA/carboxylic acid system, the three monomers have significantly different reactivity ratios and solubilities in water. The loci of polymerization and copolymer composition will highly depend on the equilibrium of monomers in the different phases. As shown in column 4 of Table 2.5, Charmot et al.²⁵ investigated the partitioning of the polymerized AA monomers between the aqueous phase, the particle surface and particle core. In a proposed model, because AA is soluble in water, they used an empirical modification to the critical chain length for radical entry to calculate the rate of AA polymerization in the aqueous phase, on the particle surface and inside the particle as well as the molecular weight of the grafted, buried and water-soluble polymer. The model was shown to be very sensitive to the partition coefficients of the AA between the water and polymer phases. Santos et al.¹² investigated the effect of pH on the reaction

kinetics and the acid group distribution of AA and MAA in different phases within the St/BA system. Compared to MAA, which is more hydrophobic, the AA monomer was more equally distributed throughout the system. MAA was found at higher concentrations inside the latex particles at the same pH. As a result, the effect of pH on the partitioning of MAA in different phases has a more significant impact on the glass transition temperature (T_g) of the copolymer. When it was in an acidic system (pH = 2.2 or 4), the rate of polymerization involving MAA was lower than the reactions at pH = 6. This was possibly caused by the fact that the acid concentration was higher inside the latex particles at these pH levels. The molecular weight of the copolymer product also depends on the pH of the reaction environment. In a more acidic environment, the polymerizations involving MAA promote radical desorption from particles, which leads to the formation of longer polymer chains (i.e. higher molecular weight) at constant monomer concentrations.

Other than experimental studies carried out in the batch reaction mode, seeded emulsion polymerizations were also used to produce St/BA/MAA latex particles with different morphologies. MAA was incorporated into semi-continuous seeded emulsion polymerization processes to prepare low viscosity high solids content (>60 wt.%) latexes with a multimodal particle size distribution.³¹⁻³⁴ The MAA polymerized in the water phase due to the homogeneous nucleation mechanism helps improve the latex shear stability. Several studies discuss the preparation of St/BA/MAA latex particles with core-shell structures. Okubo et al.³⁵ adjusted the pH of the two-stage emulsifier-free seeded emulsion polymerization process to ensure that the carboxyl groups would be located predominantly on the particle surface. Rios et al.³⁶ adjusted the MAA content in the shell

copolymer to control the latex particle shape and morphology. Mendizabal et al.³⁷ found that changing the pH of the reaction medium strongly affected the shell copolymer composition and thus, the stress-strain behaviour, the impact resistance, and the hardness of the materials. The copolymer prepared at lower pH values, with a greater incorporation of MAA, proved to be more rigid and tough.

Many studies on St/carboxylic acid or BA/carboxylic acid systems also provided useful information on the terpolymerization system. Zosel et al.³⁸ prepared BA/AA and BA/MAA copolymer latexes through batch polymerization processes. The dynamic mechanical measurements of films cast from the copolymer latexes showed that in the final BA/MAA latexes there was no water soluble copolymer in the serum, while about 90 wt.% of the MAA used was found inside the polymer particles and about 10 wt.% was located on the particle surface. Garrett et al.³⁹ developed pressure sensitive adhesives from BA/AA core-shell latex copolymers. The change of the AA content in the shell phase was correlated to the change of particle structure and was found to affect the adhesive properties of shear resistance and peel adhesion.

Saldivar et al.²⁷ studied the St/AA system and suggested that the change in the number of particles generated (through homogeneous nucleation) and the increase in the rate of radical desorption (favoured by the high solubility of AA in water) could affect the copolymerization kinetics. Their model predictions on the evolution of conversion and particle sizes were not very satisfactory due to uncertainties in parameters such as the termination rate coefficient for AA and the diffusion coefficient of both St and AA.

The influence of the pH and carboxylic acid content on the polymerization rate and the amount of carboxylic acid groups incorporated into the final latex products are

often of interest. The partitioning of carboxylic monomer between the aqueous and particulate phases is governed by its hydrophilic nature. As Shoaf and Poehlein^{11, 40} described, the increase in hydrophilicity of the oligomeric radicals can decrease the driving force for the radicals to penetrate into the hydrophobic core. Also, there is a potential barrier for penetration of these oligomeric radicals into the particles due to the build-up of AA homopolymer on the particle surface. Slawinski et al.⁴¹ indicated that at the beginning of the polymerization, pH had a minor influence on the polymerization because only St-rich oligomeric radicals entered the latex particles. However, because pH determines the hydrophilicity of the ionizing comonomers, it has a strong influence on the characteristics of the final latex polymer product. The negative charge on the dissociated (anionic) form of AA or MAA renders it more polar than the non-dissociated form, and thus increases its relative attraction for other polar molecules such as water and decreases its attraction for non-polar molecules such as St or BA. They showed the incorporation of acid groups on the surface of final latex particles was more efficient at lower pH.

Columns 5 and 6 in Table 2.5 show the ranges of initiator and emulsifier concentrations, respectively, used in various studies. These two variables, as well as their interactions, can affect the MWD and PSD of copolymer products. Garcia-Rejon et al.²⁶ used four levels of initiator and emulsifier concentrations together with two different comonomer ratios in batch processes in order to elucidate their effects on rheological properties of the molten copolymers. Changes in initiator and emulsifier content did not significantly affect the molecular weight and MWD of the final copolymers. However, their viscoelastic properties such as complex viscosity and storage modulus, changed

significantly as the amount of initiator increased. Since heterogeneous St/BA copolymers are usually obtained from batch processes, it is possible that they will display different rheological properties even though they have similar molecular weight characteristics. Yang and Yang¹³ isolated emulsifier concentration as the dominant factor affecting copolymer latex particle size. The MWD was shown to be sensitive to the interactions of initiator and emulsifier concentration changes. Chern and Lin⁴² had similar findings that the SLS concentration in the initial reactor charge is the predominant factor determining the particle size during semi-batch emulsion polymerizations of BA with AA or MAA.

Studies on CTA concentration (see column 7 in Table 2.5) are limited, though it is an important factor affecting the polymerization kinetics and the MWD of the copolymer product. Three different CTA concentrations were used in batch St/BA copolymerizations by Garcia-Rejon et al.²⁶ Kinetic analysis showed that CTA played an important role in the development of the molecular weight characteristics. An increase in CTA could cause significant reductions in both the viscosity and the storage modulus. Barudio et al.²⁴ looked at the effects of long and short chain mercaptan CTAs on kinetics and copolymer microstructure in emulsion St/BA batch and semi-batch reactions, carried out at the azeotropic composition. Experimental results were interpreted in terms of radical desorption and the diffusional limitations of the CTA between oil droplets and polymer particles. A more significant decrease in the polymerization rate was observed when mercaptans with shorter carbon chains (*t*-butanethiol compared to *n*-dodecanethiol) were added.

Zoco et al.⁴³ in line with the studies of Plessis et al.²⁹ investigated the effect of initiator, emulsifier and CTA concentrations on the copolymer microstructure in the

seeded emulsion copolymerization of St and BA (50/50 wt.%). They adjusted CTA concentration, aiming to control the MWD and the gel contents of copolymer products for coating and paint formulations.

Emulsion St/BA studies tend to be carried out at temperatures employed in industry, i.e. 50-80°C, as shown in Table 2.5 (see column 8). Temperature can greatly affect the rate of polymerization.¹³

An important aspect of the copolymerization studies described in Table 2.5, involves the process feed type (see column 9). Garcia-Rejon et al.¹⁶ used semi-batch processes to produce homogeneous St/BA copolymers in which the comonomer ratios were different. The monomer feeding rates were varied for the different cases. Reactions were run under monomer starved-feed conditions so that there was a linear relationship between the copolymerization rate and the monomer feed rate. The average copolymer molecular weight decreased as the feed rate increased, independent of the St/BA ratio. The average latex particle sizes generally increased in direct proportion to the feed rate. Agglomeration was found in the later stage of polymerization when the comonomer mixture was rich in St. Galimberti et al.¹⁹ carried out batch and semi-batch St/BA emulsion copolymerizations. They found that copolymers with constant composition were obtained during the process by properly adjusting the initial monomer/water ratio to take advantage of different monomer solubilities in the aqueous phase.

Statistical experimental design techniques can help elucidate effects from experiments with many factors. Two good examples are Yang and Yang¹³ and Saldivar et al.²⁷ Yang and Yang¹³ used a 2^{5-1} factorial design of experiments to investigate the St/BA system and found that the comonomer ratio, reaction temperature and emulsifier

concentration as well as the interactions among them were the key variables affecting the polymerization rate and MWD in their batch reactions.

Saldivar et al.²⁷ performed modeling and multiple level factorial experimental studies of styrenic emulsion copolymerization systems including St/BA copolymers. Two monomer ratios were used together with different levels of initiator and emulsifier in batch reactions to compare their model predictions with experimental results on conversion-time and particle size-conversion plots. The model quantitatively agreed with the experimental data on conversion-time but displayed lack of fit in predicting the evolution of particle size with reaction conversion.

A general review of the experimental studies mentioned above served as a good starting point to help determine the reaction conditions for our research. The next step is to look at some of those important factors guided by rigorous statistical experimental design techniques so that the effect of these variables as well as their interactions on the copolymer microstructure and product performance properties can be systematically investigated.

2.4 Performance properties of latex copolymers used for coatings

Organic coatings are used mainly to improve the appearance of, and to protect, the substrate. Most of them must withstand a certain range of potential mechanical damage. They must also adhere to the substrate, withstand the effects of weather, and protect the substrate from corrosion.⁴⁴ Their mechanical properties such as flexibility, solvent resistance, and adhesion are important to perform those functions effectively. Since the polymeric binder is the most important ingredient in a coating formulation, its

basic physical properties will determine most of those coating performance properties. Thus, the establishment of relationships between the polymer structure as well as its physical properties and coating performance is desirable because such relationships make it possible to design a polymer structure that will result in improved coating performance.⁴⁵

Tests are usually conducted to study polymer physical properties such as stress-strain, transient properties and dynamic mechanical properties. Stress-strain results include important properties such as modulus, tensile strength, and elongation. Transient property determination investigates the creep and stress relaxation of the polymer. The dynamic mechanical analysis studies the polymer viscoelasticity that is temperature and frequency dependent. These properties all depend upon the polymer structure, its molecular weight and distribution.

Mechanical tests are carried out to determine the coating performance such as its hardness, flexibility, impact resistance, solvent resistance, abrasion resistance, and adhesion to the substrate. These tests tend to be specific to the coating field. The results are often used to establish product specifications and to confirm a coating meets those specifications.

Comparing the results from these two types of tests are often very useful for developing a more complete understanding of coating performance. It helps establish the relations between the coating performance and the polymer latexes structure and basic physical properties. In this study, dynamic mechanical analysis will be used to study the viscoelastic properties of the coating polymer and coating adhesion will be used as an example to evaluate its performance. Then, the coating adhesion results can be linked to

the inherent properties of latex copolymer such as copolymer composition, molecular weight and distribution and latex particle size distribution so that meaningful predictions on performance properties from process conditions can be made.

2.4.1 Dynamic mechanical analysis (DMA)

The copolymers used to prepare coatings are *viscoelastic* in nature. An ideal *elastic* material will elongate under a tensile stress in direct proportion to the stress applied, according to Hooke's law. When the stress is released, the material will return to its original dimensions instantaneously. An ideal *viscous* material, a Newtonian fluid, will also elongate in direct proportion to the stress when a stress is applied. However, in contrast to the ideal elastic material, it will not return to its original dimensions when the stress is released, i.e. the deformation is permanent. Almost all coatings, as the polymers from which they are prepared are *viscoelastic*, they exhibit an intermediate behaviour between those two. Dynamic mechanical analysis (DMA) can provide a rather clear separation of elastic and viscous responses of viscoelastic polymeric materials.⁴⁶

In a shear DMA test, an oscillatory strain at a certain frequency is imposed on a dry film specimen and the resulting oscillatory stress is measured. Stress lags behind strain by an amount, δ , which can be expressed as an angle. The response is interpreted in terms of the dynamic Young's modulus, G^* , and the separated responses result in the "storage modulus", G' , associated with the elastic part of the response and the "loss modulus", G'' , associated with the viscous part of the response. The ratio of G''/G' is the viscous response expressed relative to the elastic response, also referred to as the

“damping factor”, $\tan \delta$. Frequency or temperature scanning can be used in DMA to determine the dependence of modulus on various frequencies or temperatures. From G'' vs. frequency or temperature and $\tan \delta$ vs. frequency or temperature plots, transient properties such as glass and other transitions can be determined. Other information that can be obtained from these loss plots includes the sample homogeneity and its gel content. In addition to its general use to reveal structure/property relationships, progress is being made in establishing property/property relationships between DMA plots and the results of coating tests for hardness, flexibility, impact resistance, and solvent resistance.⁴⁷ For example, good flexibility and impact resistance of films made from latex polymers are often associated with low temperature loss peaks. Horiuchi and Sato⁴⁸ also showed the relationship between the storage modulus of air-drying coating films and coating peel adhesion of a urethane coating. To that end, DMA testing can be a useful tool to correlate the latex polymer microstructure and end-use properties for coating applications.

There are more examples of DMA studies on styrene/acrylic latex copolymers in the literature. Mendizabal et al.³⁷ studied the effect of pH on the mechanical properties of St/BA/MAA latex copolymers. DMA showed that a more rigid material with good impact resistance was obtained when the incorporation of MAA into the particle was favoured at low pH levels (pH = 2.0). In Zhao et al.⁴⁹, DMA of latex films from copolymer of BA and other acrylic monomers such as 2-EHA and MMA indicated that there were hard polymer microdomains as the dispersed phase in the continuous soft polymer phase within the particles. There were also indications that the microdomains were bound to the continuous polymer phase. The inclusion of hard microdomains into a

soft continuous phase may lead to some mechanical property improvement such as improved film tensile strength and elongation. In Schuler et al.⁵⁰, DMA was used to verify the presence of two distinct polymer phases with the hard phase acting as transparent filler in BA/MMA/AA latex copolymers. The results showed that an increase in the amount of the hard phase (pAA) resulted in an increase in the storage modulus, leading to reduced tack and corresponding improved block resistance. Cerrada et al.⁵¹ used DMA to study viscoelastic relaxations of pBA grafted with pSt. The results showed that the transition region of the copolymer was broadened as the amount of grafted pSt increased. Young's modulus and microhardness also increased as the rigid pSt graft content increased because pSt grafts introduced stiffness into the copolymer structure. The DMA indicated that there might be a unique phase of both components in this type of graft copolymer.

2.4.2 Coating adhesion

Organic coatings are applied to a variety of substrate materials such as plastics, woods, and metals for decorative and protective applications. In each case, it is imperative that the coating adheres well to the substrate. Accordingly, adhesion assessment should be an integral part of coating development. It seems to be a straightforward task, but in fact, coating adhesion is very complex.⁵² ASTM D907 on Terminology of Adhesives defines adhesion as “the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action or both”. If the coating adhesion is interpreted as the bonding of polymeric coating with the substrates, this bonding strength should consist of two forces: the adhesive forces

sticking the coating material and the substrate together and the cohesive forces holding adjacent molecules of the coating material together.⁵³

For such interfacial forces to develop, the coating material must make intimate, molecular contact with the substrate surface. The process of establishing continuous contact between a coating and the substrate is known as “wetting”. Good wetting is a necessary criteria for adhesion. The extent of contact and resulting bond strength are functions of wetting energetics.

As indicated in Fig. 2.1, the Young equation can express the force balance between the liquid (coating material) and the solid substrate:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (19)$$

where γ_{LV} is the liquid-vapour interfacial tension, θ is the contact angle, γ_{SV} is the solid-vapour interfacial tension, and γ_{SL} is the solid-liquid interfacial tension.

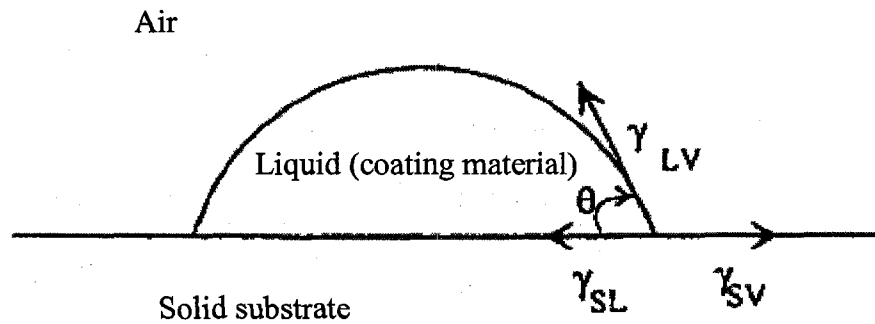


Figure 2.4 Schematic of contact angle in an air/liquid/solid substrate system

The Dupre equation expressed the work of adhesion W_A as:

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (20)$$

Substitution of the Young equation into the Dupre equation results in the Young-Dupre equation that states:

$$W_A = \gamma_{LV} (1 + \cos \theta) \quad (21)$$

The work of adhesion is approaching a maximum when the contact angle θ goes to 0, i.e. when the liquid completely spreads on the surface of the solid. This condition implies that there are stronger forces between molecules of the liquid and the substrate than between the liquid molecules themselves. Thus, the lower the contact angles, the more the interfacial area of contact, which generally yields improved adhesion. Poor wetting causes less actual area of contact between the coating and substrate, which results in lower overall coating adhesion.

The surface energy of a coating is largely controlled by the base polymer structure/composition in the coating formulation. Other factors such as the polarity and surface functionality of the polymer molecules also affect its surface tension and often account for the great improvement in adhesion. For example, addition of carboxyl functionality to polymers is usually used to improve the adhesion of acrylics, polyester, and olefin polymers to polar substrates.⁵³ In addition to initial wetting, intimate wetting shall remain intact until the coating solidifies and renders a continuous film. The coating rheology and its proper spreading kinetics are required to ensure such close contact. The major property affecting its flow is viscosity and, hence, the polymer molecular weight and molecular weight distribution.

Thermodynamic wetting is necessary but not sufficient for good coating adhesion. The next step toward getting good adhesion is to have strong bonding strength between the substrate and the coating, which requires good adhesive and cohesive forces. Both

these two forces are the result of interactions existing between atoms or molecules, which can be attributed to either primary or secondary valence forces. Primary or short-range molecular interactions include covalent and electrostatic forces that can result from chemical reactions provided by surface treatments. Secondary or long-range molecular interactions include van der Waals forces arising from hydrogen bonding and physical adsorption of polymer molecules onto the substrate.

Various mechanisms which may influence adhesion between the coating and the substrate has been reviewed as follows⁵²: **Weak boundary layer theory** suggests that a weak boundary layer near the interface between coating and substrate having a low cohesive force results in poor adhesion. Thus it is necessary to eliminate such a layer in coating film formation in order to obtain good adhesion. **Diffusion theory** explains that improved adhesion can be obtained if macromolecular diffusion between two compatible polymer materials occurs across the coating/substrate interface. **Chemical bonding theory** suggests that good adhesion is obtained when covalent bonds are formed at the interface by reactions of functional groups such as carboxyl, hydroxyl, amino, and epoxy groups. **Mechanical theory** shows better adhesion can be obtained by the mechanical anchoring of the coating to the substrate. Therefore, increasing the substrate surface roughness to allow mechanical interlocking is one of the ways to improve adhesion.

As mentioned previously, good cohesive strength is required as well to prevent rupture inside the film and keep the coating material lasting long. The cohesive forces are influenced mainly by the mobility of the polymer chain, which is affected by factors such as molecular weight and MWD, crosslinking and hydrogen bonding present in the polymer chain structure.⁵³ A certain amount of chain flexibility is desirable since it helps

spread the applied energy over a greater number of atoms and, thus, gives the bond a better chance to resist stress. Yet, too much flexibility may lead to poor temperature resistance or plastic flow under heavy load.

Examples showed that resistance to peel and shear mostly depend on the polymer MWD.⁵⁴ Intermediate molecular weight polymers have a good resistance to peel but this property is lost for high ($\geq 1,000,000$ g/mol) and low ($\leq 100,000$ g/mol) molecular weight polymers. High molecular weight polymers show a good resistance to shear but this property decreases as molecular weights decrease. Meanwhile, for intermediate molecular weight polymers, the copolymer composition profile had an impact on the adhesion as well.⁵⁵ The resistance to shear increased as the copolymer heterogeneity increased while resistance to peel was higher for copolymers with a controlled composition profile. These results suggest that polymer chains with high molecular weights provide cohesive strength and mechanical resistance while polymer chains with low molecular weights impart compatibility and adhesion. In practice, a balance among these properties is desirable, which requires polymers with a proper distribution of molecular weights.

Tobing and Klein^{56, 57} showed that polymeric networks with interconnected macromolecular structures improved the cohesive strength. It depends on several molecular parameters such as the entanglement molecular weight (M_e), weight average molecular weight (M_w), molecular weight between crosslinks (M_c), and gel content.

As we can see, coating adhesion depends mainly on the dispersion forces possessed by all molecules, then on a means of bringing these into effect by close proximity, and lastly on the cohesive behaviour of the coating material (i.e., its strength,

flexibility, and response to temperature). The bond strength is a function of all factors such as the chemical or physical nature of the bond, the degree of bond formation, and the rheological properties of the bonding phases.

Coating systems can vary in the type of base polymer binder and various formulating agents such as cross-linking agents, rheology control agents, solvents or diluents. The chemical structure and physical properties of the base polymer and these additives will influence the way in which the film is formed, the internal stresses in the cured film, and its adhesion onto the substrate. Satisfactory performance can be obtained by proper selection of its composition, MWD, gel contents, solid contents, and hence, proper polymerization conditions to make the polymer.

2.4.3 Overview of coating adhesion test methods

After the coating adhesion process is reviewed, the next question would be how to measure the adhesion. So far, there is no single test capable of assessing all aspects of coating adhesion.⁵² In practice, a series of tests are used to evaluate the adhesion by inducing rupture in different modes. The criteria that is essential for a test to warrant large-scale acceptance are: using straightforward and unambiguous procedures, being relevant to its intended application, being reproducible and quantifiable, i.e. having a meaningful rating scale for assessing performance.

There are generally two types of testing methods: implied and direct tests. Implied tests include indentation or scribe techniques, rub testing and wear testing, which is usually used to assess coating performance under actual service conditions. Direct tests such as peel, lap-shear, and direct tensile are used to measure the coating adhesion in a

single discrete quantity: the force required to fracture the bond between coating and substrate. The peel adhesion and direct tensile tests are compared below to demonstrate our choice of the adhesion test method for this study.

The tape test ASTM D3359 to measure peel adhesion has widespread popularity since it has the advantages of being simple and economical to perform. This test consists of cutting the coating into 100 1mm×1mm squares (crosshatch), applying tape to the crosshatched area, and quickly ripping the tape from the coating. The level of adhesion is rated by visually comparing the sample to a series of five standards depicted in the ASTM method.

This test was originally designed for ductile coating applied to metal substrate. Thus, it was found not being related to the coating's intended application on plastic parts and lacking reproducibility.⁵⁸ The lack of reproducibility results from the testing tape it requires and its testing procedures. There is no agreement on which tape will likely be suitable for testing all coatings. The testing procedure requires that the free end of the tape be removed rapidly at as close to a 180° angle as possible. If peel angle and rate vary, the force required to remove the tape can change dramatically. Also, the coating performance in the tape test is based on the amount of coating removed compared to a relative scale. In case of clear coatings for plastics, it is difficult to identify the regions of the coating that have been removed by the tape pull since the coating and substrate are both transparent. Both the angle and rate of tape removal and the visual assessment of the tested sample needs operator skills and thus, the testing accuracy and reproducibility rely largely upon the skill of the operator and their ability to perform the test in a consistent manner. As a result, the tape test is a semi-quantitative method. It serves as an indicator

that some minimum value for bond strength was met or exceed instead of giving an absolute value for the force required for bond rupture. With revision, it can have real meaning but more so as a quality control tool than for determining actual adhesion.

Another long-used approach to coating adhesion testing is the direct tensile test. The determination of coating removal force by direct tension shows its potential as a quantitative means of determining adhesion levels.⁵⁸ A dolly or stud is bonded to the coating film. The force that is normally applied to the joint to remove the film is then measured. If failure occurs at the film/substrate interface, this force is taken to be the “force of adhesion”. It is essential that the force is applied strictly in the normal direction to the sample and that no bending moment is active across the test area. Deviations from symmetry in the test arrangement, poor alignment, differentiation from the homogeneity and thickness of the coating and/or adhesive layer, and random variation in the strength of the bond between film and substrate can affect test results.

There are two existing ASTM standards for both laboratory and field versions of direct tension tests for coatings. ASTM D 4541 defines a class of portable pull-off adhesion testers for field evaluation of coating adhesion. ASTM D 5179 defines the test method for measuring the adhesion of organic coatings to plastic substrates using a laboratory tension test apparatus. The base substrate is a 3” diameter plastic disc. A carefully prepared aluminum stud is bonded directly to the coated, cured substrate using cyanoacrylate adhesives. The adhesive is allowed to cure for two hours at room temperature. This joint is then placed in a specially designed restraining device with only the stud protruding. The whole assembly is installed in the Instron® tensile tester which records removal forces. The tester is equipped with an upper coupling adapter, together

with a sample restraining device to provide sample alignment and minimal substrate flexing. The tension test is conducted and the pull strength is recorded.

Provided that certain variables are controlled, the coating should preferentially adhere to the plastic disc and be removed from the base substrate. A test is judged satisfactory if the stud/disc assembly is pulled clearly away from the base substrate with a minimum of or no coating material being removed. Each specimen is rated according to type of failure as follows:

- A Adhesive failure of the coating from the substrate
- C Cohesive failure in the coating
- AC Combination of adhesive failure at the coating/substrate interface and
 cohesive failure in the coating
- S Adhesive failure at the stud
- CS Combination of adhesive failure at the stud and cohesive failure in the
 coating

Coating should have pulled off uniformly over the entire stud surface either with adhesive failure from the substrate (failure mode A) or cohesive failure in the coating (failure mode C). The failure must be at least 90% A or C. Five specimens of each coated substrate are tested one day and the other five on a second day. Pull strength for the ten runs on each coating/substrate assembly are averaged and reported.

A reproducible test of this type offers the advantage to yield quantitative results of the force required for coating removal, compared to the more qualitative and subjective tape tests.

As mentioned earlier, one of the objectives of this project is to uncover mathematical relations between latex polymer properties and emulsion polymerization process conditions. To accomplish this goal, process conditions such as the monomer composition, carboxylic acid contents, and chain transfer agent contents will be manipulated to produce different copolymer products. Meanwhile the DMA test and the coating adhesion test will be used as two measures to evaluate the performance of the latex copolymer specific to its use as a coating binder. These performance properties must be linked to inherent properties such as copolymer composition, MWD, gel contents and latex PSD so that meaningful predictions on performance properties from process conditions can be made.

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**CHAPTER 3 Semi-continuous Emulsion Copolymerization of
Styrene-Butyl Acrylate with Methacrylic Acid: Screening
Design of Experiments**

(PAPER 1)

Semi-continuous Emulsion Copolymerization of Styrene-Butyl Acrylate with

Methacrylic Acid: Screening Design of Experiments

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ABSTRACT

A 2^{5-1}_{III} fractional factorial screening design of experiments was conducted to identify the effects of five variables, i.e., styrene/butyl acrylate ratio, methacrylic acid content, pH, emulsifier content, and chain transfer agent content on various product properties in the emulsion copolymerization of styrene/butyl acrylate. The monomer-starved semi-batch feed policy was used to ensure the production of homogeneous latex copolymers. The impact of these variables on the carboxylic acid distribution in the latex, the average latex particle diameter, the molecular weight and distribution of the polymer products, the glass transition temperature of the polymer, and the coating adhesion to a plastic substrate was studied.

Inside the chosen experimental region, the St/BA ratio is the key factor influencing the copolymer glass transition temperature. Results also showed that the pH of the reaction contents would affect the distribution of carboxylic acid. Higher pH led to more anionic form of the acid reacting in the water phase or on the latex particle surface. The latex particle size was found to be greatly influenced by the emulsifier content. Statistical analysis showed that the CTA concentration and the pH, as well as their 2-factor interaction significantly affected the number-averaged molecular weight. The CTA content was also the key factor influencing the weight-averaged molecular weight. The

pull-off adhesion between the latex coating and a polycarbonate substrate was found to be influenced by the pH. The adhesion forces increased as the pH of the reaction mixture increased.

3.1 INTRODUCTION

Organic coatings are used mainly to improve the appearance of, and to protect, a substrate. They must adhere to the substrate and must also withstand a certain range of potential mechanical damage.¹ Mechanical properties of coatings such as flexibility, solvent resistance, and adhesion are important to perform their functions effectively. Since the polymeric binder is the major component in a coating formulation, its microstructural properties such as polymer composition, molecular weight distribution, crosslinking and gel content will determine most of the coating performance properties. In order to maintain the structural properties in well-defined values to produce polymers useful for commercial coating and paint applications, it is necessary to understand the relationship between the polymerization conditions and polymer microstructure.²

Emulsion copolymerization of styrene (St) and n-butyl acrylate (BA) allows for the preparation of copolymer for latex paints and coatings with a wide range of properties such as colloidal stability, impact and solvent resistance, elasticity and compatibility. Systematic experimental studies have been conducted on the St/BA emulsion copolymerization to investigate different factors as well as their interactions on the copolymer microstructure and product performance. Different operational variables as well as various reactor configurations (batch, semi-batch, and continuous) and control strategies were identified which affect the polymerization process and the chemical and physical properties of the latex and copolymer products. These variables include the temperature, comonomer type and content, pH of the reaction mixture, initiator type and concentration, chain transfer agent (CTA) concentration, and surfactant type and concentration.³⁻⁹

Introducing comonomers serves to manipulate the glass transition temperature (T_g) of the formulation; and its molecular weight and distribution can also be modified to change the polymer viscoelastic properties related to its chain mobility, hence the mechanical properties of the final products.¹⁰ A wide range of comonomer ratios (St/BA) was used (from 10/90 to 90/10 weight ratio) by various research groups. This variable can greatly affect the rate of polymerization and the MWD due to the BA chain transfer to polymer reaction. Garcia-Rejon et al.³ used semi-batch processes with monomer starved-feed conditions to produce homogeneous St/BA copolymers. Their results showed a linear relationship between the copolymerization rate and the monomer feed rate. Cruz-Rivera et al.⁵ performed emulsion copolymerizations with three different comonomer ratios and obtained homogeneous copolymers using semi-batch processes. Their focus was on how the comonomer ratios and the reaction pathway affect the particle morphology, the molecular weight and colloidal properties. Models were developed to explain the evolution of copolymer composition and glass transition behaviour. The latexes displayed a particle size decrease with increasing St content. Higher molecular weights were also observed when the BA content was increased, probably due to its decreasing cross-termination rate constant. Yang and Yang⁶ found the same trends under batch conditions. Saldivar et al.⁸ also observed that the parameters for the gel effect of BA and micelle surface area covered by an emulsifier molecule increased with the increase of BA content in the monomer mixture. The kinetic studies in Cruz-Rivera et al.⁵ showed that the reactivity ratios determined in batch emulsion polymerization at low conversion were close to those obtained in bulk or solution polymerization.

In seeded semi-batch emulsion copolymerizations of St and BA at 75°C, Plessis et al.⁹ varied the St contents in the monomer feed by a small amount (less than 10 wt.%). They found that the change in the St/BA ratio had a significant impact on both the reaction kinetics and the copolymer microstructure. The higher the St content was in the monomer feed, the lower the gel fraction and the branching level and the higher the weight-average molecular weight of the sol polymer were found in the copolymers. These, in turn, influenced the properties of adhesives derived from the latexes.

Carboxylic acid monomers such as AA and MAA are typically included in emulsion polymerizations to improve overall latex properties.¹¹ The introduction of these monomers can improve the shear and freeze-thaw stability of latexes used as binding agents in paints, bring desirable viscosity profiles vs. pH, improve the polymer film mechanical properties, and have a positive effect on polymer adhesion towards substrates such as metals and clays.¹² For the St/BA/carboxylic acid system, the three monomers have significantly different reactivity ratios and solubility in water. The loci of polymerization and copolymer composition will highly depend on the equilibrium of monomers in the different phases. Charmot et al.¹³ investigated the partitioning of the polymerized AA monomers between the aqueous phase, the particle surface and particle core. The proposed model was shown to be very sensitive to the partition coefficients of the AA between the water and polymer phases. Santos et al.¹⁴ investigated the effect of pH on the reaction kinetics and the acid group distribution of AA and MAA in different phases within the St/BA system. Compared to MAA, which is more hydrophobic, the AA monomer was more equally distributed throughout the system. MAA was found at higher concentrations inside the latex particles at the same pH. As a result, the effect of pH on

the partitioning of MAA in different phases has a more significant impact on the glass transition temperature (T_g) of the copolymer. When it was in an acidic system (pH = 2.2 or 4), the rate of polymerization involving MAA was lower than the reactions at pH = 6. This was possibly caused by the fact that the acid concentration was higher inside the latex particles at these pH levels. The molecular weight of the copolymer product also depends on the pH of the reaction environment. In a more acidic environment, polymerizations involving MAA promote radical desorption from particles, which leads to the formation of longer polymer chains (i.e., higher molecular weight) at constant monomer concentrations.

Other than experimental studies carried out in the batch reaction mode, seeded emulsion polymerizations were also used to produce St/BA/MAA latex particles with different morphologies. MAA was incorporated into semi-continuous seeded emulsion polymerization processes to prepare low viscosity high solids content (>60 wt.%) latexes with a multimodal particle size distribution.¹⁵⁻¹⁸ The MAA polymerized in the water phase due to the homogeneous nucleation mechanism helps improve the latex shear stability. Several studies discuss the preparation of St/BA/MAA latex particles with core-shell structures. Okubo et al.¹⁹ adjusted the pH of the two-stage emulsifier-free seeded emulsion polymerization process to ensure that the carboxyl groups would be located predominantly on the particle surface. Rios et al.²⁰ adjusted the MAA content in the shell copolymer to control the latex particle shape and morphology. Mendizabal et al.²¹ found that changing the pH of the reaction medium strongly affected the shell copolymer composition and thus, the stress-strain behavior, the impact resistance, and the hardness

of the materials. The copolymer prepared at lower pH values, with a greater incorporation of MAA, proved to be more rigid and tough.

Studies on St/carboxylic acid or BA/carboxylic acid systems also provided useful information on the terpolymerization system. Garrett et al.²² developed pressure sensitive adhesives from BA/AA core-shell latex copolymers. The change of the AA content in the shell phase was correlated to the change of particle structure and was found to strongly influence the adhesive properties of shear resistance and peel adhesion. For a latex particle shell with overall acrylic acid contents up to 5 mol% BA, its shear resistance increased with AA content whereas peel adhesion decreased with AA content. When higher AA contents (32-49 mol%) were used in the shell formulation, both shear resistance and peel adhesion decreased with the AA content. Saldivar et al.⁸ studied the St/AA system and suggested that the change in the number of particles generated (through homogeneous nucleation) and the increase in the rate of radical desorption (favoured by the high solubility of AA in water) could affect the copolymerization kinetics. Their model predictions on the evolution of conversion and particle sizes were not very satisfactory due to uncertainties in parameters such as the termination rate coefficient for AA and the diffusion coefficient of both St and AA.

The influence of pH and the carboxylic acid monomer content on the polymerization rate and the amount of carboxylic acid groups incorporated into the final latex products are often of interest. Shoaf and Poehlein²³ investigated the partitioning of AA and MAA between the particle and the aqueous phase using a thermodynamic approach. They described how an increase in hydrophilicity of the oligomeric radicals decreased the driving force for the radicals to penetrate into the hydrophobic core of the

polymer particle. The reaction rates of both the St and carboxylic acid monomers decreased as the overall degree of acid neutralization increased. In a seeded batch emulsion polymerization of St and AA, Slawinski et al.²⁴ also showed that the incorporation of acid groups on the surface of final latex particles was more efficient at lower pH.

The surfactants play the roles in the nucleation of latex particles, emulsification of monomer droplets, and stabilizing latex particles during the polymerization and during the shelf life of the latex. Yang and Yang⁶ isolated emulsifier concentration as the dominant factor affecting copolymer latex particle size. Chern and Lin²⁵ had similar findings that the SLS concentration in the initial reactor charge is the predominant factor determining the particle size during semi-batch emulsion polymerizations of BA with AA or MAA.

The surfactant also has strong influence on the film formation as well as the latex film properties such as adhesion to various substrates and their mechanical strength.²⁶ Anionic surfactant such as sodium dodecyl sulfate (SDS) is not homogeneously distributed in the film. It tends to segregate towards the open surface of film and film-substrate interface. If the surfactant is on the film-substrate interface, a weak boundary layer may occur and can seriously damage the coating adhesion.²⁷

CTA concentration is an important factor affecting the polymerization kinetics and the MWD of the copolymer products and hence the evolution of their principle adhesive properties such as tack, peel and shear resistance. Three different CTA concentrations were used in batch St/BA copolymerizations by Garcia-Rejon and Rios.⁴ Kinetic analysis showed that an increase in CTA caused significant reductions in both the

viscosity and the storage modulus of the copolymer products. Barudio et al.²⁸ looked at the effects of long and short chain mercaptan CTAs on kinetics and copolymer microstructure in emulsion St/BA batch and semi-batch reactions, carried out at the azeotropic composition. Experimental results were interpreted in terms of radical desorption and the diffusional limitations of the CTA between oil droplets and polymer particles. A more significant decrease in the polymerization rate was observed when mercaptans with shorter carbon chains (*t*-butanethiol compared to *n*-dodecanethiol) were added.

Zoco et al.²⁹, in line with the studies of Plessis et al.⁹ investigated the effect of initiator, emulsifier and CTA concentrations on the copolymer microstructure in the seeded emulsion copolymerization of St and BA (50/50 wt.%). CTA contents were adjusted in order to control the MWD and the gel contents of copolymer products for coating and paint formulations. Zubitur et al.³⁰ studied the agitation effect on semi-batch St/BA emulsion copolymerizations and found that in the presence of CTA, the polymer molecular weights decreased with increasing agitation rate, whereas they increased in the absence of CTA. It is possibly due to the fact that there are diffusion limits on the CTA that affect the copolymer molecular weights during the reaction.

Elizalde et al.³¹ showed that while for non-linear copolymers, gel fraction and branching levels must also be taken into account when characterizing the adhesive properties with MWD data, resistance to peel and shear mostly depend on the polymer MWD for linear copolymers. Intermediate molecular weight polymers have a good resistance to peel but this property is lost for high ($\geq 1,000,000$ g/mol) and low ($\leq 100,000$ g/mol) molecular weight polymers. High molecular weight polymers show a good

resistance to shear but this property decreases as molecular weights decrease. Meanwhile, for intermediate molecular weight polymers, the copolymer composition profile had an impact on the adhesion as well.³² The resistance to shear increased as the copolymer heterogeneity increased while resistance to peel was higher for copolymers with a controlled composition profile. These results suggest that polymer chains with high molecular weights provide cohesive strength and mechanical resistance while polymer chains with low molecular weights impart compatibility and adhesion. In practice, a balance among these properties is desirable, which requires polymers with a proper distribution of molecular weights.

Statistical experimental design techniques can help elucidate effects from experiments with many factors. Two good examples are Yang and Yang⁶ and Saldivar et al.⁸ Yang and Yang⁶ used a 2^{5-1} factorial design of experiments to investigate the St/BA emulsion polymerization batch process. A detailed regression and variance estimate analysis was carried out to identify important process conditions such as the comonomer ratio, reaction temperature, initiator and emulsifier contents as well as the their interactions to affect the polymerization rate, particle size and molecular weight distribution.

Saldivar et al.⁸ performed modeling and multiple level factorial experimental studies of styrenic emulsion copolymerization systems including St/BA copolymers. Two monomer ratios were used together with different levels of initiator and emulsifier in batch reactions to compare their model predictions with experimental results on conversion-time and particle size-conversion plots. The model quantitatively agreed with

the experimental data on conversion-time but displayed lack of fit in predicting the evolution of particle size with reaction conversion.

A general review of the experimental studies mentioned above served as a good starting point to help determine the reaction conditions for our research. The next step is to look at some of those important factors such as St/BA monomer contents ratio, MAA contents, pH, SDS and CTA contents guided by rigorous statistical experimental design techniques so that the effect of these variables as well as their interactions on the copolymer microstructure and product performance properties can be systematically investigated. Screening designs of higher resolution are desirable for effects that may be hidden or difficult to interpret. Thus, a 2^{5-1} fractional factorial design of experiments was chosen to estimate the main effects of the five variables on selected properties such as T_g , molecular weight and distribution of the polymer as well as the latex film adhesion to plastic substrates.

3.2 EXPERIMENTAL SECTION

3.2.1 Materials

Monomers St (99%, Aldrich Chemical Co. Inc.), BA (99+%, Aldrich Chemical Co. Inc.), and MAA (99%, Aldrich Chemical Co. Inc.) were purified using classical methods.³³ Inhibitor was removed from St and BA according to previously described procedures. Then St and BA, as well as MAA were distilled under vacuum at most 24 h before use and stored at -10°C . Potassium persulfate (KPS, 99+%, Aldrich Chemical Co. Inc.) was used as a free-radical water-soluble initiator, sodium dodecyl sulfate (SDS, 90%, Aldrich Chemical Co. Inc.) was used as an emulsifier. Sodium bicarbonate

(NaHCO_3 , 98%, Aldrich Chemical Co. Inc.) was used as a pH buffer. The chain transfer agent (CTA) 1-dodecanethiol (98+%, Aldrich Chemical Co. Inc.) as well as all the solvents for characterization of copolymers such as ethanol, acetone- d_6 (99.9 atom% D, CDN isotopes), tetrahydrofuran (THF, 99.92%, EMD) was used as received without further purification. In all polymerization runs, distilled-deionized (DDI) water was used.

3.2.2 Experimental configuration and emulsion polymerizations

All emulsion polymerizations were conducted in semi-continuous mode. The reactions took place isothermally in a Labmax® (Mettler-Toledo) reaction system equipped with an “in-house” stainless steel reactor. The jacketed 1.2-L reactor was equipped with a condenser, feed and sampling ports, an initiator loading cell, and an anchor stirrer. There were two sets of liquid reagent charging systems each with a bottle, a pump and feed lines connected to the feed port. One was used to feed monomer mixtures into the reactor during semi-batch runs and the other was used to feed the buffer solution. The reflux condenser was equipped with a rupture disk, a relief valve and a vent line. The stirring speed (200 rpm), temperature ($60 \pm 0.1^\circ\text{C}$) and feeding rates were all controlled using the Camille™ program (Mettler-Toledo). The reactor was also coupled with a pH meter to monitor the pH during the reaction. The total reaction time for all runs was 420 min reaching high monomer conversion.

Pre-determined amounts of SDS and DDI water were first charged into the reactor. The reactor was then sealed and heated while under agitation at 200 rpm and purged for 30 min with nitrogen. When the temperature of the reactor contents reached the set point, the initiator solution was charged to the reactor. N_2 purging was continued for about 5 min thereafter.

Monomers and CTA were mixed at a particular ratio and were transferred into the reagent charging system. The monomer mixture feed was started when the temperature inside the reactor was stabilized at 60°C. The feed rate was kept constant for 360 min. The total charge was up to 1L. Samples were taken at various time intervals over the course of polymerization. After the monomer mixture in the reagent charge system was depleted, the reactor was kept running for 60 more min. Samples and final latexes were treated with hydroquinone to prevent the reaction of residual monomers.

During the polymerization, the amount of buffer solution fed to the reactor was adjusted to control the pH of the reaction contents.

3.2.3 Analytical techniques

Conversion

Samples withdrawn from the reactor during the polymerization were analyzed gravimetrically to determine the instantaneous (based upon the total monomer fed until the sampling time) and overall monomer conversions, X_i and X respectively, as shown below:

$$X_i(t) = \frac{m_p(t)}{F_m \times t} \times 100\% \quad (1)$$

$$X(t) = \frac{m_p(t)}{m_m} \times 100\% \quad (2)$$

where $m_p(t)$ is the mass of polymer produced up to time t , F_m is the feeding rate of monomer mixture, and m_m is the total mass of monomer taking part in the reaction.

Copolymer composition

The cumulative copolymer composition of dried samples was determined by ^1H -NMR using a Bruker AMX500 Fourier-transform ^1H -NMR spectrometer. Copolymer samples were prepared as ~2% (w/v) solutions in acetone- d_6 , which was used as both the solvent and the reference. Analysis was carried out at room temperature. To record the spectra, the acquisition time was 4.6 s, and 16 scans were performed per readout (for averaging). All spectra exhibited good peak separations for a straightforward interpretation of the results. The relative amounts of monomer bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. For St/BA copolymers, the copolymer compositions were determined by comparison of the integrated intensities of the resonance signals due to the five phenyl proton of St (at approximately 6.5 ppm) and that due to the two protons of the methylene group in the ester group of BA (the $-\text{OCH}_2$ group at approximately 3.5 ppm).

Particle size

The latex particle size and distribution was measured by dynamic light scattering spectroscopy, DLS (90plus, Brookhaven Instruments Corp.). Samples were prepared by diluting a drop of latex sample in approximately 5 mL DDI water. Each measurement was taken at a 90° angle and an average of 6 measurements was recorded.

Molecular weight

A Waters Associates GPC system was used to determine the resulting polymer molecular-weight averages and molecular-weight distributions. It was equipped with three Waters Styragel-HR columns (10^3 , 10^4 , and 10^6 Å pore size) installed in series, heated to 30°C , and a Waters 410 differential refractometer heated to 38°C . THF (HPLC

grade) was used as the mobile phase and the flow rate was 0.3 mL/min. It was used as both the carrier fluid and the reference. Polymer samples were dissolved in THF to produce solutions with a concentration of 0.001-0.002 g/10mL and filtered through 0.45 μ m filters to remove any high molecular weight gel. 200 μ L of each solution was injected into the GPC and the data were analyzed using the Millennium 32™ (version 3.05) chromatography manager software. Using the universal calibration principle, given the Mark-Houwink K and α parameters of polymers in THF (polystyrene, K = 1.6×10^{-2} mL/g, α = 0.700³⁴; polybutyl acrylate, K = 1.1×10^{-2} mL/g, α = 0.708³⁵), polymer molecular weights were determined. The K and α values for the copolymers were obtained using weighted averages based on the cumulative copolymer composition data.

Gel content

An extraction process modified from Plessis et al.⁹ was used to determine possible gel contents of the dried polymer samples. About 0.1 g of polymer sample was weighed and placed between two PVDF membrane filters (pore size 0.45 μ m, diameter 47 mm, Waters). The rim of the two membrane filters was then heated and sealed to make a pouch. The weight of the membrane and the polymer sample was recorded. The pouch containing the polymer sample was immersed into a bottle of about 50 g THF solvent; the amount of THF was also recorded. In order to extract the soluble polymer continuously, the bottle containing THF and the polymer sample pouch was shaken for 24 h in a mechanical shaker. After 24 h, the pouch was rinsed with THF; dried and weighed. The gel fraction, gel%, was calculated using the following equation (3.3):

$$gel\% = \frac{m_{gel}}{m_{polymer}} \times 100\% \quad (3.3)$$

where m_{gel} and $m_{polymer}$ are the weights of insoluble polymer and the whole sample, respectively.

Glass transition temperature (T_g)

T_g of each copolymer samples were measured using a TA Instruments differential scanning calorimeter (DSC) MDSC Q100. Approximately 10 μ g sample was put into an aluminium sample pan and heated to 150°C to eliminate any thermal history. Then the sample was cooled from 110 to -60°C followed by a 2 min isothermal step. It was heated again from -60 to 110°C to determine the T_g . Cooling and heating steps were conducted at a rate of 10°C/min. The T_g values of each sample were taken through two replicate runs. The standard deviation for T_g measurements was determined to be 1.0 degree for each individual samples.

Carboxylic acid distribution

The distribution of carboxylic groups in the final latex was given by the amount of functional groups present in the aqueous phase, on the latex particle surface, and inside the particles. Hen³⁶ developed a conductometric titration method to determine the concentration of carboxyl groups bound at the surface of St/itaconic acid latex particles. Vijayendran³⁷ used the same method to study the effect of carboxylic acid concentrations and latex particle size on the acid distribution. The back titration conductometric analysis was also used to evaluate the amount of carboxylic groups present at the surface of the polystyrene (1) /poly(butyl acrylate – methacrylic acid) (2) core-shell latex particles.²⁰ About 12 g of latex sample were accurately weighted and then were diluted to approximately 4% solid contents with DDI water in a 400 mL beaker. Both sets of pH

meter (Orion Research Inc.) and the conductometer (Orion Research Inc.) were placed in the diluted latex. A magnetic stirring bar was used to ensure good mixing. The pH of the latex was adjusted to a pH of 11.5 ± 0.2 with addition of a 0.4098 mol/L NaOH solution. The latex was then titrated with a standard 0.02413 mol/L H_2SO_4 solution in a rate of about 1.0 mL/min. Both the conductance and pH of the latex were recorded as a function of the volume of standard H_2SO_4 consumed until a pH about 2.4 was reached.

Since all methods involving weak acid-base titration are very sensitive to the presence of CO_2 , the experiment was conducted with N_2 continuously purging the latex.

Adhesion testing

A laboratory tension test apparatus was built to measure the adhesion of sample coatings to plastic substrates according to the standard ASTM D 5179. The substrate was a 3-inch diameter Lexan[®] polycarbonate (PC) disc. Each final latex samples were cast on the substrate to obtain 100 μm dry film thickness. The coating film was then dried and conditioned for 1 week prior to testing at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. A carefully prepared aluminum stud was bonded directly onto the dry coating film on the PC disc with using cyanoacrylate adhesives. The Aluminum stud had a $\frac{3}{4}$ inch diameter. The stud face was sanded with a piece of 80-grit sandpaper, cleaned with acetone and heated in an oven at 120°C for 1 h. After the stud cooled down, 4 drops of cyanoacrylate adhesive was spread on the stud surface. Then the stud was quickly pressed onto the coated PC substrate. 2-kg weights were placed on the stud to ensure good contact between the stud, adhesive, and the coating surface. The adhesive was allowed to cure for 2 h and the testing specimen was conditioned for 24 h under $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity.

The stud-adhesive-coating-PC substrate joint was installed in an Instron® tensile tester with only the stud protruding. The Instron® tester recorded the forces to remove the coating film from the PC substrate. It had an upper coupling adapter, together with a sample restraining device made in the lab to provide sample alignment and minimal substrate flexing. The tension test was then conducted pulling the crosshead at 5 cm/min, and the pull strength was recorded with chart speed 30 cm/min.

A test was judged satisfactory if the testing joint was pulled clearly away from the base substrate with a minimum of or no coating material being removed. Each specimen was rated according to 5 types of failure as follows:

- A Adhesive failure of the coating from the substrate
- C Cohesive failure in the coating
- AC Combination of adhesive failure at the coating/substrate interface and cohesive failure in the coating
- S Adhesive failure at the stud
- CS Combination of adhesive failure at the stud and cohesive failure in the coating

Coating should have pulled off uniformly over the entire stud surface either with adhesive failure from the substrate (failure mode A) or cohesive failure in the coating (failure mode C). The failure must be at least 90% A or C in order to register a valid pull strength reading. Five specimens of each coated substrate were tested one day and the other five on a second day. Statistical analyses have shown no sample-to-sample differences on the pull-off strength results. Thus, the 10 readings of adhesion forces on each coating/substrate assembly were averaged and reported.

3.2.4 Experimental design

The effect of five variables: the weight ratio between the two monomers St and BA (St/BA, x_1), MAA concentration ([MAA], x_2), the pH of the reaction content (pH, x_3), the emulsifier concentration ([SLS], x_4), and the CTA concentration ([CTA], x_5) were examined using a 2^{5-1}_V factorial design as shown in Table 3.1. The design levels are coded “-” and “+” for the low and high values of each variable respectively. The unit “phm” in the table stands for parts per hundred parts monomer in the reaction contents. Other factors were kept constant: the desired latex solid contents (x_6) was around 38 wt%, the initiator concentration ([KPS], x_7) was 0.5 phm, and the reaction temperature (x_8) was 60°C.

Table 3.1 Variable levels for 2^{5-1}_V design with 5 factors

Variable	Name	Levels	
		-	+
x_1	Comonomer ratio (St/BA wt/wt)	25/75	35/65
x_2	[MAA]	2.5 phm	5.0 phm
x_3	pH	3.5	5.5
x_4	[SLS]	0.8 phm	1.5 phm
x_5	[CTA]	0.2 phm	0.6 phm

A 2^{5-1}_V factorial design was chosen to estimate the main effects and interactions of the five variables inside the experimental region. The overall design matrix of factors and levels for the 16 experimental runs is listed in Table 3.2. The sequence of individual runs was randomized when the experiments were carried out. The design was of resolution V, which means that the main effects were confounded with four-factor and greater interactions. Confounding was also present between two-factor and three-factor interactions. Although they cannot be completely neglected, three-factor and greater interactions in chemical process are generally assumed to be negligible.³⁸

Table 3.2 2^{5-1}_V design matrix with 5 factors

Run	x_1	x_2	x_3	x_4	x_5
1	-	-	-	-	+
2	+	-	-	-	-
3	-	+	-	-	-
4	+	+	-	-	+
5	-	-	+	-	-
6	+	-	+	-	+
7	-	+	+	-	+
8	+	+	+	-	-
9	-	-	-	+	-
10	+	-	-	+	+
11	-	+	-	+	+
12	+	+	-	+	-
13	-	-	+	+	+
14	+	-	+	+	-
15	-	+	+	+	-
16	+	+	+	+	+

3.3 RESULTS AND DISCUSSION

Emulsion copolymerization experiments with different St, BA, and MAA contents were conducted using semi-batch processes with a monomer starved feed policy. Table 3.3 lists the levels of the 5 variables for the 16 runs as well as the properties of their final latex products such as the molecular weights and distribution, latex particle sizes, the T_g of the copolymer, and the adhesion of the coating film to the polycarbonate substrates.

Figure 3.1 shows an example of monomer conversion profiles of reactions with same monomer St/BA/MAA mass ratio of 35/65/5.0 (runs 4, 8, 12, and 16). The overall monomer conversion was defined as the ratio of total polymerized monomer at sampling time over the total monomer fed into the reactor. The instantaneous monomer conversion was higher than 85wt% indicating that the monomers were reacted instantaneously as they were fed into the reactor. Despite the difference in monomer reactivity ratios, the semi-continuous reactions carried out under starved monomer conditions led to the formation of a constant composition polymer with the same composition as the monomer feed. In these 16 reaction runs, their instantaneous monomer conversion was not affected by monomer feed ratio, the pH, nor the SDS contents or the CTA contents. The rate of polymerization was dependent of monomer feed rate.

Two levels of St/BA monomer feed ratio ($\text{St/BA} = 25/75$, and $35/65$) were set in the design of experiments. The molar fractions of St in the feed were 30 and 40 mol%, respectively. Figure 3.2 shows St/BA copolymer composition profile during the reaction.

Table 3.3 2^{5-1} design experiment result

Runs	St/BA/MAA (phm)	pH	SDS (phm)	CTA (phm)	M_n	M_w	M_w/M_n	T_g (K)	D_p (nm)	Pull-off adhesion (N)
9	St25BA75M2.5	3.5	1.5	0.2	46900	302600	6.45	261.1	61.2	112.1 ± 5.6
1	St25BA75M2.5	3.5	0.8	0.6	26800	97300	3.63	259.4	73.4	107.3 ± 3.4
5	St25BA75M2.5	5.5	0.8	0.2	67000	294000	4.39	273.0	79.1	383.4 ± 10.2
13	St25BA75M2.5	5.5	1.5	0.6	27500	142900	5.20	258.3	60.8	251.3 ± 9.6
3	St25BA75M5.0	3.5	0.8	0.2	68800	319100	4.64	268.0	76.4	245.5 ± 5.4
11	St25BA75M5.0	3.5	1.5	0.6	26100	85500	3.28	264.3	55.8	162.3 ± 5.9
15	St25BA75M5.0	5.5	1.5	0.2	91500	378900	4.14	264.2	71.7	747.6 ± 28.4
7	St25BA75M5.0	5.5	0.8	0.6	30600	131000	4.28	264.1	97.3	473.6 ± 6.7
2	St35BA65M2.5	3.5	0.8	0.2	50700	308900	6.09	277.6	70.1	175.8 ± 5.6
10	St35BA65M2.5	3.5	1.5	0.6	32800	102900	3.14	272.9	55.9	145.8 ± 7.4
14	St35BA65M2.5	5.5	1.5	0.2	84500	343000	4.06	276.0	46.9	655.6 ± 28.2
6	St35BA65M2.5	5.5	0.8	0.6	31000	138200	4.46	273.3	103	722.8 ± 25.1
12	St35BA65M5.0	3.5	1.5	0.2	49600	251100	5.06	280.6	62.9	219.1 ± 8.5
4	St35BA65M5.0	3.5	0.8	0.6	27600	107800	3.91	277.4	68.2	210.1 ± 8.0
8	St35BA65M5.0	5.5	0.8	0.2	88400	281400	3.18	278.6	88.5	843.3 ± 26.6
16	St35BA65M5.0	5.5	1.5	0.6	31100	124500	4.00	277.9	69.4	714.1 ± 41.5

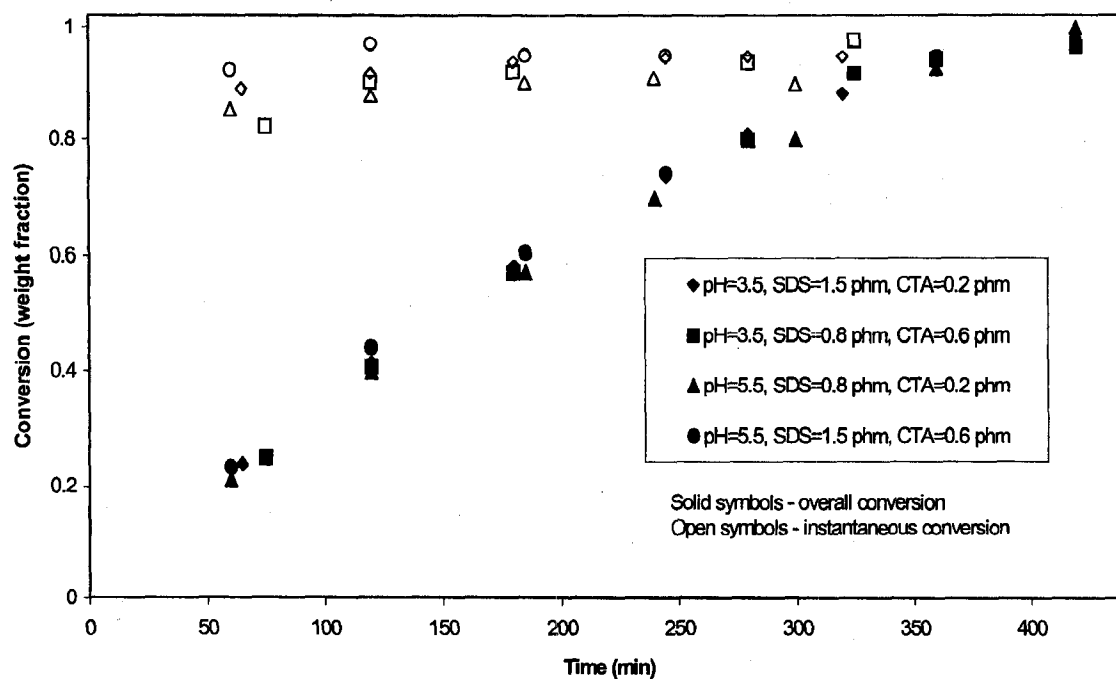


Figure 3.1 St/BA/MAA emulsion copolymerization runs 4, 8, 12 and 16: conversion vs. time

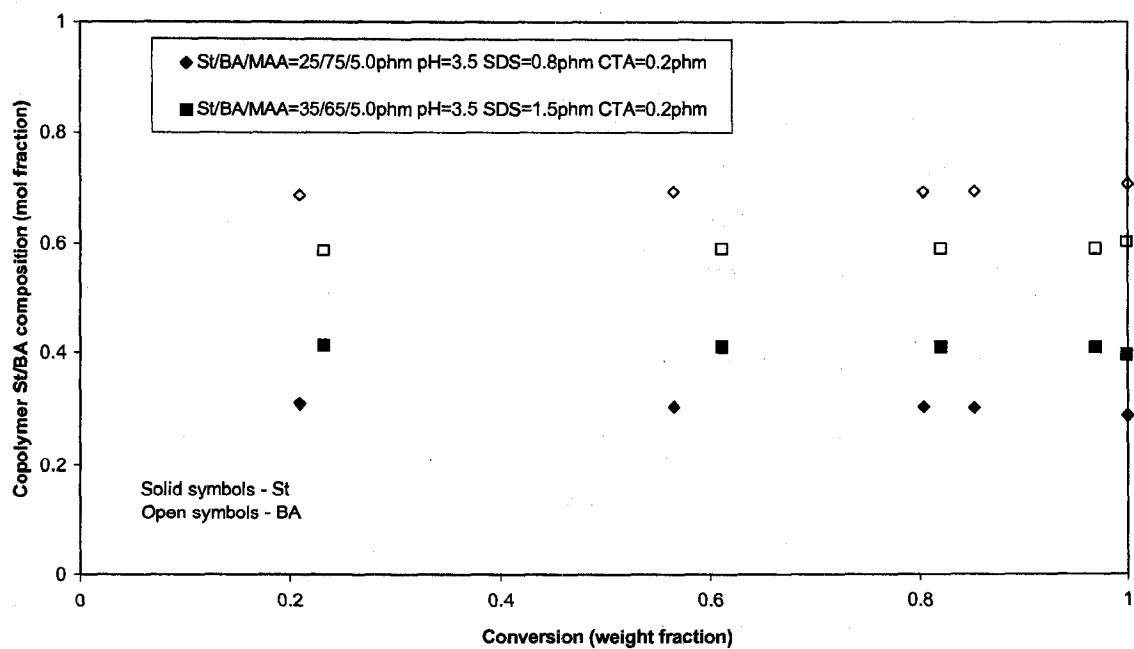


Figure 3.2 St/BA/MAA emulsion copolymerization runs 3 and 12: composition vs. conversion

The ^1H -NMR analysis was used to determine the copolymer St/BA composition. The results of experiments 3 and 12 with different St molar fractions indicated that copolymer compositions were equal to the monomer feed composition in the two runs.

Because MAA monomer has a dissociation constant $pK_a = 4.36$ in water, the partitioning of MAA between the aqueous phase and particles depends on the pH of the reaction environment.²³ In the case of St/BA/MAA emulsion copolymerization, the MAA was either in the form of monomer, soluble homopolymer or copolymer with St/BA inside the particles.^{13, 20} Hen³⁶ and Vijayendran³⁷ developed conductometric titration method to measure the content of acid groups bound at the latex particle surface and the content of “free” MAA in the aqueous phase. Since the total amount of MAA added was known, the content of MAA “buried” or polymerized with St/BA inside the particle was calculated as the difference between the total amount of MAA and the sum of the “surface bound” and “free” MAA content.

As shown in Figures 3.3 to 3.6, for example in experimental run 1 at pH of 3.5, 28 mol% of the total MAA remained in the aqueous, 57 mol% was bonded on the surface, and 15 mol% was inside the particle. Compared to experimental run 5 at pH of 5.5, more MAA was found in the aqueous phase (51 mol%), 34 mol% bonded on the particle surface and 14mol% remained inside the particle.

Dissociated (anionic) MAA with negative charges is more polar than its non-dissociated form, and thus will be relatively more attractive to other polar molecules such as water and less attractive to non-polar species such as St and BA. Increasing the pH led to higher concentrations of the anionic form of the acid, and the MAA contents found in the organic phase decreased correspondingly. As a result, the increase in the

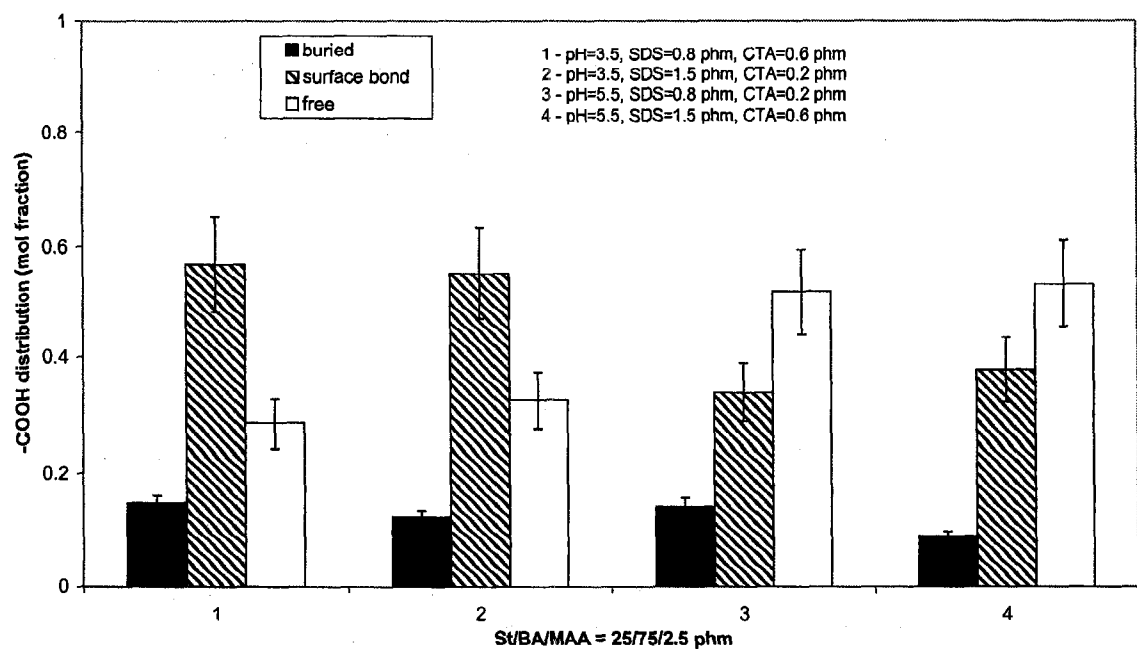


Figure 3.3 St/BA/MAA emulsion copolymerization runs 9, 1, 5 and 13: distribution of carboxylic acid groups

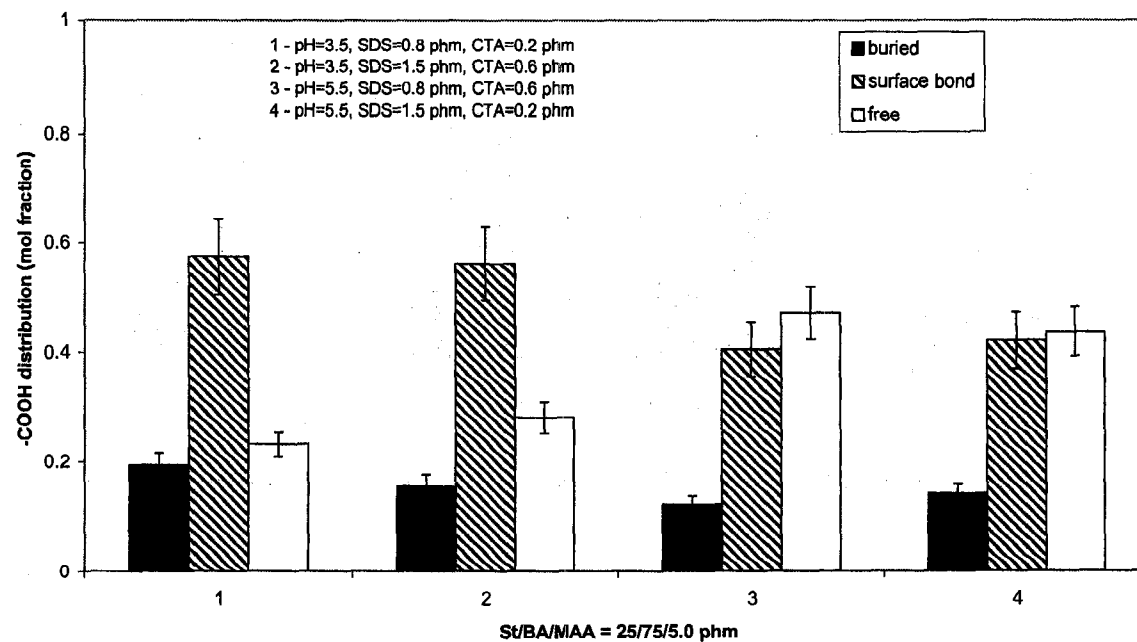


Figure 3.4 St/BA/MAA emulsion copolymerization runs 3, 11, 15 and 7: distribution of carboxylic acid groups

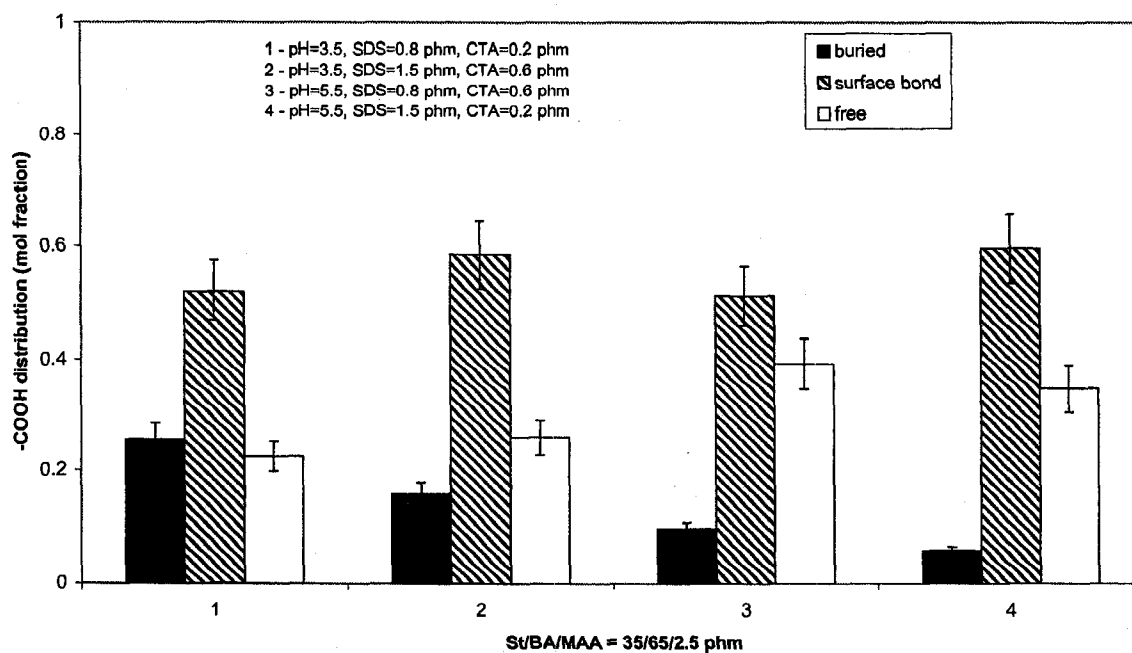


Figure 3.5 S/BA/MAA emulsion copolymerization runs 2, 10, 14 and 6: distribution of carboxylic acid groups

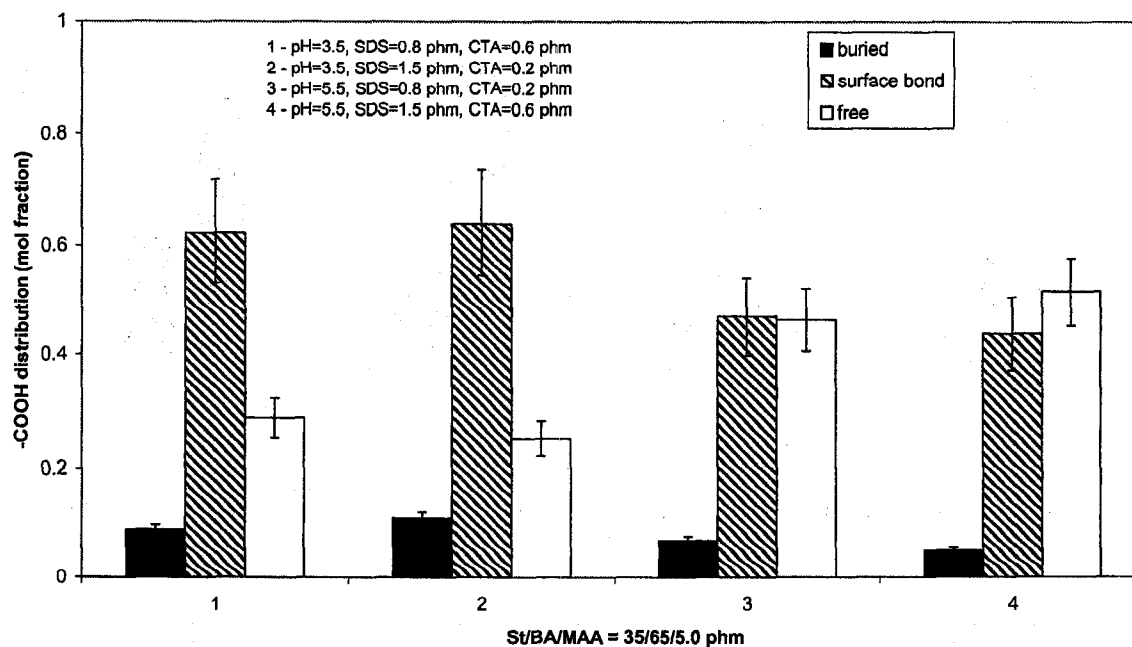


Figure 3.6 S/BA/MAA emulsion copolymerization runs 12, 4, 8 and 16: distribution of carboxylic acid groups

hydrophilicity of the oligomeric radicals formed in the aqueous phase can decrease the driving force for the radicals to penetrate into the hydrophobic particulate phase. Also there is a potential barrier for penetration of these oligomeric radicals due to the build-up of MAA homopolymer at the surface of the polymer particles, which would decrease the rate of polymerization at higher pH.²³

Figures 3.7 and 3.8 illustrate the variation of average particle diameter D_p measured by dynamic light scattering spectroscopy during the reaction. It is worth noting the inaccuracy of the particle size measurements at <20% monomer conversion due to the fact that the light scattering averages tend to weigh more heavily larger particles.⁸ At low conversions particles are small and the presence of a few large particles arising from latex instability may shift the measurement to larger particle sizes.

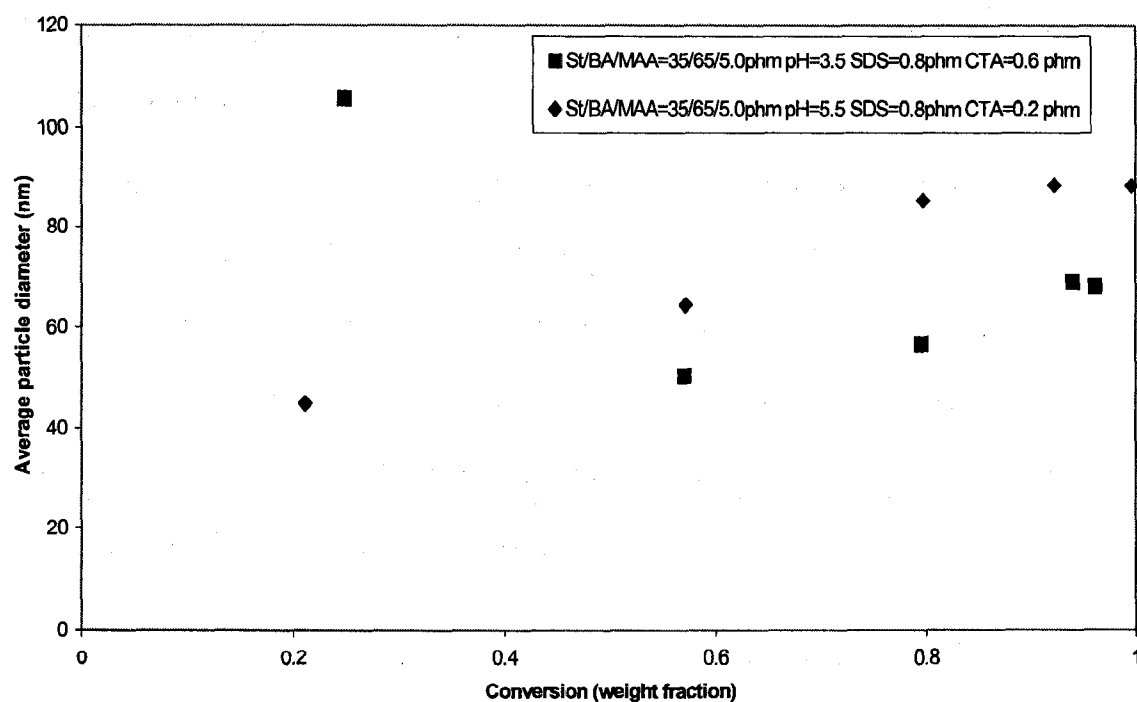


Figure 3.7 St/BA/MAA emulsion copolymerization runs 4 and 8: average particle diameter vs. conversion

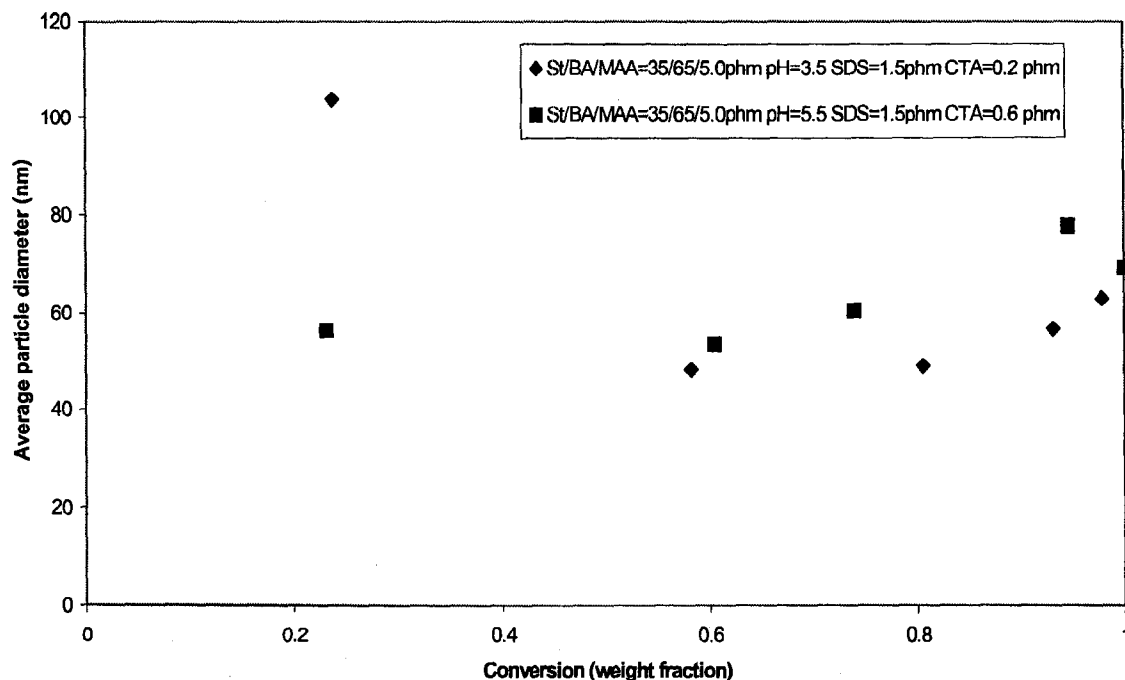


Figure 3.8 St/BA/MAA emulsion copolymerization runs 12 and 16: average particle diameter vs. conversion

The four copolymerization runs 4, 8, 12, and 16 had the same monomer ratio of St/BA/MAA = 35/65/5.0 (weight ratio) and all showed similar histories of average particle size evolution over conversion. With higher [SDS] in the reaction, particles with smaller D_p were formed. As shown in Table 3.4, estimate of the variables effects on the particle size from the 2^{5-1} fractional factorial experiments also indicates that variable x_4 ([SDS]) is the key factors influencing particle size.

Average molecular weight variation over the polymerization process was plotted in Figures 3.9 and 3.10 for four reaction runs. M_n remained roughly constant over the reaction process while M_w profile varied under different conditions. The intermolecular chain transfer to polymer reaction is very important in emulsion polymerizations with BA, which can lead to the formation of long chain braches. Additionally, crosslinking can

Table 3.4 Average particle diameter estimates of the effect from the 2^{5-1}_{IV} fractional factorial design

Variables	Coded coefficients
Constant	71.3
x_1	-0.7
x_2	2.5
x_3	5.8
* x_4	-10.7
x_5	1.7
x_1x_2	-0.8
x_1x_3	0.5
x_1x_4	-1.1
x_1x_5	1.8
x_2x_3	2.2
x_2x_4	1.9
x_2x_5	-2.8
x_3x_4	-4.2
x_3x_5	3.9
x_4x_5	-1.8

*Denotes a variable that is significant to affect D_p

occur if propagating branches terminate by combination.³⁹ If crosslinking does not occur, the M_n is unaffected by chain transfer to polymer while the molecular weight distribution was broadened and the higher ordered molecular weight averages such M_w increases. Instantaneous monomer conversion over 85 wt% was achieved during the reactions which resulted in high polymer concentration in the system. Chain transfer to polymer became the natural consequence of such monomer-starved semi-batch processes.

Estimate of the variables effects on M_n is shown in Table 3.5. Analysis shows that variables x_5 (CTA concentration, [CTA]) and x_3 (pH) are the key factors influencing the M_n . The M_n decreased with the increase of CTA contents and the decrease of reaction mixture pH. The 2-factor interaction of [CTA] and the pH of the reaction environment on M_n was also significant. Table 3.6 shows the estimate of the variables effects on M_w . The

variable x_5 ($[CTA]$) is the key factor influencing M_w . The molecular weights decreased with increasing CTA concentration.

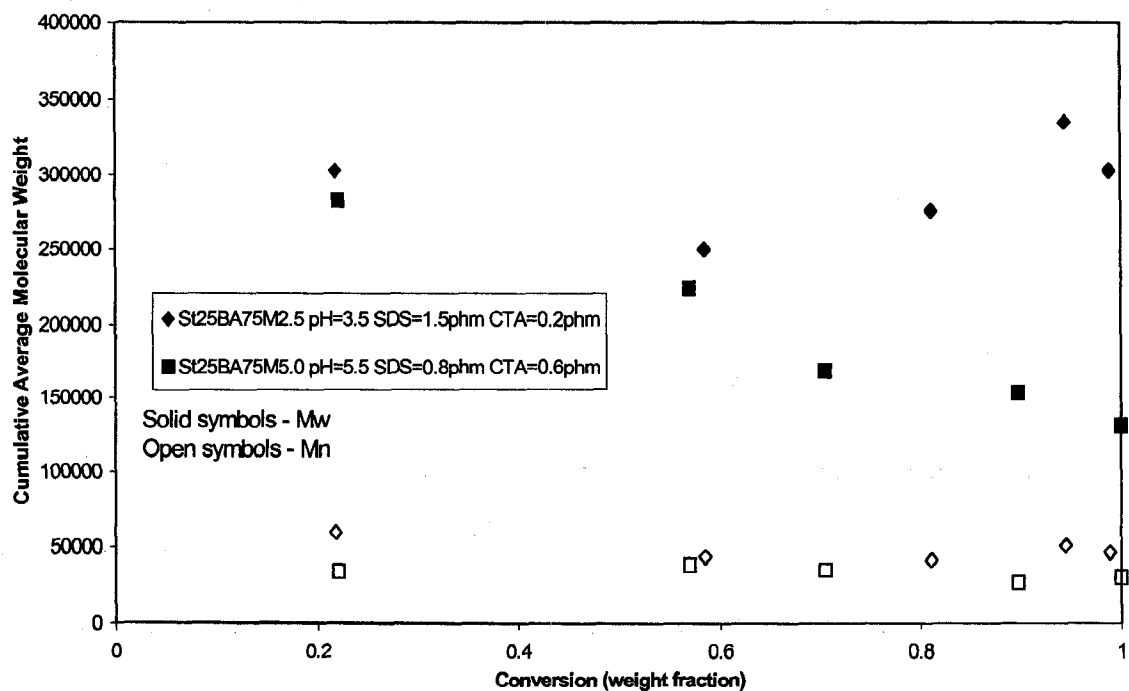


Figure 3.9 St/BA/MAA emulsion copolymerization runs 9 and 7: cumulative number- and weight-average molecular weight vs. conversion

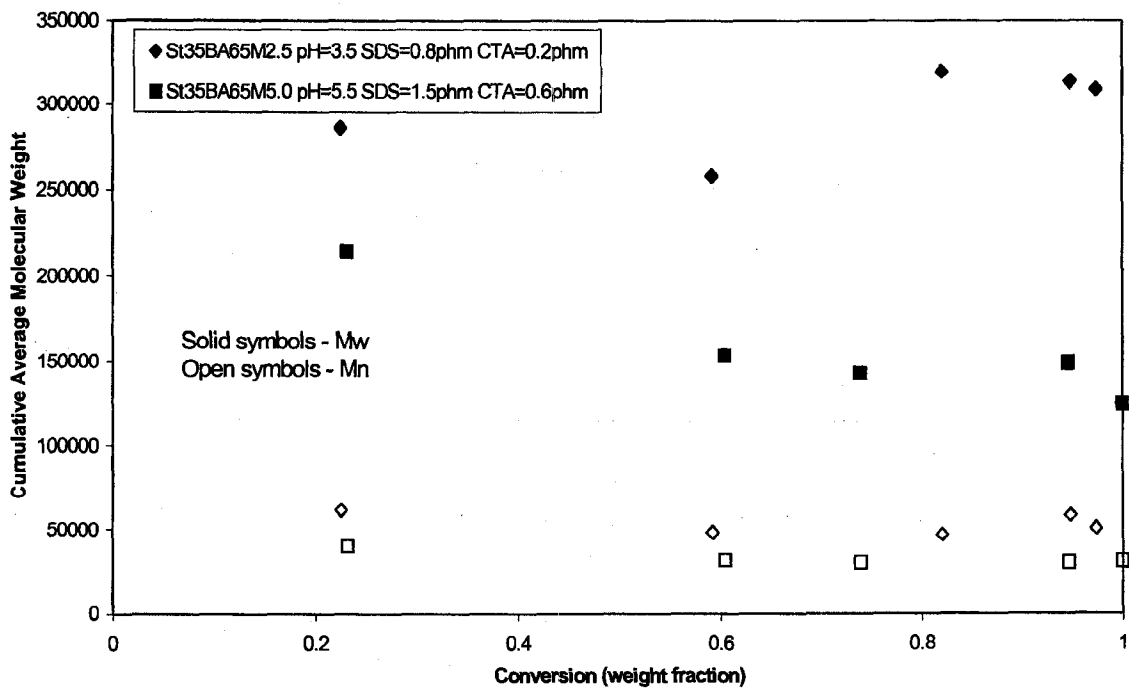


Figure 3.10 St/BA/MAA emulsion copolymerization runs 2 and 16: cumulative number- and weight-average molecular weight vs. conversion

Table 3.5 M_n estimates of the effects from the 2^{5-1}_V fractional factorial design

Variables	Coded Coefficients
Constant	48815.4
x_1	656.5
x_2	2909.7
* x_3	7654.4
x_4	-72.3
* x_5	-19612.7
x_1x_2	-3188.6
x_1x_3	1645.8
x_1x_4	105.6
x_1x_5	777.2
x_2x_3	1044.8
x_2x_4	-2077.6
x_2x_5	-3250.9
x_3x_4	2260.9
* x_3x_5	-6772.7
x_4x_5	244.7

*Denotes a variable that is significant to affect M_n

Table 3.6 M_w estimates of the effects from the 2^{5-1}_V fractional factorial design

Variables	Coded Coefficients
Constant	213074.1
x_1	-5846.1
x_2	-3153.1
x_3	16176.2
x_4	3357.3
* x_5	-96810.3
x_1x_2	-12873.5
x_1x_3	-1617.0
x_1x_4	-5204.6
x_1x_5	7936.8
x_2x_3	2876.9
x_2x_4	-3272.5
x_2x_5	-915.7
x_3x_4	14712.1
x_3x_5	1720.0
x_4x_5	-5669.1

*Denotes a variable that is significant to affect M_w

Several papers reported the St contents influenced the final M_w .^{5, 6, and 9} The evolution of M_w was largely influenced by the gel contents. Gel formation involves chain transfer to large polymer chains followed by radical termination reaction by combination. It was shown that 10 wt% of styrene in the monomer feed was enough to avoid the formation of gel. With the increase of styrene contents, the probability of having secondary butyl acrylate radicals decreased and the styrene radicals were less reactive for the intermolecular chain transfer to polymer. In addition, the larger termination rate constant of styrene radicals reduced average number of radicals per particle, which in turn lowered the probability of termination by combination of long radicals.

About 13-16wt% of gel was found only in latex polymer produced from experimental runs 5, 8, and 15. The polydispersities of the final polymer products were all greater than 2. Such broad molecular weight distribution suggested although the chain transfer to the CTA might have been the main termination event, a transfer to the polymer was also present.⁴⁰

An estimate of the variables' effects on the polymer T_g is shown in Table 3.7. Analysis shows that variable x_1 (St/BA) is the key factor influencing T_g . The final polymer products had a higher T_g as the St content increased in the monomer feed. DSC measurements exhibited only one glass transition region in each polymer sample despite the difference of the three monomers, which confirmed that the monomer-starved semi-batch feed policy led to the production of homogeneous copolymers.

The coating adhesion to a polycarbonate (PC) substrate is regarded as one of the coating performance properties related to the microstructural property of the coating

material. The pull-off adhesion measured per ASTM D5179 gave quantitative evaluation on the adhesion forces between the latex coating and the PC substrate.

Table 3.7 T_g estimates of the effects from the 2^{5-1}_V fractional factorial design

Variables	Coded Coefficients
Constant	270.42
* x_1	6.4
x_2	1.5
x_3	0.2
x_4	-1.0
x_5	-2.0
x_1x_2	0.4
x_1x_3	-0.6
x_1x_4	1.1
x_1x_5	0.6
x_2x_3	-0.9
x_2x_4	0.9
x_2x_5	1.0
x_3x_4	-0.6
x_3x_5	-0.3
x_4x_5	0.9

*Denotes a variable that is significant to affect T_g

Over 95% either adhesive or cohesive failure was recorded as the failure mode during the pull-off testing, which indicated that the coating adhesion forces would depend to a large extent on the bulk properties of the latex polymer.

An estimate of the variables' effects on coating adhesion is shown in Table 3.8. Analysis shows that variable x_3 (pH) is the key factor affecting the coating adhesion. The adhesion forces increased as the pH of the reaction mixture increased. As shown in a previous analysis of carboxylic acid distribution in the latex, a higher pH resulted in a higher MAA content and the carboxylic acids were found either on the particle surface or homopolymerized in the water phase. Garrett et al.²² showed that the PSA made of PBA/AA became stiffer and the shear resistance of the adhesive increased (provided that

both substrates were wetted by the adhesive) as there was a greater AA content in the outer layer of the latex particle. The increase in the adhesion force that is similar to the shear resistance may be interpreted in terms of the increasing proportion of the outer MAA polymer layer leading to a material that is increasingly stiffer due to hydrogen-bonding and ionic interactions arising from the partially neutralized MAA repeat units.

The composition and molecular weight distributions of the latex copolymers were also report to influence the shear resistance of the adhesive materials.^{9, 31, 32} However, the St/BA ratio and the CTA contents that affected the latex copolymer composition and molecular weight distribution were not identified as significant factors affecting the coating adhesion in these experiments. A broader experimental space than that used in this study might be required to identify such effects.

Table 3.8 Coating adhesion estimates of the effects from the 2^{5-1}_V fractional factorial design

Variables	Coded coefficients
Constant	385.60
x_1	75.2
x_2	66.3
* x_3	213.4
x_4	-9.6
x_5	-37.2
x_1x_2	-30.5
x_1x_3	59.7
x_1x_4	-17.6
x_1x_5	24.6
x_2x_3	29.3
x_2x_4	18.4
x_2x_5	-24.7
x_3x_4	2.8
x_3x_5	-21.3
x_4x_5	-20.4

*Denotes a variable that is significant to affect the coating adhesion

3.4 CONCLUSIONS

A 2^{5-1}_{III} fractional factorial screening design of experiments was conducted to identify the effects of five variables, i.e., St/BA ratio, MAA content, pH, emulsifier content, and CTA content on various product properties in the semi-continuous emulsion copolymerization of St/BA. The effects of the of these variables on the carboxylic acid distribution in the latex, the average latex particle diameter, the molecular weight and distribution of the polymer products, the glass transition temperature of the polymer, and the coating adhesion to a plastic substrate were experimentally investigated.

Inside the chosen experimental region, the St/BA ratio is the key factor influencing T_g of copolymer. The final polymer products had a higher T_g as the St content increased in the monomer feed. DSC measurements confirmed that the monomer-starved semi-batch feed policy led to the production of homogeneous copolymers. Results also showed that the pH of the reaction contents would affect the distribution of carboxylic acid. Higher pH led to more anionic form of the acid staying in the water phase or on the latex particle surface. The latex particle size was found to be greatly influenced by the emulsifier content. Analysis showed that the CTA concentration and the pH, as well as their 2-factor interaction significantly affected the M_n . M_n decreased with the increase of CTA contents and the decrease of pH. The CTA content was also the key factor influencing M_w . M_w decreased with increasing CTA concentration. The pull-off adhesion between the latex coating and a polycarbonate substrate was found to be influenced by the pH. The adhesion forces increased as the pH of the reaction mixture increased.

The experimental studies showed that the microstructural properties of the polymer latex could be manipulated by changing variables such as monomer feed

composition, pH, emulsifier content, as well as CTA content. Hence, performance properties such as the coating adhesion could also be optimized over a properly selected experimental region.

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**CHAPTER 4 Semi-continuous Emulsion Copolymerization of
Styrene-Butyl Acrylate with Methacrylic Acid: Box-Behnken
Design of Experiments**

(PAPER 2)

Semi-continuous Emulsion Copolymerization of Styrene-Butyl Acrylate with Methacrylic Acid: Box-Behnken Design of Experiments

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ABSTRACT

Following a previous factorial screening design of experiments, a 3-factor 3-level Box-Behnken design was conducted to study the semi-continuous emulsion copolymerization of styrene (St) - butyl acrylate (BA) with methacrylic acid (MAA). The effects of three variables, i.e., St/BA ratio, MAA content, and pH, on the carboxylic acid distribution in the latex, the polymer glass transition temperature (T_g), the average latex particle diameter, the molecular weight and distribution of the polymer products, and the coating adhesion to a polycarbonate (PC) substrate were investigated. Correlation between the variables and the performance properties was studied over the experimental region with the chain transfer agent (CTA) and the emulsifier content being held constant.

Experimental results showed how the pH affected the distribution of carboxylic acid in the polymer particles. The regression analysis of the Box-Behnken design revealed how the St/BA ratio, MAA content, and pH influence the copolymer T_g ; the latex particle size; the number-average molecular weight M_n as well as the weight-average molecular weight M_w . Contour plots were made based on equations from the

regression analysis. An empirical model to correlate the pull-off adhesion of the latex coating to the PC substrate was also obtained through the regression analysis.

4.1 INTRODUCTION

The emulsion copolymerization of styrene (St) and *n*-butyl acrylate (BA) monomers provides to the paint and coating industry, latex copolymers with a variety of end-use properties. These properties are determined by factors such as the copolymer composition, molecular weight distribution (MWD), latex particle morphology and particle size distribution (PSD) which can be manipulated through different reaction conditions such as reaction temperature, co-monomer ratio (St/BA), initiator, emulsifier, and chain transfer agent (CTA) concentrations as well as different polymerization processes and control policies.

Because of its wide commercial use, extensive studies have been carried out to investigate the relations between polymerization conditions and latex polymer properties. Garcia-Rejon et al.¹ used semi-batch starved monomer feeding policies to produce homogeneous latex copolymers in the co-monomer composition range of St/BA = 20/80-80/20 (weight ratio). They showed that the rate of polymerization was controlled by the monomer feed rate, ensuring that the copolymer composition was equal to the co-monomer composition in the feed. Yang and Yang² investigated the St/BA batch emulsion polymerization process with a 2^{5-1} factorial experimental design and chose the St/BA ratio, reaction temperature, initiator and emulsifier concentrations, and agitation speed as factors. They found that the St/BA ratio, reaction temperature and the surfactant concentrations were the key variables influencing the rate of polymerization and the MWD of the polymer products. Araujo et al.³ and Saldivar et al.⁴ also used a mixed experimental design to study several batch emulsion copolymerization systems which included St/BA and St/acrylic acid (AA). The effects of reaction temperature, initiator

and emulsifier concentrations, co-monomer molar ratio and total monomer concentration were investigated. They developed a mathematical model able to predict the evolution of monomer conversion and latex particle size during the reaction. Plessis et al.⁵ studied the seeded semibatch emulsion copolymerization of St and BA. They focused on chain transfer to polymer reactions and gel formation during the polymerization. The St content in the monomer feed was less than 10 wt% while the change in the St/BA ratio had a significant impact on both the reaction kinetics and the microstructure of the polymer products. The higher the St content in the monomer feed, the lower the gel fraction and the branching level and the higher the weight-average molecular weight of the sol polymer were in the copolymers. These, in turn, influenced the adhesive properties of the product latex when the latex was applied as a pressure sensitive adhesive (PSA).

The paints and coatings industry usually employs carboxylic acid monomers such as AA and methacrylic acid (MAA) in emulsion polymerizations to improve overall latex properties.⁶ Introducing these monomers can improve the shear and freeze-thaw stability of latexes used as bonding agents in paints, improve the mechanical properties of films formed from the polymer latex, and have a positive effect on polymer adhesion towards substrates such as metals and clays.⁷

The three monomers St, BA, and carboxylic acid have significantly different reactivity ratios and solubility in water. The loci of polymerization and copolymer composition will strongly depend on the equilibrium concentration of monomers in the different phases. The influence of pH and the carboxylic acid monomer content on the polymerization rate and the amount of carboxylic acid groups incorporated into the final latex products are often of interest. Shoaf and Poehlein⁸ (1990) found that the partitioning

of carboxylic monomer between the aqueous and particulate phases is governed by its hydrophilic nature. They described how an increase in hydrophilicity of the oligomeric radicals decreased the driving force for the radicals to penetrate into the hydrophobic core of the polymer particle.⁹ In addition there is a potential barrier for penetration of these oligomeric radicals into the particles due to the build-up of AA homopolymer on the particle surface. Slawinski et al.¹⁰ indicated that at the beginning of the polymerization, pH had a minor influence on the polymerization because only St-rich oligomeric radicals entered the latex particles. However, because pH determines the hydrophilicity of the ionizing comonomers, it has a strong influence on the characteristics of the final latex polymer product. The negative charge on the dissociated (anionic) form of AA or MAA renders it more polar than the non-dissociated form, and thus increases its relative attraction for other polar molecules such as water and decreases its attraction for non-polar molecules such as St or BA. They showed the incorporation of acid groups on the surface of final latex particles was more efficient at lower pH.

Santos et al.¹¹ investigated the batch emulsion copolymerization of St with BA in the presence of AA and MAA. They examined the effect of pH levels, which led to different levels of ionization on the reaction kinetics and carboxyl group distribution in the different phases. MAA, which is more hydrophobic compared to AA, was found at higher concentrations inside the latex particles at the same pH. As a result, the effect of pH on the partitioning of MAA in different phases has a more significant impact on the glass transition temperature (T_g) of the copolymer, which is a function of the copolymer composition. When it was in a more acidic system (pH = 2.2 or 4), the rate of polymerization involving MAA was lower than that at pH = 6. This was possibly caused

by the fact that the MAA concentration was higher inside the latex particles in a more acidic environment. The molecular weight of the copolymer product also depends on the pH of the reaction environment. Increasing the pH decreased the average molecular weight of the copolymer formed in the presence of MAA.

Trejo-O'Reilly et al.¹² showed that the presence of MAA, even in a relatively small amount in several St/BA/MAA batch emulsion polymerization processes led to significant changes in the mechanical properties of the final polymers. Mendizabal et al.¹³ studied the influence of pH on the incorporation of MAA monomer in St/BA core-shell copolymer during a two-stage reaction process. They found that a decrease in pH would increase the amount of MAA incorporated into the shell, which in turn improved the mechanical properties such as ultimate elongation, ultimate strength, and toughness of the dried latex films.

Extensive studies described in the literature¹³⁻¹⁸ have identified many factors that can be manipulated to influence the microstructural properties of the St/BA polymer latex. Previously a 2^{5-1}_{IV} fractional factorial screening design of experiments was conducted to identify the effects of five variables, i.e., St/BA ratio, MAA content, pH, emulsifier content, and CTA content on various product properties.¹⁴ The impact of these variables on the carboxylic acid distribution in the latex, the average latex particle diameter, the molecular weight and distribution of the polymer products, the polymer glass transition temperature (T_g), and the coating adhesion to a polycarbonate (PC) substrate was studied. It is of interest to uncover correlations between the variables and the performance properties such as the coating adhesion over certain experimental regions.

A Box-Behnken design is a response surface method used to investigate the relationship between one or more response variables and a set of quantitative experimental parameters, especially when curvature in the response surface is suspected.^{20, 21} Response surface methods are often used once preliminary screening designs such as factorial designs of experiments have been carried out. Box-Behnken designs do not have axial points in the experimental space and each factor requires three levels that may be experimentally more convenient and less expensive to run than other response surface design methods with the same number of factors.²⁰⁻²²

In a previous study, we showed that the St/BA ratio was the key factor influencing the copolymer T_g , pH affected the distribution of carboxylic acid in the polymer particles, the CTA concentration and the pH, as well as their 2-factor interaction significantly affected the number-average molecular weight (M_n), the CTA content was the key factor influencing the weight-average molecular weight (M_w), and the pull-off adhesion between the latex coating and the PC substrate was influenced by the pH.¹⁹ Thus, a design of experiments with more levels of the 3 factors: the pH, the St/BA ratio, and the MAA content, which will result in copolymers with a broad range of T_g (while other variables are kept constant) will help correlate their effects and interactions on latex polymer properties. The CTA content will be 0.6 phm throughout the experiments to avoid gel formation. A Box-Behnken design for three variables with 3-level experimentation requires 15 experimental runs.

4.2 EXPERIMENTAL SECTION

4.2.1 Materials

Purification of reagents was performed by classical methods. Inhibitor was removed from St (99%, Aldrich Chemical Co. Inc.) and BA (99%, Aldrich Chemical Co. Inc.) according to previously described procedures.²³ The initiator was potassium persulfate (KPS, 99+%, Aldrich Chemical Co. Inc.) and the emulsifier was sodium dodecyl sulfate (SDS, 90%, Aldrich Chemical Co. Inc.). Sodium bicarbonate (NaHCO_3 , 98%, Aldrich Chemical Co. Inc) buffer was used to control the pH level in the emulsion polymerizations. The initiator, emulsifier, and buffer were all used as received without further purification. Distilled-deionized (DDI) water was used in all polymerization runs. The chain transfer agent (CTA), 1-dodecanethiol (98+%, Aldrich Chemical Co. Inc.) was used as received. All of the solvents used in these experiments and for characterization of the copolymers (i.e., ethanol, acetone- d_6 (99.9 atom% D, CDN isotopes), tetrahydrofuran (THF, 99.92%, EMD) were also used as packaged.

4.2.2 Polymerization method

Details of the experimental set-up have been described previously¹⁹. High conversion emulsion copolymerizations of St/BA/MAA were run at 60°C in a semi-batch starved feed mode in a 1.25 L LabMax™ reactor. The total reaction time for all runs was 420 min.

Predetermined amounts of SDS and DDI water were first charged into the reactor. The reactor was sealed and heated while the contents were mixed at 200 rpm and purged

for 30 min with nitrogen gas. The initiator solution in DDI water was first deoxygenated by purging with nitrogen gas for ~10 min, and was then charged to the initiator loading cell. When the temperature of the reactor contents reached the set point, the initiator solution was charged to the reactor. N₂ purging was continued for about 5 min thereafter.

The prepared monomer mixture (monomers and CTA at a particular ratio) was transferred into the reagent charging system. When the temperature inside the reactor was stabilized at 60°C, the monomer mixture feed was started; this corresponded to time zero. The feed rate was kept constant for 360 min. During the polymerization, the pH of the reactor contents was controlled by varying the amount of buffer solution fed to the reactor. After the monomer mixture in the reagent charge system was depleted, the reactor was kept running for an additional 60 min. Samples were taken at various time intervals during the course of each experimental run. Samples and final latexes were treated with hydroquinone to quench the reaction.

4.2.3 Product characterization

Conversion

The instantaneous and overall monomer conversions, X_i and X , respectively, were based on the total polymer in the reaction mixture and were measured by gravimetry. X_i and X are given by:

$$X_i(t) = \frac{m_p(t)}{F_m \times t} \times 100\% \quad (4.1)$$

$$X(t) = \frac{m_p(t)}{m_m} \times 100\% \quad (4.2)$$

where $m_p(t)$ is the mass of polymer produced up to time t , F_m is the feeding rate of monomer mixture, and m_m is the total mass of monomer taking part in the reaction.

Copolymer composition

The sampled dried polymers were analyzed for cumulative polymer composition through ^1H -NMR spectra taken by a Bruker AMX500 Fourier-transform ^1H -NMR spectrometer. Analyses were carried out at room temperature in acetone- d_6 (~2% (w/v) solutions), which was used as both the solvent and the reference. Acquisition time was 4.6 s, and 16 scans were performed per readout (for averaging). All spectra exhibited good peak separations for a straightforward interpretation of the results. The relative amounts of monomer bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. For St/BA copolymers, the five protons on the aromatic ring of St absorbed at approximately 6.5 ppm and the two protons of the methylene closest to the oxygen in the ester portion of the BA absorbed at approximately 3.5 ppm (the $-\text{OCH}_2$ group). The copolymer compositions were determined by comparison of the integrated intensities of the resonance signals due to the phenyl proton of St and that of the methylene group in the BA.

Carboxylic acid distribution

The distribution of carboxylic groups in the final latex was given by the amount of functional groups present in the aqueous phase, on the latex particle surface, and inside the particles. A conductometric analysis was used to evaluate the amount of carboxylic groups present at the surface of the particles. The method developed by Hen²⁴ and Vijayendran²⁵ was followed. About 12 g of latex were weighed and then diluted to approximately 4% solids content with DDI water in a 400 mL beaker. Both the pH meter

(Orion Research Inc.) and the conductivity meter (Orion Research Inc.) probes were placed in the diluted latex. A magnetic stirring bar was used to ensure good mixing. The pH of the latex was adjusted to 11.5 ± 0.2 with the addition of a 0.4098 mol/L NaOH solution. The latex was then titrated with a standard 0.02413 mol/L H_2SO_4 solution at a rate of about 1.0 mL/min. Both the conductivity and pH of the latex were recorded as a function of the volume of standard H_2SO_4 consumed until a pH of about 2.4 was reached. Since all methods involving weak acid-base titration are very sensitive to the presence of CO_2 , the experiment was conducted with N_2 continuously purging the latex.

Particle size

Dynamic light scattering (90plus, Brookhaven Instruments Corp.) was used to analyze the latex particle size and distribution. The particle diameter measurements were carried out by diluting a drop of latex sample in approximately 5 mL DDI water. Measurements were recorded at a 90° angle and an average of 6 measurements was recorded.

Molecular weight

The resulting polymer molecular-weight averages and molecular-weight distributions were determined with a Waters Associates GPC system equipped with three Waters Styragel-HR columns (10^3 , 10^4 , and 10^6 Å pore size) installed in series, heated to 30°C , and a Waters 410 differential refractometer heated to 38°C . THF (HPLC grade) was used as the mobile phase and was delivered at 0.3 mL/min. It was used as both the carrier fluid and the reference. Polymer samples were dissolved in THF to produce solutions with a concentration of 0.001-0.002 g/10 mL and filtered through $0.45\ \mu\text{m}$

filters to remove any high molecular weight gel. 200 μL of each solution was injected into the GPC and the data were analyzed using the Millennium 32™ (version 3.05) chromatography manager software. Polymer molecular weights were calculated using the universal calibration principle, given the Mark-Houwink K and α parameters of polymers in THF (polystyrene, $K = 1.6 \times 10^{-2} \text{ mL/g}$, $\alpha = 0.700^{26}$; polybutyl acrylate, $K = 1.1 \times 10^{-2} \text{ mL/g}$, $\alpha = 0.708^{27}$). K and α values for the copolymers were obtained using weighted averages based on the cumulative copolymer composition data.

Gel content

Emulsion polymerizations involving BA may yield polymer products containing a certain amount of insoluble gel.⁵ An extraction process was used to determine the polymer gel content. About 0.1 g of polymer sample was weighed and placed between two PVDF membrane filters (pore size 0.45 μm , diameter 47 mm, Waters). The rim of the two membrane filters was then heated and sealed to make a pouch. The weight of the membrane and the polymer sample was recorded. The pouch containing the polymer sample was immersed into a bottle of about 50 g THF solvent; the amount of THF was also recorded. The bottle containing THF and the polymer sample pouch was shaken for 24 h in a mechanical shaker to extract the soluble polymer. After 24 h, the pouch was rinsed with THF; dried and weighed. The gel fraction, gel%, was calculated as follows:

$$\text{gel}\% = \frac{m_{\text{gel}}}{m_{\text{polymer}}} \times 100\% \quad (4.3)$$

where m_{gel} and m_{polymer} are the weights of insoluble polymer and the whole sample, respectively.

Glass transition temperature (T_g)

T_g of each copolymer samples were measured using a TA Instruments differential scanning calorimeter (DSC) MDSC Q100. Approximately 10 μg sample was put into an aluminium sample pan and heated to 150°C to eliminate any thermal history. Then the sample was cooled from 110 to -60°C followed by a 2 min isothermal step. It was heated again from -60 to 110°C to determine the T_g . Cooling and heating steps were conducted at a rate of 10°C/min. The T_g values of each sample were taken through two replicate runs. The standard deviation for T_g measurements was determined to be 1.0 degree for each individual samples.

Adhesion testing

A laboratory tension test apparatus was built to measure the adhesion of sample coatings to plastic substrates according to the standard ASTM D 5179. The substrate was a 3-inch diameter Lexan[®] polycarbonate (PC) disc. Each final latex samples were cast on the substrate to obtain 100 μm dry film thickness. The coating film was then dried and conditioned for 1 week prior to testing at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. A carefully prepared aluminum stud was bonded directly onto the dry coating film on the PC disc with using cyanoacrylate adhesives. The Aluminum stud had a $\frac{3}{4}$ inch diameter. The stud face was sanded with a piece of 80-grit sandpaper, cleaned with acetone and heated in an oven at 120°C for 1 h. After the stud cooled down, 4 drops of cyanoacrylate adhesive was spread on the stud surface. Then the stud was quickly pressed onto the coated PC substrate. 2-kg weights were placed on the stud to ensure good contact between the stud, adhesive, and the coating surface. The adhesive was allowed to cure for

2 h and the testing specimen was conditioned for 24 h under $23 \pm 2^{\circ}\text{C}$ and $50 \pm 5\%$ relative humidity.

The stud-adhesive-coating-PC substrate joint was installed in an Instron® tensile tester with only the stud protruding. The Instron® tester recorded the forces to remove the coating film from the PC substrate. It had an upper coupling adapter, together with a sample restraining device made in the lab to provide sample alignment and minimal substrate flexing. The tension test was then conducted pulling the crosshead at 5 cm/min, and the pull strength was recorded with chart speed 30 cm/min.

A test was judged satisfactory if the testing joint was pulled clearly away from the base substrate with a minimum of or no coating material being removed. Each specimen was rated according to 5 types of failure as follows:

- A Adhesive failure of the coating from the substrate
- C Cohesive failure in the coating
- AC Combination of adhesive failure at the coating/substrate interface and
cohesive failure in the coating
- S Adhesive failure at the stud
- CS Combination of adhesive failure at the stud and cohesive failure in the
coating

Coating should have pulled off uniformly over the entire stud surface either with adhesive failure from the substrate (failure mode A) or cohesive failure in the coating (failure mode C). The failure must be at least 90% A or C in order to register a valid pull strength reading. Five specimens of each coated substrate were tested one day and the other five on a second day. Statistical analyses have shown no sample-to-sample

differences on the pull-off strength results. Thus, the 10 readings of adhesion forces on each coating/substrate assembly were averaged and reported.

4.2.4 Experimental design

Table 4.1 shows the three factors used for the present experimental design: the weight ratio between the two monomers St and BA (St/BA, x_1), MAA concentration ([MAA], x_2), and the pH of the reaction content (pH, x_3). The low, medium, and high levels of each variable are coded as -1, 0, and +1, respectively. The unit “phm” in the table stands for parts per hundred parts monomer in the reaction contents. Other factors were kept constant, as shown in Table 4.2.

Table 4.3 provides the overall experimentation matrix according to the Box-Behnken design, i.e., the reaction conditions for each of the 15 experimental runs. The sequence of individual runs was randomized when the experiments were carried out.

Table 4.1 Factors and levels for the Box-Behnken design of experiments

Variable	Factors	Level		
		-1	0	+1
x_1	St/BA	20/80 wt%	35/65 wt%	50/50 wt%
x_2	[MAA]	2.5 phm	5.0 phm	7.5 phm
x_3	pH	Low (3.5±0.2)	Medium (4.7±0.2)	High (6.0±0.2)

Table 4.2 Variables kept constant in experiments

Variable	Factors	
X_4	[SLS]	1.5 phm
X_5	[CTA]	0.6 phm
X_6	[KPS]	0.5 phm
X_7	Solid contents	38 wt%
X_8	Temperature	60°C

Table 4.3 Box-Behnken design matrix with 3 factors

Runs	x_1	x_2	x_3
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

4.3 RESULTS AND DISCUSSION

As mentioned earlier, a monomer starved feed policy was used in the semi-batch emulsion polymerization with different St, BA, and MAA contents. Table 4.4 lists the change of the 3 variables for the 15 experimental runs as well as the properties of their final latex products.

Figure 4.1 shows a conversion vs. time plot for runs with a St/BA weight ratio of 50/50 as an example. In each run, the instantaneous monomer conversion was more than 85 wt%, which meant that the monomers were consumed almost as fast as they entered the reactor, a starved-feed polymerization. In this case, the rate of polymerization was dependent on the monomer feed rate.

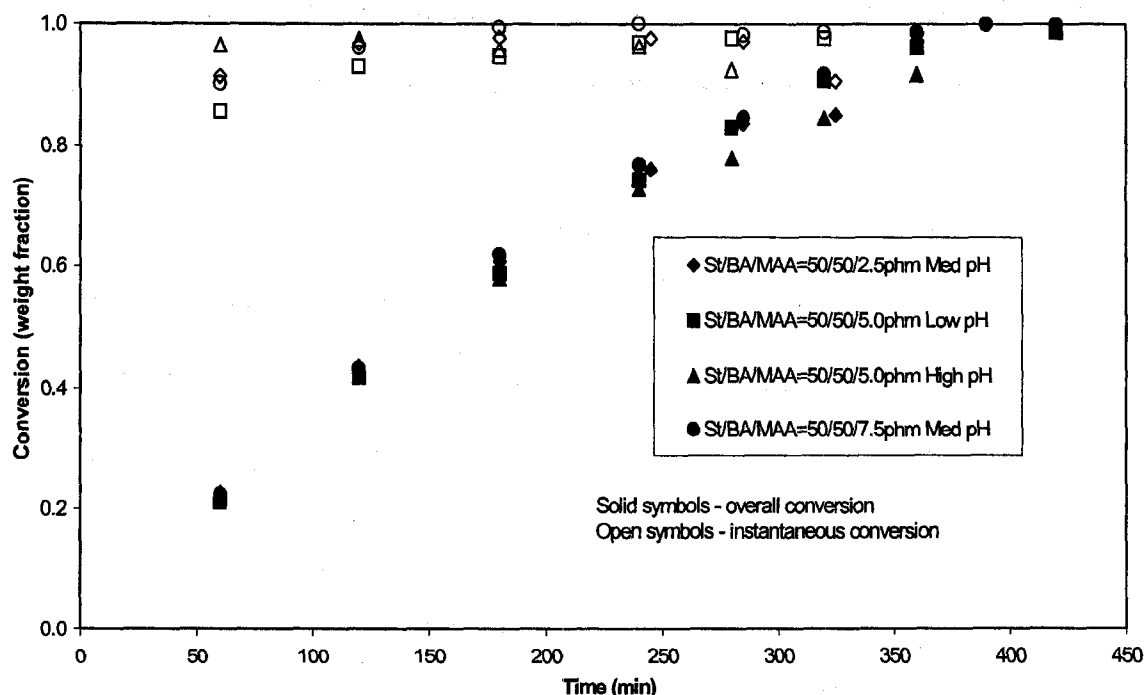


Figure 4.1 St/BA/MAA emulsion copolymerization runs 2, 6, 8 and 4: conversion vs. time

Table 4.4 Box-Behnken design, experimental results

Runs	St/BA/MAA (phm)	pH	T _g (K)	D _p (nm)	M _n	M _w	M _w /M _n	Pull-off adhesion (N)
1	20/80/2.5	Med	251.0	42.2	29000	95100	3.28	81.0 ± 6.1
5	20/80/5.0	Low	255.0	47.3	27200	74200	2.73	178.1 ± 8.3
7	20/80/5.0	High	253.1	115.6	17300	155400	8.98	331.3 ± 24.9
3	20/80/7.5	Med	262.0	53.7	20800	95300	4.58	238.1 ± 15.1
9	35/65/2.5	Low	280.2	52.2	18900	75000	3.97	201.5 ± 6.5
11	35/65/2.5	High	278.2	44.9	23400	86000	3.68	586.0 ± 18.6
13	35/65/5.0	Med	278.2	40.8	17400	62400	3.59	249.9 ± 12.8
14	35/65/5.0	Med	275.4	37.8	26400	91500	3.47	295.2 ± 18.2
15	35/65/5.0	Med	276.2	44.8	18200	65600	3.60	289.6 ± 13.5
10	35/65/7.5	Low	282.9	62.6	22000	75700	3.44	284.4 ± 13.7
12	35/65/7.5	High	278.2	109.4	20000	108200	5.41	802.8 ± 46.0
2	50/50/2.5	Med	294.4	31.4	11700	67300	5.75	330.1 ± 11.2
6	50/50/5.0	Low	300.3	43	10400	59700	5.74	399.4 ± 26.5
8	50/50/5.0	High	293.5	90.7	10100	84100	8.33	821.0 ± 57.0
4	50/50/7.5	Med	305.7	45.8	20600	68500	3.33	640.5 ± 26.5

The pH and MAA concentration were expected to influence the rate of polymerization and the distribution of acid groups in the latex particles. During the semi-batch polymerization process, however, the effect of pH on the course of the reaction was not very pronounced. As shown in Figure 4.1, in the run with St/BA/MAA = 50/50/5.0, the higher pH only caused a rather slight decrease in the polymerization rate at the higher monomer conversion in the final stages of the reaction.

Three St/BA monomer feed ratios were used in the experimental design. The molar fractions of St in the feed were 24, 40, and 55 mol%, respectively. Figure 4.2 shows results of the copolymer St/BA composition analysis of three runs 7, 14, and 8 with different St mole fractions in the feed. The copolymer compositions were equal to the monomer feed composition in each case. In addition, DSC measurements exhibited only one glass transition in each polymer sample, which confirmed the production of homogeneous copolymers using the monomer-starved semi-batch feed policy.

Figures 4.3 to 4.5 show the distribution of acid groups in latexes with different St/BA ratios. The conductimetric titration method developed by Hen²⁴ and Vijayendran²⁵ was used to measure the content of acid groups bound at the latex particle surface and the content of “free” MAA in the aqueous phase. The MAA was either in the form of monomer, soluble homopolymer or copolymer with St/BA. Since the total amount of MAA added was known, the content of MAA “buried” or polymerized with St/BA inside the particle was calculated as the difference between the total amount of MAA and the sum of the “surface bound” and “free” MAA.^{24, 25} At low (pH = 3.5) or medium (pH = 4.7) pH conditions, more carboxylic acid groups were found bound to the surface of

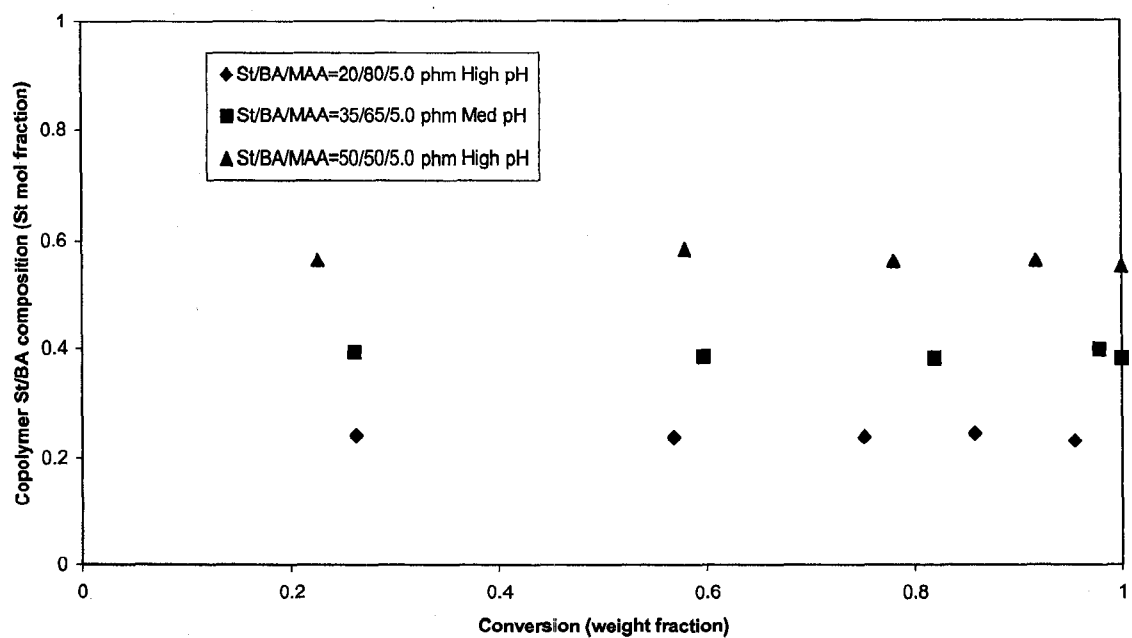


Figure 4.2 St/BA/MAA emulsion copolymerization runs 7, 14, and 8: composition vs. conversion

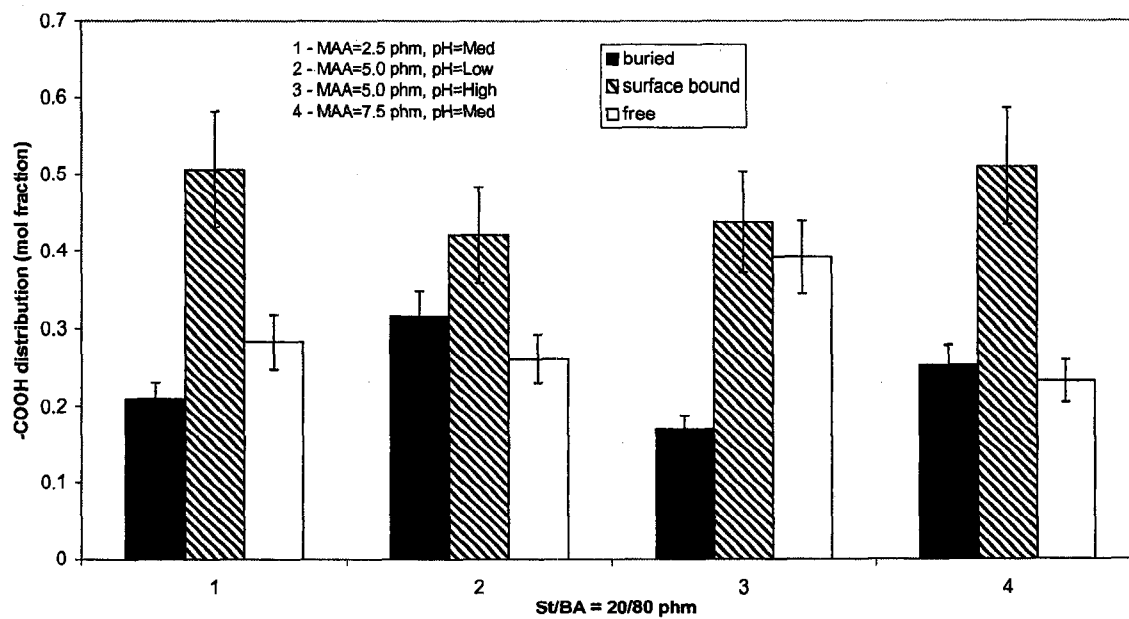


Figure 4.3 St/BA = 20/80 phm emulsion copolymerization runs 1, 5, 7 and 3: distribution of carboxylic acid groups

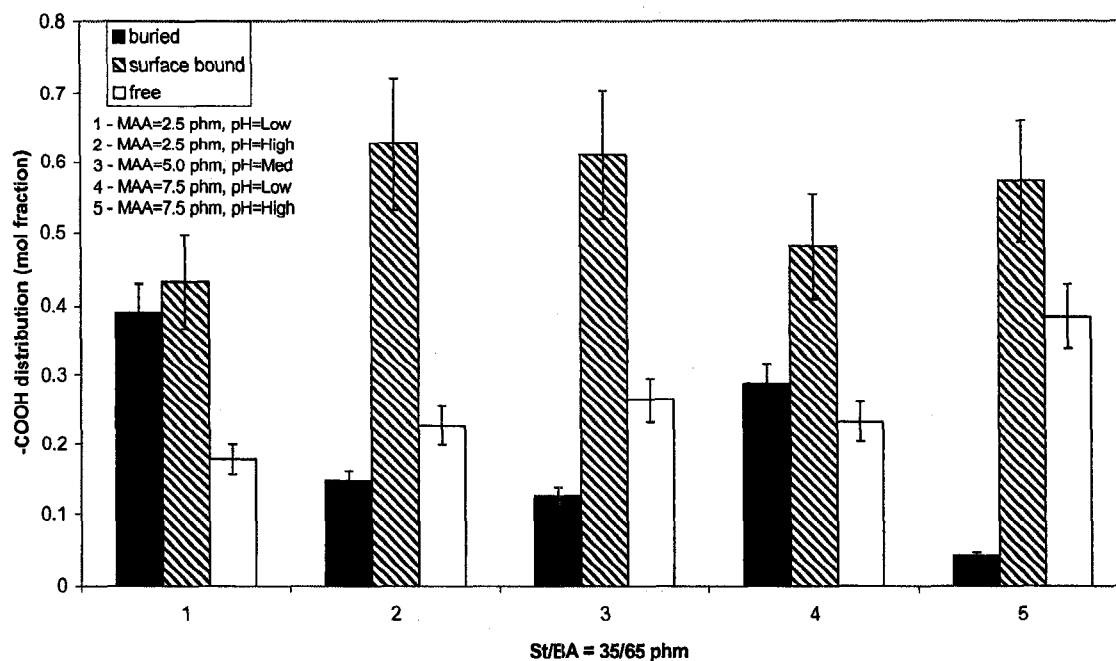


Figure 4.4 St/BA = 35/65 phm emulsion copolymerization runs 9, 11, 14, 10 and 12: distribution of carboxylic acid groups

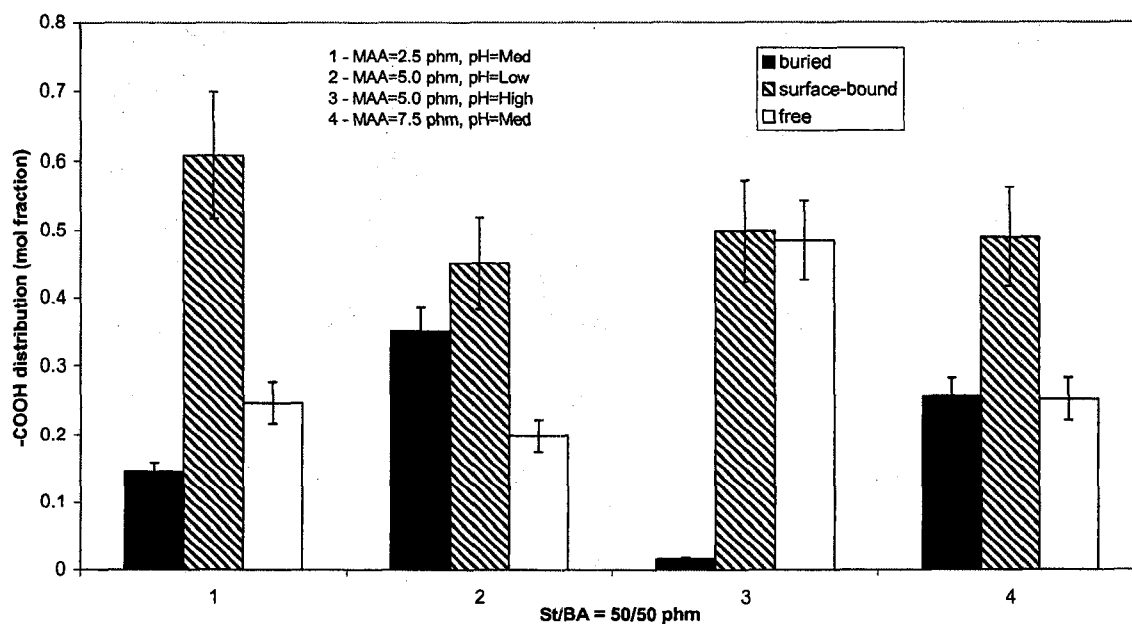


Figure 4.5 St/BA = 50/50 phm emulsion copolymerization runs 2, 6, 8, and 4: distribution of carboxylic acid groups

the latex particles and inside the polymer particles. When pH increased to about 6.0, more MAA was polymerized in the aqueous phase.

Since MAA monomer is soluble in water and has a dissociation constant $pK_a = 4.36$, the partitioning of MAA between the aqueous phase and particles depends on the pH of the reaction environment.⁹ Increasing the pH led to higher concentrations of the dissociated form of the acid, and the quantity of MAA found in the organic phase decreased correspondingly. As a result, the increase in the hydrophilicity of the oligomeric radicals formed in the aqueous phase can decrease the driving force for the radicals to penetrate into the hydrophobic particulate phase. Because of the MAA homopolymer at the surface of the polymer particles, the potential barrier for penetration of oligomeric radicals could decrease the rate of polymerization at higher pH.⁹

The MAA homopolymer has a T_g of 458.15K and the T_g of St and BA are 373.15K and 219.15K, respectively.²⁶ Only one glass transition was found in each polymer sample from DSC measurements, which confirmed the production of homogeneous copolymers using the monomer-starved semi-batch feed policy. The regression analysis of the design of experiments show that variables x_1 (St/BA mass ratio) and x_2 (MAA content) were the key factors influencing the polymer T_g . Figure 4.6 shows contour lines of constant polymer T_g vs. the St/BA ratio and the MAA content (at pH = 4.7). The plot was constructed based on the regression of experimental results indicating that more St and MAA contents in the monomer feed can increase the T_g of the polymer products.

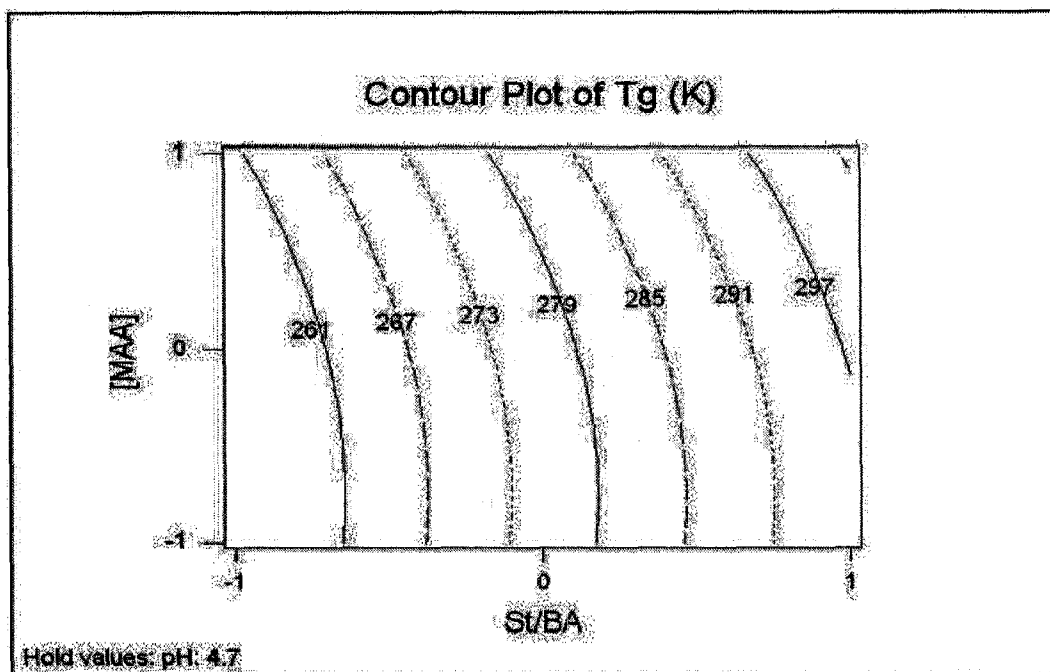


Figure 4.6 Contour plot of constant polymer T_g vs. St/BA ratio and MAA content (pH = 4.7)

Figure 4.7 shows typical results for the average particle diameter and average particle number as a function of monomer conversion. For runs with a St/BA mass ratio of 50/50, the plot shows that the average particle diameter decreased before reaching a constant value at the high conversion stage of the reaction. In the semi-batch polymerization process with monomer-starved feed, a large portion of monomer fed into the reactor could be absorbed by previously formed particles, favoring the formation of larger particles at the early stage of the reaction.²⁷⁻²⁹ Because MAA is soluble in water and BA is partially soluble in water, new particles in smaller sizes were formed through the homogeneous nucleation mechanism when fresh monomer was continuously fed into the reactor during the reaction. For the run with St/BA/MAA = 50/50/5.0 under a low pH reaction environment, the slight increase in the average particle diameter could be due to the agglomeration of latex particles.

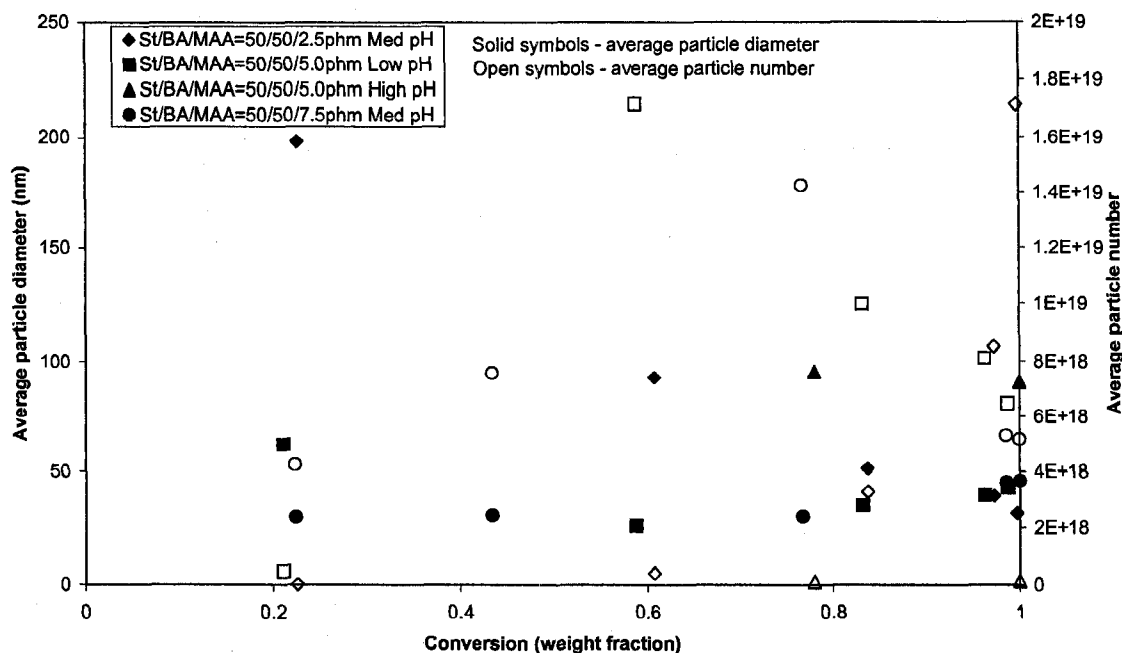


Figure 4.7 St/BA = 50/50 phm emulsion copolymerization runs 2, 6, 8, and 4: Average diameter and number of particles vs. conversion

Previous studies showed that the latex particle size was greatly influenced by the emulsifier content.¹⁹ Regression of the Box-Behnken design of experiments indicates that when the surfactant content was held constant at 1.5 phm, variables x_2 (MAA content), x_3 (pH), as well as their interaction had a significant influence on the average particle diameters. Following the regression model, the response surface and the contour plot were constructed to show the interactions between the MAA content and the pH. Both the response surface plots (Fig 4.8a) and the contour plot (Fig 4.8b) of D_p vs. MAA content and pH when St/BA = 35/65 show that bigger particles were produced with the increasing amount of MAA ($[MAA] = 7.5$ phm) and the increase of pH (pH = 6.0). This could be attributed to more MAA polymerized outside the particle at higher pH.⁹⁻¹¹

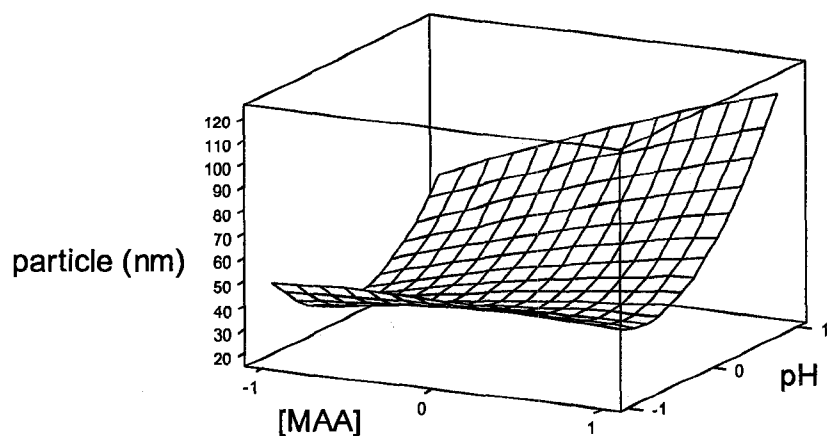
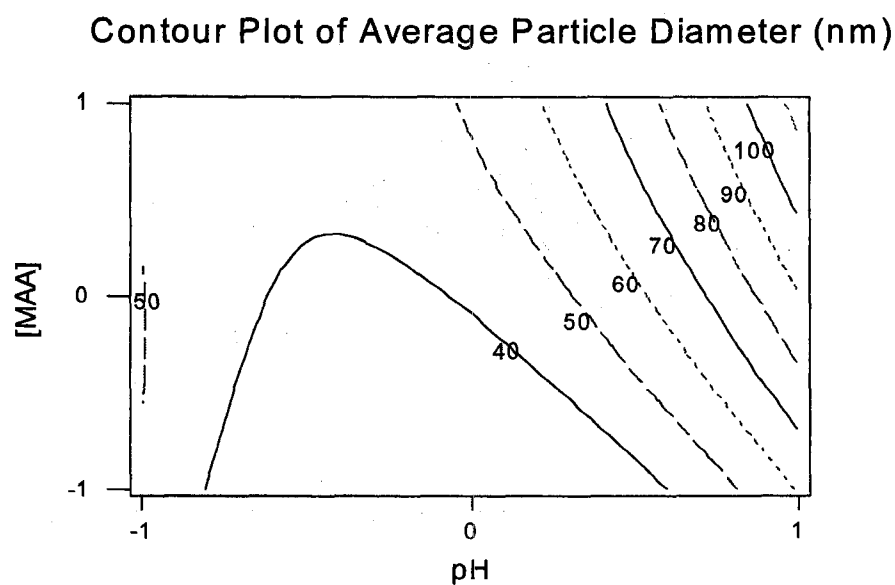


Figure 4.8a Response surface plots of latex average particle diameter D_p vs. MAA content and pH

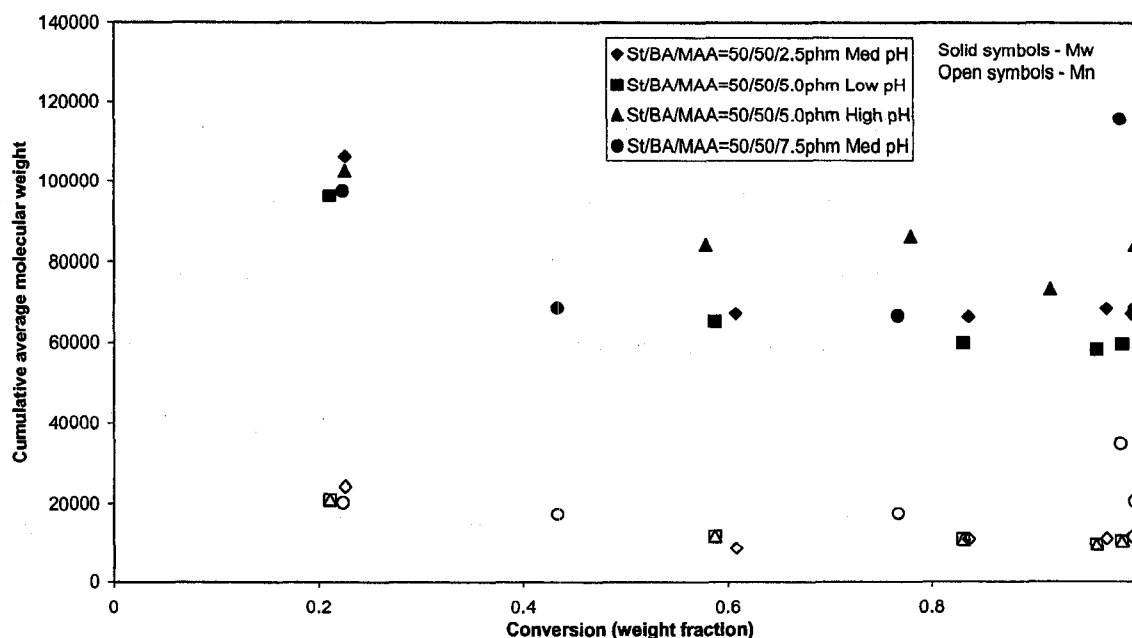


Hold values: St/BA: 35/65 wt%

Figure 4.8b Contour plots of constant latex average particle diameter D_p vs. MAA content and pH
(St/BA = 35/65 wt%)

Figure 4.9 shows the evolution of polymer molecular weight for runs with a monomer feed composition of St/BA = 50/50 wt%. Similar trends were observed in all other runs. Throughout the reactions, the M_n remained almost unchanged while the M_w decreased slightly at the early stage of the polymerization and reached a constant value at higher conversions (>60 wt%).

Figure 4.9 St/BA = 50/50 wt% emulsion copolymerization runs 2, 6, 8, and 4: cumulative M_n and M_w vs. monomer conversion



During the semibatch polymerization process, due to the use of a monomer-starved feed policy, the instantaneous monomer conversions were very high and the rate of polymerization was controlled by the rate of monomer addition. Hence, inside the monomer swollen latex particle, the monomer concentration was low and the fraction of polymer was very high, thereby increasing the chance of chain radical transfer to polymer reactions and producing polymers with a broad molecular weight distribution. As shown

in previous experimental studies,¹⁹ the use of CTA during the polymerizations produced polymers with a narrower molecular weight distribution.

Intermolecular chain transfer to polymer reactions can lead to the formation of long chain branches⁵. Additionally, crosslinking can occur if the chain transfer to polymer reaction is followed by termination by combination. If crosslinking does not occur, the M_n of the polymer product is unaffected by chain transfer to polymer reactions while the higher-order molecular weights such as M_w will increase and the molecular weight distribution will be broadened.³⁰ Plessis et al.⁵ showed that more than 10 wt% of St in the St/BA monomer feed would avoid gel formation. There was more than 20 wt% of St in the monomer feed in our polymerizations and the gel content measurement experiments revealed that no gel was formed in any of the latex products. The M_w decreased as the amount of St increased in the recipe due to lower probability of termination by combination of long radicals caused by the reduction of the average number of radicals per particle because of the larger termination rate constant of St radicals.⁵

A previous screening design showed that the CTA concentration and the pH significantly affected the M_n and that the CTA content was the key factor influencing M_w . With the CTA content being held constant at 0.6 phm throughout the current experiments, the regression analysis revealed that M_n was affected by the St/BA ratio and the MAA content, M_w was affected by the St/BA ratio and the pH, and the St/BA ratio as well as the pH had significant effects on the polydispersity. The response surface and contour plots in Figures 4.10 to 4.12 show the effect of variables and their interactions on the molecular weight properties of the latex polymer.

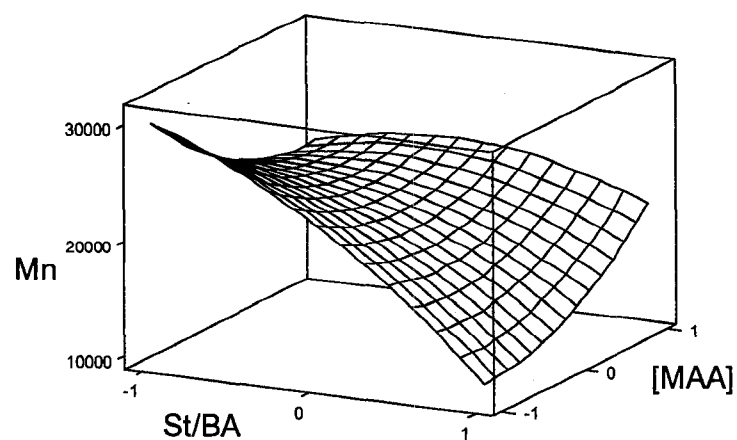
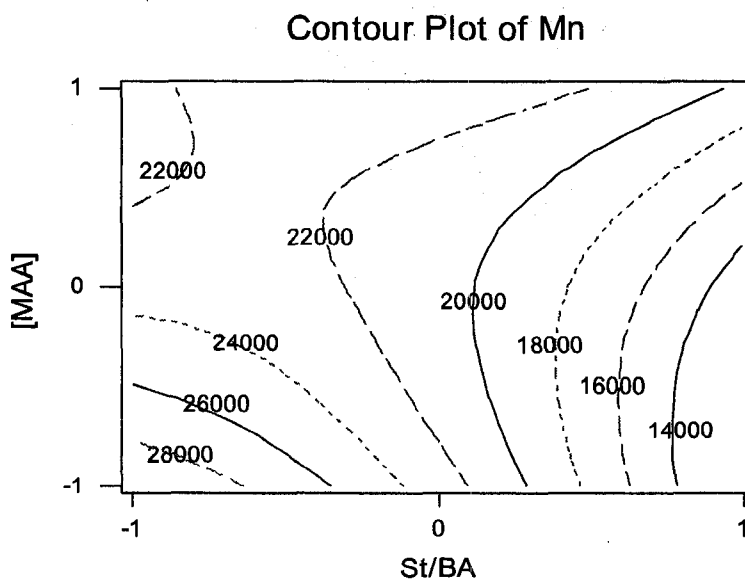


Figure 4.10a Response surface plots: latex polymer cumulative number-average molecular weight vs. St/BA ratio and MAA content



Hold values: pH: 4.7

Figure 4.10b Contour plots: constant cumulative number-average molecular weight vs. St/BA ratio and MAA content (pH = 4.7)

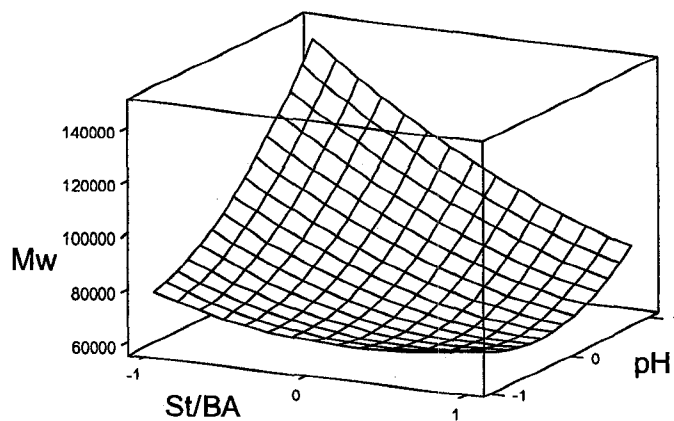
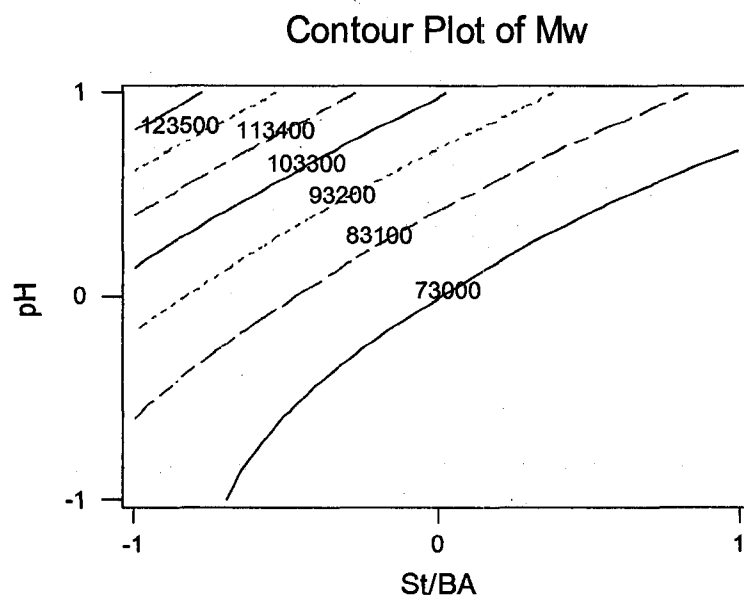


Figure 4.11a Response surface plots: latex polymer cumulative weight-average molecular weight vs. St/BA ratio and pH



Hold values: [MAA]: 5.0phm

Figure 4.11b Contour plots: constant cumulative weight-average molecular weight vs. St/BA ratio and pH ([MAA] = 5.0 phm)

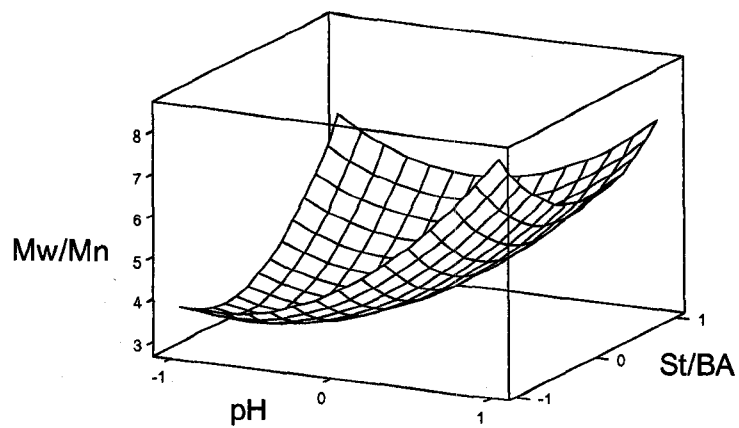
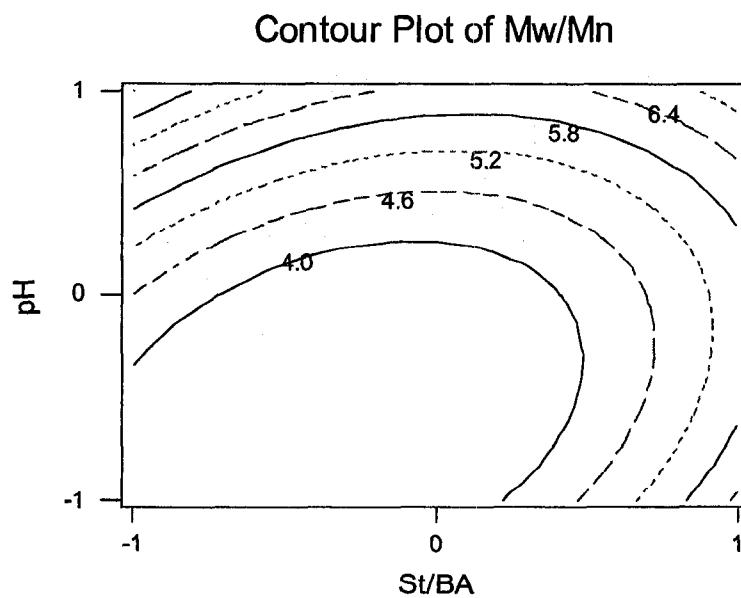


Figure 4.12a Response surface plots: latex polymer M_w/M_n vs. St/BA ratio and pH



Hold values: [MAA]: 5.0phm

Figure 4.12b Contour plots: constant M_w/M_n vs. St/BA ratio and pH ([MAA] = 5.0 phm)

Figures 4.10a and b indicate that M_n increased with the decrease of St to 20 wt%. Figures 4.11a and b indicate that higher M_w can be achieved with lower pH (close to 3.5) and less St (close to 20 wt%) in the monomer feed. In a more acidic environment there will be more MAA taking part in the copolymerization with St and BA inside the particle. Through the “lumped” kinetic constant $k_p / k_t^{0.5}$ (where k_p is the propagation rate constant and k_t is the termination rate constant) approach used by McKenna et al.³¹, it was found that M_w was lower in the St/BA copolymerization with the addition of MAA compared to St/BA copolymers without MAA since MAA has a larger value of k_t .³² Figures 4.12a and b show that under the current conditions, polymer with narrower polydispersity can be obtained close to the center point, i.e., St/BA = 35/65 wt%, pH = 4.7.

In a previous screening design, it was found that the coating adhesion to the Lexan® polycarbonate (PC) was greatly influenced by the pH of the reaction mixture. When the adhesion of the latex polymers to the PC substrates was subjected to regression analysis by the Box-Behnken design, the following regression equation is generated:

$$E(\text{pull-off adhesion}) = 278.2 + 170.4x_1 + 95.9x_2 + 184.8x_3 + 4.1x_1^2 + 40.1x_2^2 + 150.3x_3^2 + 38.3x_1x_2 + 67.3x_1x_3 + 33.5x_2x_3 \quad (4.3)$$

Table 4.4 summarizes the analysis of variance. The test statistics F and R^2 are defined as $F = \text{MSR}/\text{MSE}$ and $R^2 = 1 - \text{SSE}/\text{SST}$, where MSR is the mean square of regression obtained by dividing the sum of square of regression with the degrees of freedom. MSE is the mean square of residual error from the analysis of variance. Table 4.4 shows $F = 20.77$ larger than $F_{0.01}(9, 5)$ of 10.16 indicating the significance of the

model. The multiple correlation coefficient R^2 is 0.974 (close to 1). Thus the equation 4.3 is considered to fit well with the experimental data.

Table 4.4. Analysis of variance for pull-off adhesion

Source	Degrees of Freedom	Sum of Squares	Mean Square	F	P
Regression	9	694524	77169	20.77	0.002
Linear	3	579214	193071	51.96	0.000
Square	3	86821	28940	7.79	0.025
Interaction	3	28488	9496	2.56	0.169
Residual Error	5	18578	3716		
Lack-of-Fit	3	17358	5786	9.49	0.097
Pure Error	2	1220	610		
Total	14				

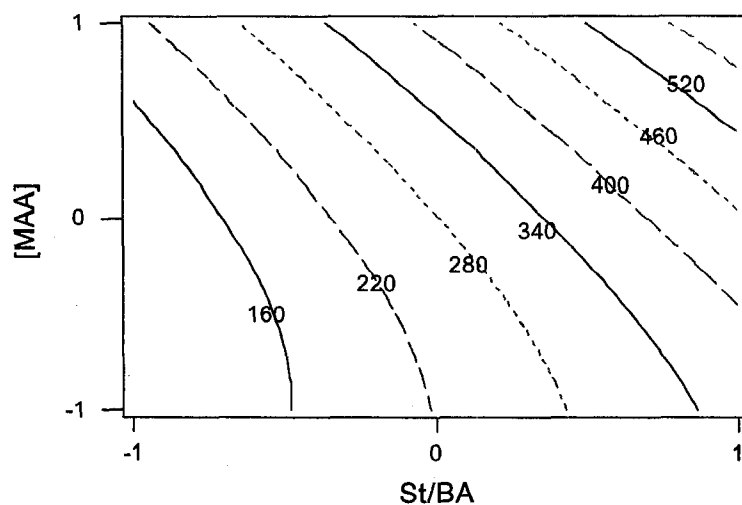
Response surface and contour plots were constructed based on the regression analysis to illustrate the effect of variables and their interactions on the adhesion properties of the latex polymer as shown in Figures 4.13a-d. Figure 4.13a showed that with the increase of St/BA ratio (to 50/50 wt%) and MAA contents (to 7.5 phm), latex polymer with higher coating adhesion could be obtained. It was also shown in Figure 4.13b show that a higher St content in the monomer and a higher pH lead to higher coating adhesion. Figures 4.13 c-d showed that more MAA and higher pH were required to get higher coating adhesion forces.

Based on estimates of factors that had significant impact on the adhesion forces (shown in Table 4.5), a reduced model was built without the interaction terms:

$$E(\text{pull-off adhesion}) = 303.5 + 170.4x_1 + 95.9x_2 + 184.8x_3 + 147.2x_3^2 \quad (4.4)$$

Its analysis of variance was summarized in Table 4.6. The multiple correlation coefficient R^2 is 0.926.

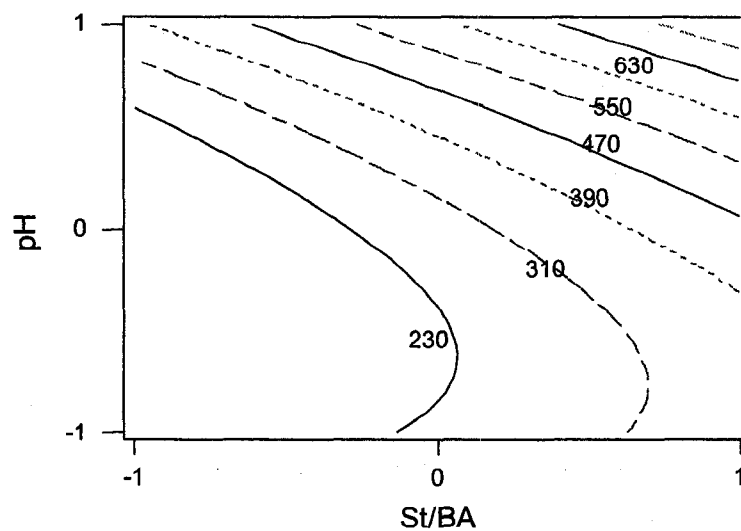
Contour Plot of Pull-off Adhesion (N)



Hold values: pH: 4.7

Figure 4.13a Contour plots: constant adhesion forces vs. St/BA ratio and [MAA] (pH = 4.7 phm)

Contour Plot of Pull-off Adhesion (N)



Hold values: [MAA]: 5.0phm

Figure 4.13b Contour plots: constant adhesion forces vs. St/BA ratio and pH ([MAA] = 5.0 phm)

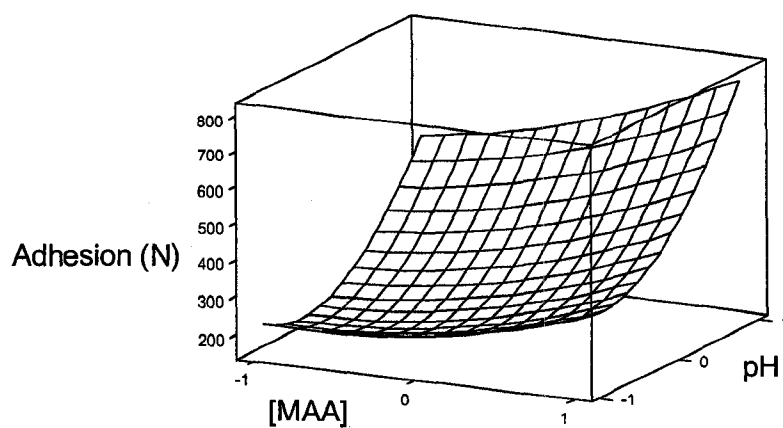
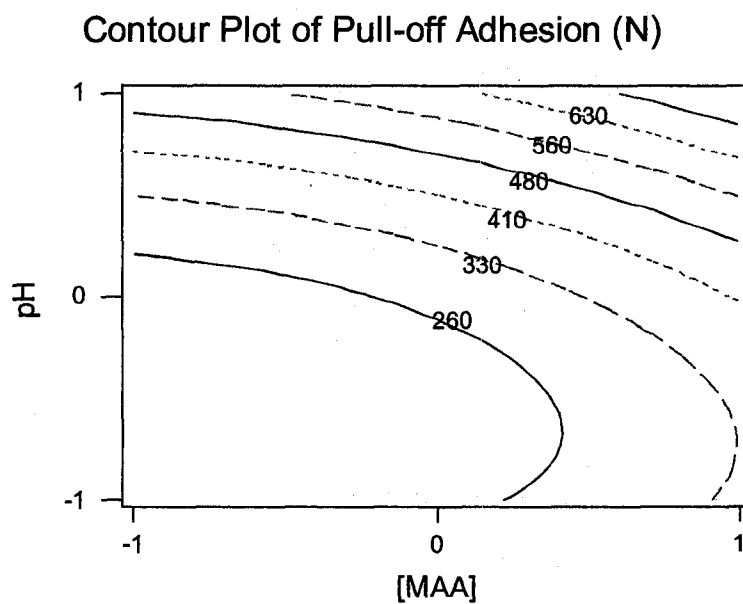


Figure 4.13c Response surface plots: pull-off adhesion vs. MAA contents and pH



Hold values: St/BA: 35/65 wt%

Figure 4.13d Contour plots: constant adhesion forces vs. [MAA] and pH (St/BA ratio = 35/65 wt%)

Table 4.5 Estimated regression coefficients for pull-off adhesion

Terms	Coded Coefficients	T	P	95% Confidence Interval
constant	278.2	7.906	0.001	(209.9, 346.6)
x_1	170.4	7.908	0.001	(128.6, 212.3)
x_2	95.9	4.45	0.007	(54.0, 137.8)
x_3	184.8	8.576	0.000	(143.0, 226.7)
x_1^2	4.1	0.129	0.902	(-57.5, 65.7)
x_2^2	40.1	1.264	0.262	(-21.5, 101.7)
x_3^2	150.3	4.739	0.005	(88.7, 212.0)
x_1x_2	38.3	1.257	0.264	(-20.9, 97.5)
x_1x_3	67.3	2.209	0.078	(8.1, 126.5)
x_2x_3	33.5	1.098	0.382	(-25.7, 92.7)

Table 4.6 Analysis of variance for pull-off adhesion: a reduced model

Source	Degrees of Freedom	Sum of Squares	Mean Square	F	P
Regression	4	660096	165024	31.13	0.000
Linear	3	579214	193071	36.92	0.000
Square	1	80881	80881	15.26	0.003
Residual Error	10	53006	5301		
Lack-of-Fit	8	51786	6473	10.61	0.089
Pure Error	2	1220	610		
Total	14				

Variables from previous runs were put into equation 4.4 for verification.¹⁹ For example, for an experimental run at pH = 3.5 with St/BA/MAA = 35/65/2.5 phm, [SLS] = 1.5 phm, [CTA] = 0.6 phm the model predicted the adhesion forces to be 170N comparable to 145.8N from the real products. For another experimental run at pH = 5.5 with St/BA/MAA = 35/65/5.0 phm, [SLS] = 1.5 phm, [CTA] = 0.6 phm the model gave prediction on the adhesion forces to be 635.5N comparable to 714.1N from the real products.

4.4 CONCLUSIONS

A 3-factor 3-level Box-Behnken design was conducted to study the semi-continuous emulsion copolymerization of St/BA with MAA. The experimental design investigated the effects of three variables, i.e., St/BA ratio, MAA content, and pH on various product properties. The experimental region was set as – St/BA = 20/80 wt% to 50/50 wt%, [MAA] = 2.5 to 7.5 phm, pH = 3.5 to 6.0 with CTA and emulsifier contents being held constant. Model correlation between the variables and the performance properties was studied using regression analysis.

Within the experimental region, the pH of the reaction contents would affect the distribution of carboxylic acid. The regression analysis of the Box-Behnken design also showed that the St/BA ratio and MAA content were the key factors influencing the copolymer T_g ; the MAA content and the pH significantly affected the latex particle size; the St/BA ratio and MAA content affected the number-average molecular weight M_n ; the St/BA ratio and pH affected the weight-average molecular weight M_w . The pull-off adhesion of the latex coating to the PC substrate was influenced by the three factors. The empirical model shows that more [MAA] (7.5 phm) and higher pH (6.0) are required to improve the coating adhesion

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**CHAPTER 5 Semi-continuous Emulsion Copolymerization of
Styrene-Butyl Acrylate with Methacrylic Acid: Latex Polymer
Viscoelastic Properties and Its Adhesion to Plastic Substrates
(PAPER 3)**

**Semi-continuous Emulsion Copolymerization of Styrene-Butyl Acrylate with
Methacrylic Acid: Latex Polymer Viscoelastic Properties and Its Film Adhesion to
Plastic Substrates**

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ABSTRACT

Styrene (St) – butyl acrylate (BA) – methacrylic acid (MAA) copolymer lattices of various composition, molecular weight and distribution as well as particle sizes were obtained from semi-continuous emulsion polymerizations. The viscoelastic behavior of the polymer was studied by dynamic mechanic analysis (DMA) to investigate the reaction variable influence on the structure of latex particles and the structural effect on their coating adhesion performance. Particularly the distribution of carboxylic acid group resulted from the pH of the reaction was investigated using the isothermal frequency dependent moduli master curve. The features of either ionic or hydrogen bonding interactions which lead to the interfacial crosslinking of particles were correlated to the results of carboxylic group distribution analysis. This combination of techniques offers the opportunity to investigate the evidence of improving the cohesive strength of the latex film.

5.1 INTRODUCTION

Organic coatings are applied to a variety of substrate materials such as plastics, woods, and metals for decorative and protective applications. Most of them must withstand a certain range of potential mechanical damage. Their mechanical properties such as flexibility, solvent resistance, and adhesion are important to perform the function effectively.¹ The polymeric binder in a coating formulation has to cope with such a demand and its basic physical properties will determine most of those coating performance properties. Thus, the establishment of relationships between the polymer structure as well as its physical properties and coating performance is desirable because such relationships make it possible to design a polymer structure that will result in improved coating performance.²

Mechanical tests are carried out to determine the coating performance such as its hardness, flexibility, abrasion resistance, and adhesion to the substrate. These tests tend to be specific to the coating field. The results are often used to establish product specifications and to confirm a coating meets those specifications. For the polymeric binder tests are usually conducted to study its physical properties such as stress-strain and dynamic mechanical properties. Stress-strain results include properties such as modulus, tensile strength, and elongation. The dynamic mechanical analysis (DMA) studies the polymer viscoelasticity that is temperature and frequency dependent. These properties all depend upon the polymer structure, its molecular weight and distribution. Comparing the results from the mechanical testing and the polymer tests helps establish the relations between the coating performance and the polymer latexes structure and basic physical properties.²

Since the coating needs to adhere well to the substrate, adhesion assessment should be an integral part of coating development. It seems to be a straightforward task, but in fact, coating adhesion is very complex.³ If the coating adhesion is interpreted as the bonding of polymeric coating with the substrates, this bonding strength should consist of two forces: the adhesive forces sticking the coating material and the substrate together and the cohesive forces holding adjacent molecules of the coating material together.⁴

For such interfacial forces to develop, the coating material must make intimate, molecular contact with the substrate surface. The process of establishing continuous contact between a coating and the substrate is known as “wetting”. Good wetting is a necessary criterion for adhesion. Poor wetting causes less actual area of contact between the coating and substrate, which results in lower overall coating adhesion. The extent of contact and resulting bond strength are functions of wetting energetics including both the surface energy of the coating as well as the substrate surface energy.³

In addition to initial wetting, intimate wetting shall remain intact until the coating solidifies and renders a continuous film. The coating rheology and its proper spreading kinetics are required to ensure such close contact. The major property affecting its flow is viscosity and, hence, the polymer molecular weight and molecular weight distribution (MWD).

Thermodynamic wetting is necessary but not sufficient for good coating adhesion. The next step toward getting good adhesion is to have strong bonding strength between the substrate and the coating, which requires good adhesive and cohesive forces. Besides the close contact between the coating and the substrate, good cohesive strength is required as well to prevent rupture inside the film and keep the coating material lasting

long. The cohesive forces are influenced mainly by the mobility of the polymer chain, which is affected by factors such as molecular weight and MWD, crosslinking and hydrogen bonding present in the polymer chain structure.⁴ A certain amount of chain flexibility is desirable since it helps spread the applied energy over a greater number of atoms and, thus, gives the bond a better chance to resist stress. Yet, too much flexibility may lead to poor temperature resistance or plastic flow under heavy load.

Examples showed that resistance to peel and shear forces mostly depend on the polymer MWD.⁵ Intermediate molecular weight polymers have a good resistance to peel but this property is lost for high ($\geq 1,000,000$ g/mol) and low ($\leq 100,000$ g/mol) molecular weight polymers. High molecular weight polymers show a good resistance to shear but this property decreases as molecular weights decrease. Meanwhile, for intermediate molecular weight polymers, the copolymer composition profile had an impact on the adhesion as well.⁶ The resistance to shear increased as the copolymer heterogeneity increased while resistance to peel was higher for copolymers with a controlled composition profile. These results suggest that polymer chains with high molecular weights provide cohesive strength and mechanical resistance while polymer chains with low molecular weights impart compatibility and adhesion. In practice, a balance among these properties is desirable, which requires polymers with a proper distribution of molecular weights.

Tobing and Klein^{7, 8} showed that polymeric networks with interconnected macromolecular structures improved the cohesive strength. It depends on several molecular parameters such as the entanglement molecular weight (M_e), weight average molecular weight (M_w), molecular weight between crosslinks (M_c), and gel content.

As we can see, coating adhesion depends mainly on the dispersion forces possessed by all molecules, then on a means of bringing these into effect by close proximity, and lastly on the cohesive behavior of the coating material (i.e., its strength, flexibility, and response to temperature). The bond strength is a function of all factors such as the chemical or physical nature of the bond, the degree of bond formation, and the rheological properties of the bonding phases. Coating systems can vary in the type of base polymer binder and various formulating agents such as cross-linking agents, rheology control agents, solvents or diluents. The chemical structure and physical properties of the base polymer and these additives will influence the way in which the film is formed, the stresses within the cured film, and its adhesion onto the substrate. Satisfactory performance can be obtained by proper selection of its composition, MWD, gel contents, solid contents, and hence, proper polymerization conditions to make the polymer.

The polymeric binder in coating formulations is *viscoelastic* in nature. In contrast to an ideal elastic or viscous material, it exhibits an intermediate behaviour between those two. Dynamic mechanical analysis (DMA) can provide a rather clear separation of elastic and viscous responses of viscoelastic polymeric materials.⁹⁻¹¹ In a DMA test, an oscillatory strain at a certain frequency is imposed on a dry film specimen and the resulting oscillatory stress is measured. Stress lags behind strain by an amount, δ , which can be expressed as an angle. The response is interpreted in terms of the dynamic Young's modulus, G^* , and the separated responses result in the "storage modulus", G' , associated with the elastic part of the response and the "loss modulus", G'' , associated with the viscous part of the response. The ratio of G''/G' is the viscous response

expressed relative to the elastic response, also referred to as the “damping factor”, $\tan \delta$. Frequency or temperature scanning can be used in DMA to determine the dependence of modulus on various frequencies or temperatures. From G'' vs. frequency or temperature and $\tan \delta$ vs. frequency or temperature plots, transient properties such as glass and other transitions can be determined. Other information that can be obtained from these loss plots includes the sample homogeneity and its gel content. In addition to its general use to reveal structure/property relationships, progress is being made in establishing property/property relationships between DMA plots and the results of coating tests for hardness, flexibility, impact resistance, and solvent resistance.¹² For example, good flexibility and impact resistance of films made from latex polymers are often associated with low temperature loss peaks. Kan et al. illustrated the correlation between the paper coating gloss and its storage modulus.¹³ Horiuchi and Sato¹⁴ also showed the relationship between the storage modulus of air-drying coating films and coating peel adhesion of a urethane coating. To that end, DMA testing can be a useful tool to correlate the latex polymer microstructure and end-use properties for coating applications.

Mendizabal et al.¹⁵ found that increasing the amount of incorporated methacrylic acid (MAA) in the shell would improve mechanical properties of the coating film such as ultimate elongation and strength and toughness. The DMA results showed that a more rigid material with good impact resistance was obtained when the incorporation of MAA into the particle was favoured at low pH levels (pH = 2.0). In Zhao et al.¹⁶, DMA of latex films from copolymer of BA and other acrylic monomers such as methyl methacrylate (MMA) and 2-EHA (2-Ethylhexyl Acrylate) indicated that there were hard polymer microdomains as the dispersed phase in the continuous soft polymer phase within the

particles. There were also indications that the microdomains were bound to the continuous polymer phase. The inclusion of hard microdomains into a soft continuous phase may lead to some mechanical property improvement such as improved film tensile strength and elongation.

In Schuler et al.¹⁷, DMA was used to verify the presence of two distinct polymer phases with the hard phase acting as transparent filler in BA/MMA/AA latex copolymers. The results showed that an increase in the amount of the hard phase (pAA) resulted in an increase in the storage modulus, leading to reduced tack and corresponding improved block resistance.

Cerrada et al.¹⁸ used DMA to study viscoelastic relaxations of pBA grafted with pSt. The results showed that the transition region of the copolymer was broadened as the amount of grafted pSt increased. Young's modulus and microhardness also increased as the rigid pSt graft content increased because pSt grafts introduced stiffness into the copolymer structure. The DMA indicated that there might be a unique phase of both components in this type of graft copolymer.

In practice, a series of tests are used to evaluate the adhesion by inducing rupture in different modes.³ There are generally two types of testing methods: implied and direct tests. Implied tests include indentation or scribe techniques, rub testing and wear testing, which is usually used to assess coating performance under actual service conditions. Direct tests such as peel, lap-shear, and direct tensile are used to measure the coating adhesion in a single discrete quantity: the force required to fracture the bond between coating and substrate. A reproducible test of this type offers the advantage to yield quantitative results of the force required for coating removal, compared to the more

qualitative and subjective tape tests. The peel adhesion and direct tensile tests are compared below to demonstrate our choice of the adhesion test method for this study.

The tape test ASTM D3359 to measure peel adhesion has widespread popularity since it has the advantages of being simple and economical to perform. But because it was originally designed for ductile coating applied to metal substrates, it was found not being related to the coating's intended application on plastic parts and lacking reproducibility due to its testing procedures and the testing tape it requires.¹⁶ As a result, the tape test is a semi-quantitative method and serves more so as an indicator that some minimum value for bond strength was met or exceed rather than giving an absolute value for the force required for bond rupture.

Another long-used approach to coating adhesion testing is the direct tensile test such as existing ASTM standards ASTM D4541 or ASTM D5179 for both laboratory and field uses. The determination of coating removal force by direct tension shows its potential as a quantitative means of determining adhesion levels.¹⁹ Provided that certain variables such as the test apparatus alignment, the coating and/or adhesive thickness are controlled, the coating should preferentially adhere to the plastic disc and be removed from the base substrate. A test is judged satisfactory if the stud/disc assembly is pulled clearly away from the base substrate with a minimum of or no coating material being removed. Coating should have pulled off uniformly over the entire stud surface either with adhesive failure from the substrate or cohesive failure in the coating. Five specimens of each coated substrate are tested one day and the other five on a second day. Pull strength for the ten runs on each coating/substrate assembly are averaged and reported.

In this project process conditions such as the monomer composition, the amount of carboxylic acid, chain transfer agent and emulsifier contents, as well as the pH of the reaction mixture were manipulated to produce different copolymer products. A fractional factorial screening design followed by a Box-Behnken response surface design of experiments were used to examine the relationship between the process variables and the micro-structural properties of the latex polymer. Meanwhile the DMA test was used to study the viscoelastic properties of the coating polymer and the adhesion test was used to evaluate the performance of the latex copolymer specific to its use as a coating binder. The objective is to look for the correlation between the coating adhesion results and the inherent properties of latex copolymer such as copolymer composition, molecular weight and distribution so that meaningful predictions on performance properties from process conditions can be made in the future.

5.2 EXPERIMENTAL SECTION

5.2.1 Preparation and characterization of the latex samples

Polymer latex samples were prepared using emulsion polymerization processes. The effect of variables such as the monomer contents [St], [BA], and [MAA] as well as the pH of the reaction content, the emulsifier concentration, and the CTA concentration were examined according to a 5-factor 2^{5-1}_{III} fractional factorial followed by a 3-factor Box-Behnken design of experiments.^{20, 21} Experimental conditions for the two designs were listed in Tables 5.1 – 5.4. All emulsion polymerizations were conducted at 60°C in semi-batch starved feed mode in a 1.25 L LabMax™ reactor to ensure final products with homogeneous copolymer composition. During the polymerization, the pH of the reaction

contents was controlled by varying the amount of sodium bicarbonate buffer solution fed to the reactor.

Table 5.1 Variable levels for 2^{5-1} design of experiments with 5 factors

Variable	Name	Levels	
		-	+
x ₁	Comonomer ratio (St/BA wt%)	25/75	35/65
x ₂	[MAA]	2.5 phm	5.0 phm
x ₃	pH	3.5	5.5
x ₄	[SLS]	0.8 phm	1.5 phm
x ₅	[CTA]	0.2 phm	0.6 phm

Table 5.2 Variables kept constant in 2^{5-1} design of experiments

Variable	Factors	
X ₆	[KPS]	0.5 phm
X ₇	Solid contents	38 wt%
X ₈	Temperature	60°C

Table 5.3 Factors and levels for Box-Behnken design of experiments

Variable	Factors	Level		
		-1	0	+1
x ₁	St/BA	20/80 wt%	35/65 wt%	50/50 wt%
x ₂	[MAA]	2.5 phm	5.0 phm	7.5 phm
x ₃	pH	Low (3.5±0.2)	Medium (4.7±0.2)	High (6.0±0.2)

Table 5.4 Variables kept constant in Box-Behnken design of experiments

Variable	Factors	
X ₄	[SLS]	1.5 phm
X ₅	[CTA]	0.6 phm
X ₆	[KPS]	0.5 phm
X ₇	Solid contents	38 wt%
X ₈	Temperature	60°C

Polymer latex products were analyzed to determine their copolymer composition, molecular weights and distribution, particle size and distribution, gel contents, glass transition temperature (T_g), as well as carboxylic acid distribution.^{20, 21}

5.2.2 Dynamic mechanical analysis (DMA)

To investigate the viscoelastic properties of polymer samples, the dynamic mechanical analyses were conducted using a dynamic mechanical analyzer (RDA III, Rheometric Scientific Inc.) in the oscillatory shear mode. Parallel plate geometry was used and the diameter of the plate was 25mm. To prepare the samples for DMA experiments, latex samples were poured into petri dishes with a piece of silicone paper covering the bottom and dried at room temperature. The thickness of the dry film sample was about 3.8mm. Discs with a diameter of 25mm were cut from these films for testing.

Latex polymers prepared with monomer ratio of St/BA = 50/50 wt% had T_g very close to or above room temperature (293.15 K). The film samples were too brittle for DMA tests at room temperature. Film samples were cast from latexes with less than 50wt% of St for DMA testing.

Strain-controlled frequency/temperature sweep tests on the polymer film samples were made by measuring the complex shear modulus (G' and G'') as a function of frequency, ω , at various temperatures. These dynamic mechanical analyses were performed in the frequency range (10^{-1} -100 rad/s). A strain in a range of 0.1-3% was chosen for each individual test, which was sufficiently small that G' and G'' were independent of the applied strain. The measurements were performed over a frequency range of 10^{-1} -100 rad/s, as well as a temperature range of 0-60°C where measurements were recorded at each 5°C increment.

5.2.3 Adhesion test

A laboratory tension test apparatus was built to measure the adhesion of sample coatings to plastic substrates according to the standard ASTM D 5179. The substrate was

a 3-inch diameter Lexan[®] polycarbonate (PC) disc. Each final latex samples were cast on the substrate to obtain 100 μm dry film thickness. The coating film was then dried and conditioned for 1 week prior to testing at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. A carefully prepared aluminum stud was bonded directly onto the dry coating film on the PC disc with using cyanoacrylate adhesives. The Aluminum stud had a $\frac{3}{4}$ inch diameter. The stud face was sanded with a piece of 80-grit sandpaper, cleaned with acetone and heated in an oven at 120°C for 1 h. After the stud cooled down, 4 drops of cyanoacrylate adhesive was spread on the stud surface. Then the stud was quickly pressed onto the coated PC substrate. 2-kg weights were placed on the stud to ensure good contact between the stud, adhesive, and the coating surface. The adhesive was allowed to cure for 2 h and the testing specimen was conditioned for 24 h under $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity.

The stud-adhesive-coating-PC substrate joint was installed in an Instron[®] tensile tester with only the stud protruding. The Instron[®] tester recorded the forces to remove the coating film from the PC substrate. It had an upper coupling adapter, together with a sample restraining device made in the lab to provide sample alignment and minimal substrate flexing. The tension test was then conducted pulling the crosshead at 5 cm/min, and the pull strength was recorded with chart speed 30 cm/min.

A test was judged satisfactory if the testing joint was pulled clearly away from the base substrate with a minimum of or no coating material being removed. Each specimen was rated according to 5 types of failure as follows:

- A Adhesive failure of the coating from the substrate
- C Cohesive failure in the coating

- AC Combination of adhesive failure at the coating/substrate interface and cohesive failure in the coating
- S Adhesive failure at the stud
- CS Combination of adhesive failure at the stud and cohesive failure in the coating

Coating should have pulled off uniformly over the entire stud surface either with adhesive failure from the substrate (failure mode A) or cohesive failure in the coating (failure mode C). The failure must be at least 90% A or C in order to register a valid pull strength reading. Five specimens of each coated substrate were tested one day and the other five on a second day. Statistical analyses have shown no sample-to-sample differences on the pull-off strength results. Thus, the 10 readings of adhesion forces on each coating/substrate assembly were averaged and reported.

5.3 RESULTS AND DISCUSSION

In previous studies, a 2^{5-1}_{IV} fractional factorial screening design of experiments was conducted to identify the effects of five variables, i.e., St/BA ratio, MAA contents, pH, emulsifier contents, and chain transfer agent content on various product properties.²⁰ Inside the chosen experimental region, results showed that the St/BA ratio is the key factor influencing T_g of copolymer and the pH of the reaction contents would affect the distribution of carboxylic acid. Higher pH led to more anionic form of the acid staying in the water phase or on the latex particle surface. Analysis showed that the CTA concentration and the pH, as well as their 2-factor interaction significantly affected the copolymer molecular weights. The pull-off adhesion between the latex and a polycarbonate substrate was measured as one of the performance properties of the final products. The adhesion forces were found to increase as the pH of the reaction mixture increased. A Box-Behnken response surface design of experiments was then conducted to study factors St/BA ratio, MAA contents, and pH to improve the coating adhesion performance.

St/BA/MAA copolymer lattices were produced in the semi-batch emulsion polymerization. A monomer starved feed policy was used to make copolymer with homogeneous composition. 31 latex polymer samples in total were obtained from the two design of experiment. Tables 5.5 and 5.6 listed the process variables of the experimental runs as well as the properties of the latex products are

Table 5.5 ^{2⁵⁻¹} design, experimental results

Runs	St/BA/MAA (phm)	pH	SDS (phm)	CTA (phm)	M _n	M _w	M _w /M _n	T _g (K)	D _p (nm)	Pull-off adhesion (N)
9	St25BA75M2.5	3.5	1.5	0.2	46900	302600	6.45	261.1	61.2	112.1 ± 5.6
1	St25BA75M2.5	3.5	0.8	0.6	26800	97300	3.63	259.4	73.4	107.3 ± 3.4
5	St25BA75M2.5	5.5	0.8	0.2	67000	294000	4.39	273.0	79.1	383.4 ± 10.2
13	St25BA75M2.5	5.5	1.5	0.6	27500	142900	5.20	258.3	60.8	251.3 ± 9.6
3	St25BA75M5.0	3.5	0.8	0.2	68800	319100	4.64	268.0	76.4	245.5 ± 5.4
11	St25BA75M5.0	3.5	1.5	0.6	26100	85500	3.28	264.3	55.8	162.3 ± 5.9
15	St25BA75M5.0	5.5	1.5	0.2	91500	378900	4.14	264.2	71.7	747.6 ± 28.4
7	St25BA75M5.0	5.5	0.8	0.6	30600	131000	4.28	264.1	97.3	473.6 ± 6.7
2	St35BA65M2.5	3.5	0.8	0.2	50700	308900	6.09	277.6	70.1	175.8 ± 5.6
10	St35BA65M2.5	3.5	1.5	0.6	32800	102900	3.14	272.9	55.9	145.8 ± 7.4
14	St35BA65M2.5	5.5	1.5	0.2	84500	343000	4.06	276.0	46.9	655.6 ± 28.2
6	St35BA65M2.5	5.5	0.8	0.6	31000	138200	4.46	273.3	103	722.8 ± 25.1
12	St35BA65M5.0	3.5	1.5	0.2	49600	251100	5.06	280.6	62.9	219.1 ± 8.5
4	St35BA65M5.0	3.5	0.8	0.6	27600	107800	3.91	277.4	68.2	210.1 ± 8.0
8	St35BA65M5.0	5.5	0.8	0.2	88400	281400	3.18	278.6	88.5	843.3 ± 26.6
16	St35BA65M5.0	5.5	1.5	0.6	31100	124500	4.00	277.9	69.4	714.1 ± 41.5

Table 5.6 Box-Behnken design, experimental results

Runs	St/BA/MAA (phm)	pH	M _n	M _w	M _w /M _n	T _g (K)	D _p (nm)	Pull-off adhesion (N)
1	20/80/2.5	Med	29000	95100	3.28	251.0	42.2	81.0 ± 6.1
5	20/80/5.0	Low	27200	74200	2.73	255.0	47.3	178.1 ± 8.3
7	20/80/5.0	High	17300	155400	8.98	253.1	115.6	331.3 ± 24.9
3	20/80/7.5	Med	20800	95300	4.58	262.0	53.7	238.1 ± 15.1
9	35/65/2.5	Low	18900	75000	3.97	280.2	52.2	201.5 ± 6.5
11	35/65/2.5	High	23400	86000	3.68	278.2	44.9	586.0 ± 18.6
13	35/65/5.0	Med	17400	62400	3.59	278.2	40.8	249.9 ± 12.8
14	35/65/5.0	Med	26400	91500	3.47	275.4	37.8	295.2 ± 18.2
15	35/65/5.0	Med	18200	65600	3.60	276.2	44.8	289.6 ± 13.5
10	35/65/7.5	Low	22000	75700	3.44	282.9	62.6	284.4 ± 13.7
12	35/65/7.5	High	20000	108200	5.41	278.2	109.4	802.8 ± 46.0
2	50/50/2.5	Med	11700	67300	5.75	294.4	31.4	330.1 ± 11.2
6	50/50/5.0	Low	10400	59700	5.74	300.3	43	399.4 ± 26.5
8	50/50/5.0	High	10100	84100	8.33	293.5	90.7	821.0 ± 57.0
4	50/50/7.5	Med	20600	68500	3.33	305.7	45.8	640.5 ± 26.5

Film samples were cast for DMA testing from latexes with less than 50wt% of St. Latex prepared with monomer ratio of St/BA = 50/50 wt% has T_g above 293.15 K which made the film sample too brittle for the test under the room temperature.

DMA plots in Figures 5.1 a-d showed the rheological behavior of latex polymers with St/BA ratio of 20/80 wt% as an example. The MAA contents as well as the pH of the reaction were varied according to the screening design of experiments. The time-temperature superposition principle was used to extend the frequency range to $10^{-4} - 10^4$ rad/s at the reference temperature of 25°C to obtain the isothermal master curves of the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ plot.²² The curves showed similar viscoelastic behaviour over three frequency ranges: (1) a small portion of the glass transition range at high frequencies where both G' and G'' increased with the angular frequency; (2) a plateau zone where G'' was smaller than G' and both moduli were

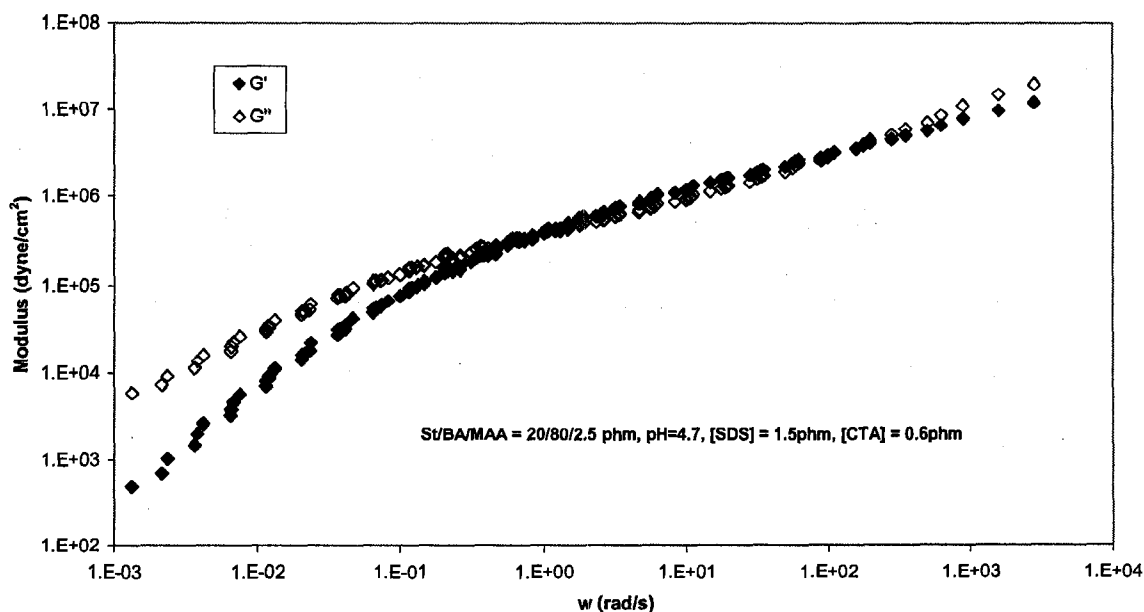


Figure 5.1a Copolymer St20BA80MAA2.5 (pH=Med): G' (G'') vs. frequency plot

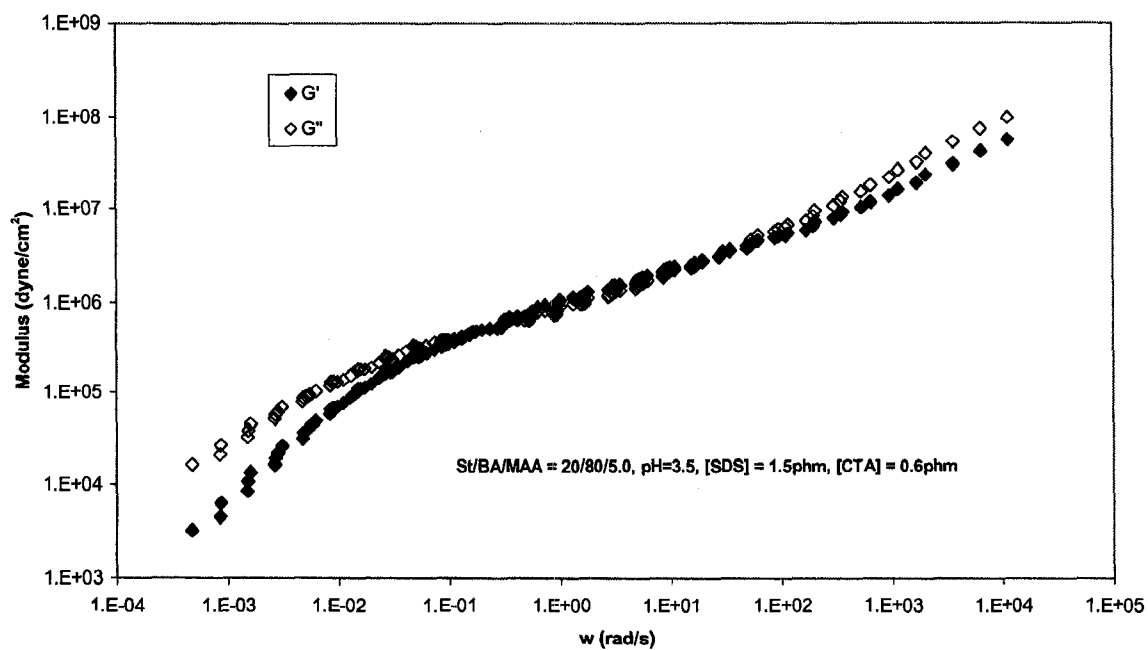


Figure 5.1b Copolymer St20BA80MAA5.0 (pH=Low): G' (G'') vs. frequency plot

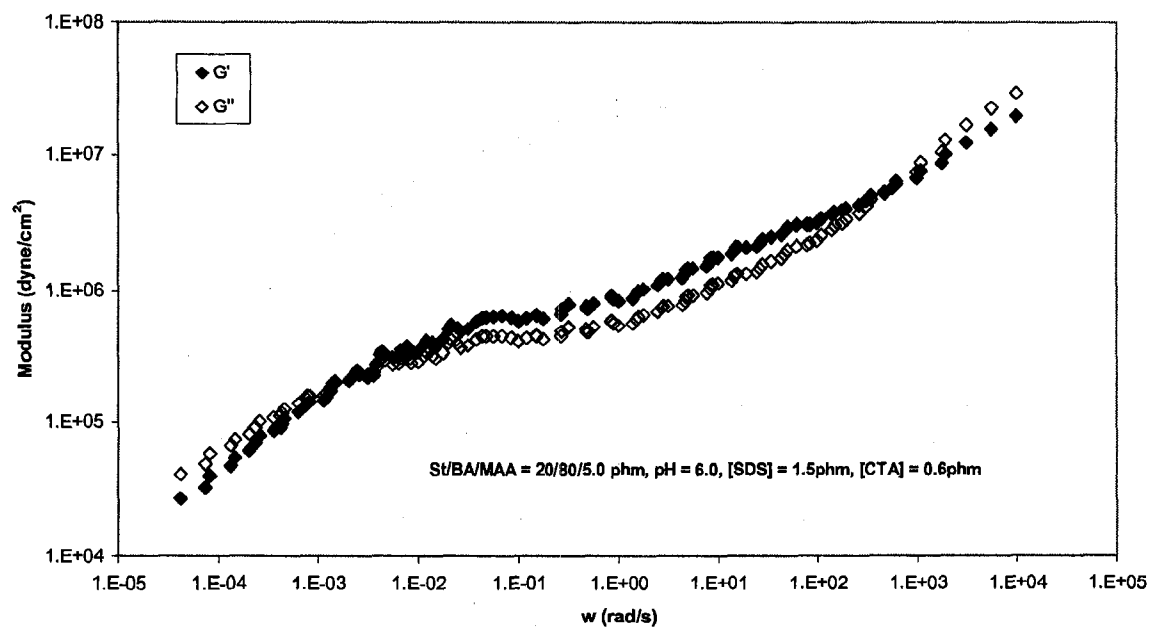


Figure 5.1c Copolymer St20BA80MAA5.0 (pH=High): G' (G'') vs. frequency plot

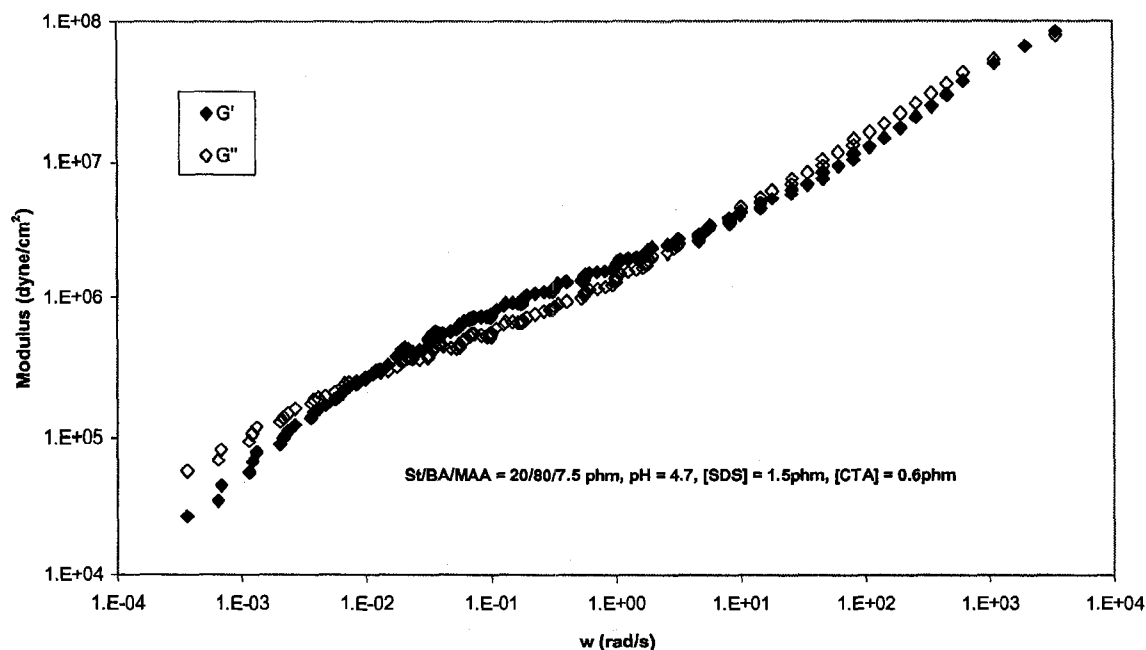


Figure 5.1d Copolymer St20BA80MAA7.5 (pH = Med): G' (G'') vs. frequency plot

slightly frequency dependent; (3) a terminal zone at low frequency where G' and G'' decreased with decreasing frequencies and the mechanical properties were more controlled by viscous flow. The location of the plateau zone and the magnitude of the moduli varied depending on different reaction conditions. The crossover was more significant in the sample with St/BA/MAA = 20/80/5.0 phm at pH = 6.0, which showed a plateau at $G'' = 7.0 \times 10^5$ dyne/cm² indicating the existence of entanglement network. The polymer was generally elastic as G' was larger than G'' in this frequency range.

Figures 5.2 a and b illustrated different viscoelastic behaviour in four copolymer samples with different monomer compositions prepared with different St, BA, and MAA composition, using the same CTA and SDS contents. These four samples had homogeneous composition and average similar molecular weight. With increasing

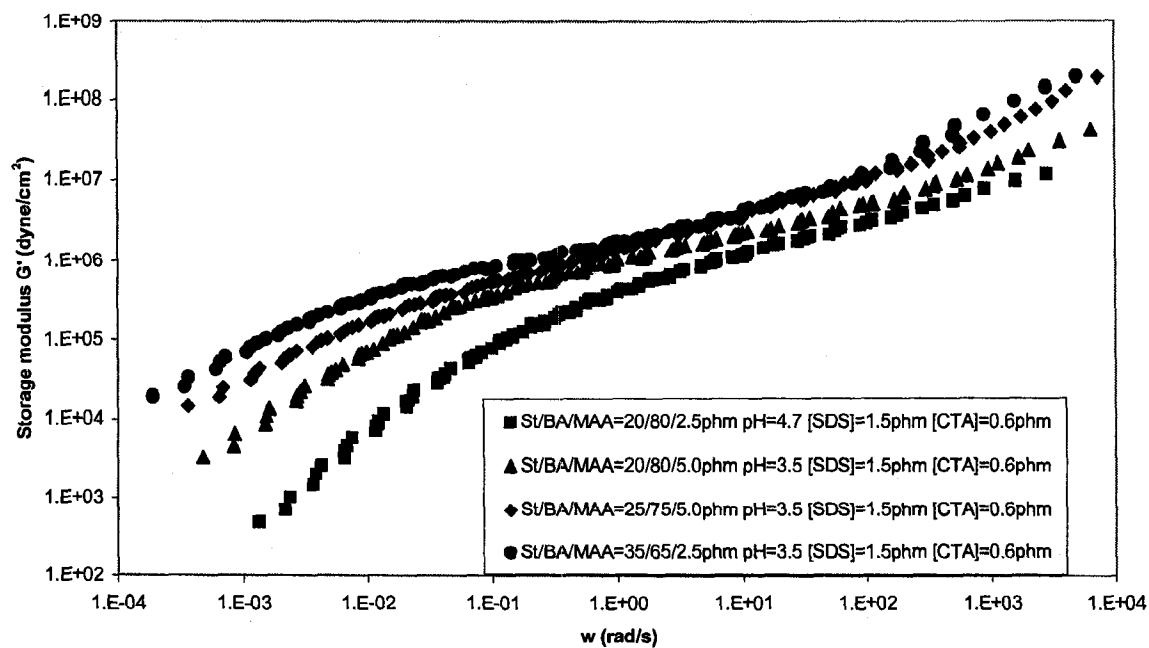


Figure 5.2a Copolymers St20BA80MAA2.5, St20BA80MAA5.0, St25BA75MAA5.0 and St35BA65MAA2.5: G' vs. frequency plots

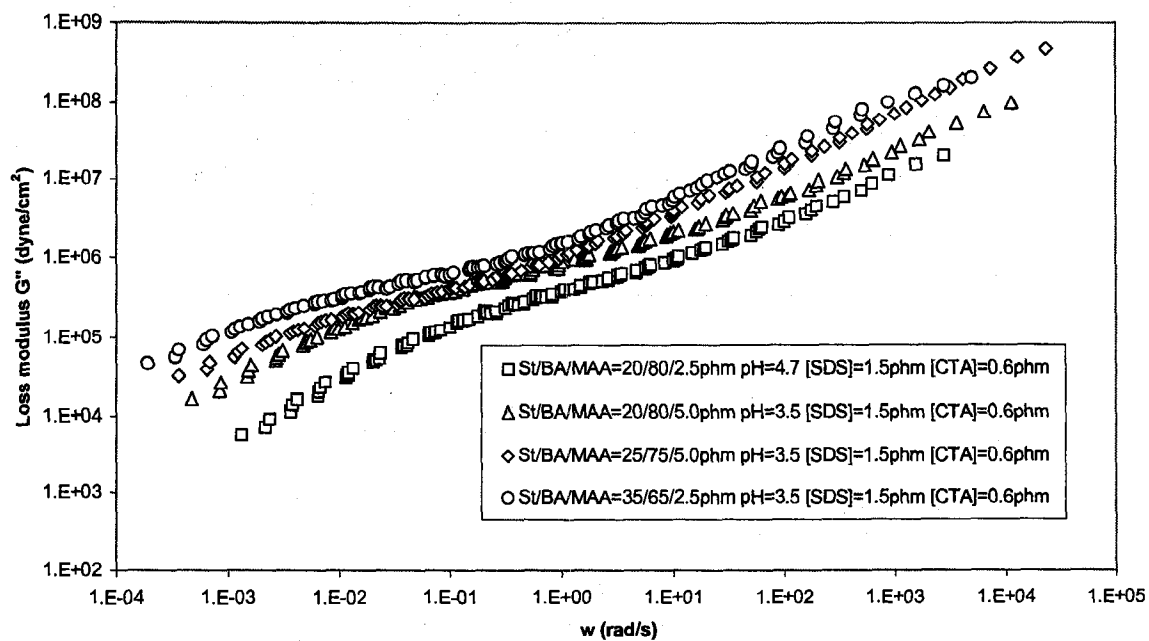


Figure 5.2a Copolymers St20BA80MAA2.5, St20BA80MAA5.0, St25BA75MAA5.0 and St35BA65MAA2.5: G'' vs. frequency plots

St contents in the copolymer samples (from 20 wt% to 35 wt%), both G' and G'' increased over the whole frequency of 10^{-4} to 10^4 rad/s. The increased St contents produced more elastic polymer products and their transition zone shifted to higher frequency ranges.^{10-11, 22} The same trend was found from formulations with increased MAA contents. The increases in G' and G'' were more significant in the terminal zone of low angular frequency range of 10^{-3} to 10^{-1} rad/s.

CTA contents also had influence on the viscoelastic properties of the polymer samples as shown in Figures 5.3a and b. Polymer samples with the same composition of St/BA/MAA = 25/75/2.5 were generated with different CTA contents to have different average molecular weights. With increasing amount of CTA from 0.2 phm to 0.6 phm, the location of the transition zone on the frequency range was displaced to higher frequencies. This observation is consistent with the shift in Figures 5.2 a and b with decreasing St contents, which both reflected a decrease in the relaxation time of the polymer chain.²² Both G' and G'' at low frequency also decreased indicating a decrease in the elasticity with lower molecular weight.

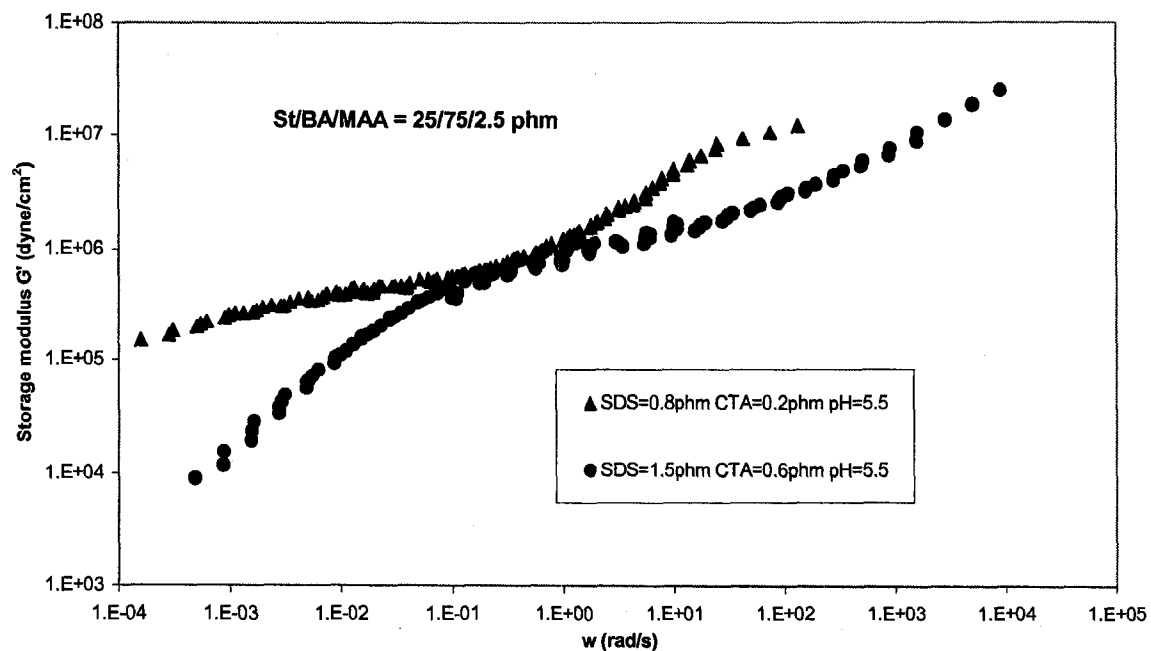


Figure 5.3a Copolymer St₂₅BA₇₅MAA_{2.5}: G' vs. frequency plots

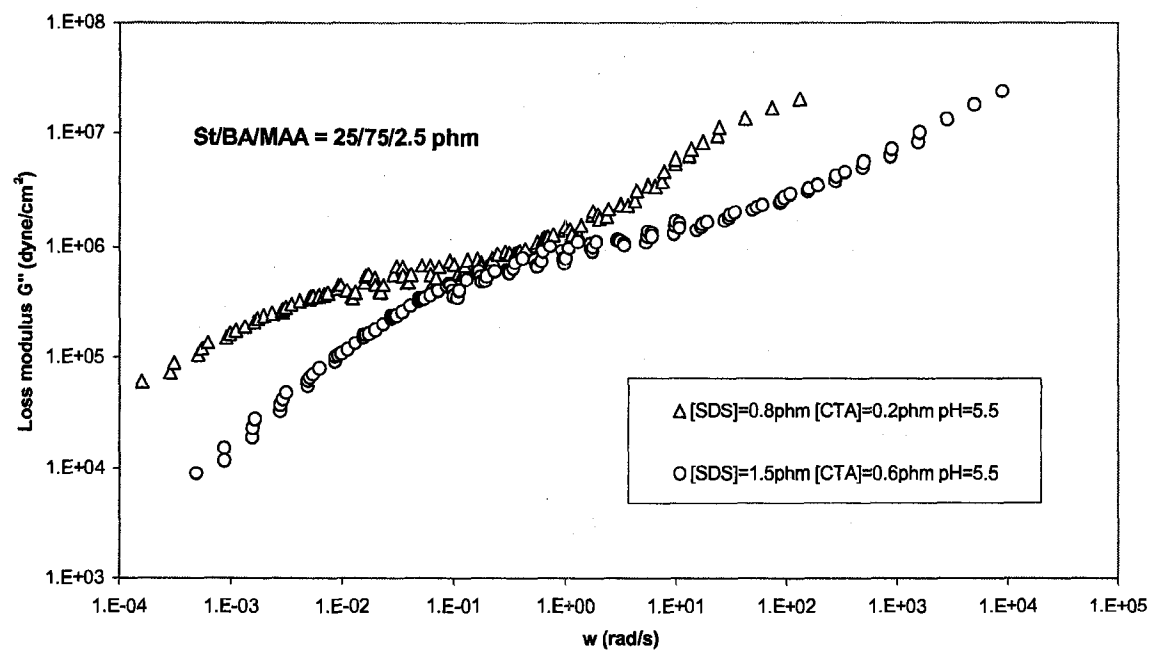


Figure 5.3b Copolymer St₂₅BA₇₅MAA_{2.5}: G'' vs. frequency plots

As mentioned earlier, gel contents were found in latex samples listed in Table 5.7. As shown in Figure 5.3 for example, samples with the presence of gel or polymer chain entanglement showed a plateau range between 10^{-2} to 10^2 rad/s where G' (G'') is only slightly dependent on the frequency.²⁶ The increase in the CTA contents from 0.2 phm to 0.6 phm eliminated the gel in the sample.^{20, 21}

Table 5.7 Latex samples with gel contents

St/BA/MAA (phm)	pH	[SDS] (phm)	[CTA] (phm)	Gel content (wt%)
St25BA75M2.5	5.5	0.8	0.2	15
St25BA75M5.0	5.5	1.5	0.2	13
St35BA65M5.0	5.5	0.8	0.2	16

In un-crosslinked polymer systems, the crossover of storage and loss moduli indicates the existence of entangled coupling in the sample.²² Entanglement coupling is a temporary network structure in which the junctions are not chemical crosslinks but are formed from chains looped through one another and moving slowly. The entanglements can provide additional rigidity to the polymer products, which will exhibit a higher modulus.

For reaction systems with carboxylic acids, such entanglement can be from interactions among carboxylic groups that give rise to acid dimers through hydrogen bonding.^{23, 24} More carboxylic groups present in the system resulted in higher storage modulus of the polymer. As shown in both Figures 5.2 and 5.3, the G' of the latex films increased with an increasing amount of MAA in the reaction contents.

Figures 5.4a and b compared the moduli from polymer samples with the same monomer composition yet prepared under different pH conditions. Polymer samples

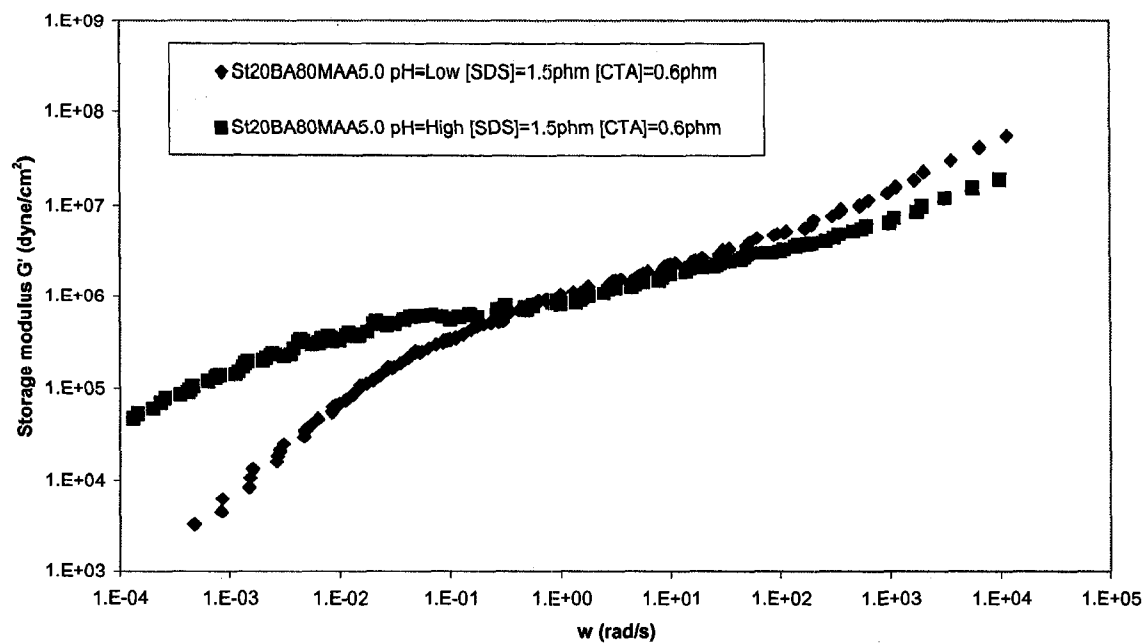


Figure 5.4a Copolymer St20BA80MAA5.0: G' vs. frequency plot

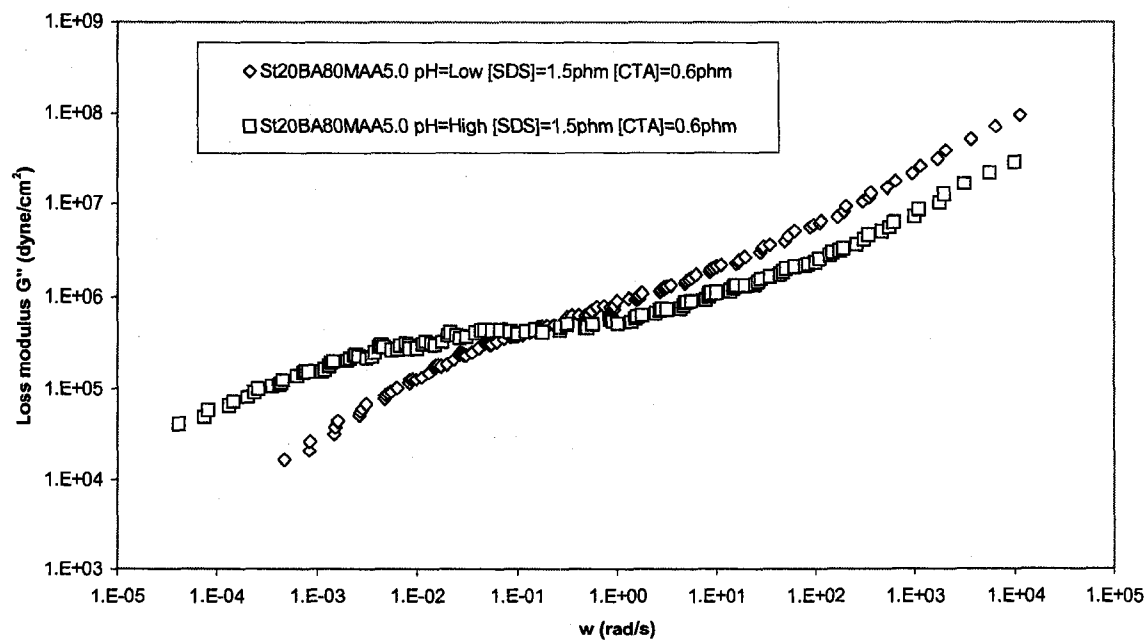


Figure 5.4b Copolymer St20BA80MAA5.0: G'' vs. frequency plot

produced in higher pH (pH = 6.0) environment showed a longer and flatter plateau that extended to the low frequency region due to their higher weight-average molecular weight M_w . Polymer samples produced in a lower pH (pH = 3.5) environment exhibited a lower modulus at low frequency ($\omega < 1$ rad/s), indicating a decrease in elasticity with lower molecular weights.²² Previous studies showed that the pH of the reaction contents greatly affect the distribution of carboxylic groups in the latex.^{20, 21} In an environment with pH = 6.0 close to the pK_a of the MAA, the acid monomer tends to polymerize on the particle surface or homo-polymerize outside the particle. This will result in the creation of ionic moieties at the boundaries between particles.²³ Thus, the G' exhibits a much higher value in the terminal zone than the one obtained from latex prepared at pH = 3.5 due to the presence of new ionic crosslinking knots.

In the coating and pressure sensitive adhesive (PSA) industry, the product performance has been correlated to fundamental polymer parameters such as its molecular weight, entangle molecular weight, T_g , and crosslinking density through linear viscoelastic theory.^{7, 8, 24-26} The performance properties such as their applicability, adhesion, and shear holding properties require looking at both the bonding and the debonding processes. Both steps can be related to the viscoelastic behaviour of the polymer products. Bonding is established in a frequency range of about 1 rad/s because of its low application speed. The polymer material with small G' in this region has less elasticity, which favours the flow and the initial contact with the substrate when used for coating application. Debonding, on the other hand occurs at higher frequencies such as 100-1000 rad/s and the forces required for debonding are related to the G'' of the polymer material in this region.^{27, 28}

In our cases, the adhesion forces of all latex coating seemed not to be proportional to $1/G'$ in the terminal zone. The bonding step is critical for good initial contact to develop good adhesion between the coating and the substrate. Meanwhile, a strong cohesive strength within the coating film is also required to keep it staying on the substrate. This is similar to the shear holding properties of the PSA performance from the testing point of view.^{28, 30} As demonstrated in previous studies, the pH affected the distribution of carboxylic group in the latex and hence significantly influenced the coating adhesion.¹⁷⁻¹⁸ The DMA results show that because the cohesive strength within the film is improved through the hydrogen bonding between the carboxylic groups, it is possible to change the MAA distribution by varying the pH and optimize the coating adhesion forces.

5.4 CONCLUSIONS

DMA was used to study the rheological behaviour of polymer film made from St/BA/MAA latex. It followed the isothermal master curves of the frequency dependent storage and loss moduli (G' and G''). The time-temperature superposition principle was used to extend the frequency range to $10^{-4} - 10^4$ rad/s at the reference temperature of 25°C. The DMA results show that because the cohesive strength within the film is improved through the hydrogen bonding between the carboxylic groups, it is possible to change the MAA distribution by varying the pH and optimize the coating adhesion forces.

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Thesis General Discussion

The objective of this project is to look for the correlation between the coating adhesion results and the inherent properties of latex copolymer such as copolymer composition, molecular weight and distribution so that meaningful predictions on performance properties from process conditions can be made in the future. In this project process conditions such as the monomer composition, carboxylic acid contents, and chain transfer agent contents were manipulated to produce different copolymer products. DMA testing was used to study the viscoelastic properties of the coating polymer and the adhesion testing was used to evaluate the performance of the latex copolymer specific to its application as a coating binder.

Emulsion polymerization of St/BA with MAA

Semi-continuous emulsion polymerizations of St/BA with MAA were conducted at 60°C. The monomer-starved semi-batch feed policy was able to ensure the production of homogeneous latex copolymers.

Design of experiments

The 2^{5-1}_{IV} fractional factorial screening design of experiments was conducted to identify the effects of five variables, i.e., styrene/butyl acrylate ratio, methacrylic acid content, pH, emulsifier content, and chain transfer agent content on various product properties in the emulsion copolymerization of styrene/butyl acrylate. The impact of these variables on the carboxylic acid distribution in the latex, the average latex particle diameter, the molecular weight and distribution of the polymer products, the glass

transition temperature of the polymer, and the coating adhesion to a plastic substrate was studied.

Inside the chosen experimental region, the St/BA ratio is the key factor influencing the copolymer glass transition temperature. Results also showed that the pH of the reaction contents would affect the distribution of carboxylic acid. Higher pH led to more anionic form of the acid reacting in the water phase or on the latex particle surface. The latex particle size was found to be greatly influenced by the emulsifier content. Statistical analysis showed that the CTA concentration and the pH, as well as their 2-factor interaction significantly affected the number-averaged molecular weight. The CTA content was also the key factor influencing the number-averaged molecular weight. The pull-off adhesion between the latex coating and a polycarbonate substrate was found to be influenced by the pH. The adhesion forces increased as the pH of the reaction mixture increased.

pH being the only factor affecting the adhesion performance was a bit out of the expectation. One possible explanation was the experimental region that had been explored was rather limited. Thus, over wider experimental region than the screening design as – St/BA = 20/80 wt% to 50/50 wt%, [MAA] = 2.5 to 7.5 phm, pH = 3.5 to 6.0 a 3-factor 3-level Box-Behnken design was then conducted to investigate the effects of three variables, i.e., St/BA ratio, MAA content, and pH with CTA and SLS contents being held constant. Model correlation between the variables and the performance properties was studied using regression analysis.

Within the experimental region, the pH of the reaction contents would affect the distribution of carboxylic acid. The regression analysis of the Box-Behnken design also

showed that the St/BA ratio and MAA content were the key factors influencing the copolymer T_g ; the MAA content and the pH significantly affected the latex particle size; the St/BA ratio and MAA content affected the number-average molecular weight M_n ; the St/BA ratio and pH affected the weight-average molecular weight M_w . The pull-off adhesion of the latex coating to the PC substrate was influenced by the three factors. The empirical model shows that more [MAA] (7.5 phm) and higher pH (6.0) are required to improve the coating adhesion. The empirical model was able to give predictions on the adhesion forces comparable to real experimental results within the design region

Latex coating adhesion performance

St/BA/MAA polymer lattices were cast on the PC substrate to investigate its coating adhesion to the plastic substrate. The pull-off adhesion was used to evaluate the coating adhesion. It demonstrated that the adhesion performance could be related to the values and frequencies of the storage and loss moduli; whereas the frequency dependent G' and G'' reflected the polymer properties generated under different conditions

DMA evidence showed that because the cohesive strength within the film is improved through the hydrogen bonding between the carboxylic groups at higher pH, it is possible to change the MAA distribution by varying the pH and optimize the coating adhesion forces. This is in agreement with those from carboxylic acid group distribution analyses. DMA evidence did not show the changes in G' in the terminal zone of polymer samples to favour the flow hence improving the contact between the coating and the substrate. One possible explanation is that the dry film thickness also affects the adhesion performance. Since coating films with only one thickness were prepared for testing in this project, such correlation might not be observed within the current film thickness range.

Future works

The work described in this thesis was particularly applied to St/BA semi-continuous emulsion polymerization with MAA. Similar experimental investigation for other monomers with functional groups such as acrylic acid should continue.

APPENDIX A Experimental Run Recipes and Records

Table A1-1 Recipe – Run I-9 St/BA/MAA = 25/75/2.5, pH = 3.5, SDS = 1.5 phm, CTA = 0.2 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	84.2	25.1	0.1	0.81	0.28
	BA	251.5	74.9	0.29	1.96	0.68
	MAA	8.68	2.6	0.01	0.10	0.04
CTA	Dodecanethiol	0.72	0.2	0.001	0.004	
Medium	Water	515.7	153.6	0.59		
Emulsifier	SDS	5.1734	1.5	0.006	0.02	
Initiator	KPS	1.65	0.5	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		867.6234				
Initial charges	Water+SDS+KPS+NaHCO ₃	522.5234				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	Monomer + CTA	345.1	0.96			

Table A1-2 Raw Data - Run I-9 St/BA/MAA = 25/75/2.5, pH = 3.5, SDS = 1.5 phm, CTA = 0.2 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.6	0.31	0.69	0.88	0.22	59204.7	302735.5	5.11	181.8	0.217
180	3.5	0.30	0.70	0.92	0.58	43872.7	249756.7	5.69	399.2	0.26
280	3.4	0.30	0.70	0.94	0.80	41931.2	275718.5	6.58	94.2	0.181
360	3.4	0.30	0.71	0.92	0.92	51180.6	335153.8	6.55	59.7	0.22
420	3.6	0.30	0.70	0.98	0.98	46857.2	302626.3	6.46	61.2	0.197

Table A2-1 Recipe – Run I-1 St/BA/MAA = 25/75/2.5, pH = 3.5, SDS = 0.8 phm, CTA = 0.6 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	84.2	25.2	0.1	0.81	0.28
	BA	250.2	74.8	0.3	1.95	0.68
	MAA	8.8	2.63	0.01	0.10	0.04
CTA	Dodecanethiol	2.095	0.6	0.002	0.01	
Medium	Water	507.917	152.0	0.6		
Emulsifier	SDS	2.6479	0.8	0.003	0.01	
Initiator	KPS	2.241	0.7	0.003	0.01	
Buffer	NaHCO ₃	0	0	0	0	
Total		858.1009				
Initial charges	Water+SDS+KPS+NaHCO ₃	512.8059				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	Monomer + CTA	345.295	0.96			

Table A2-2 Raw Data - Run I-1 St/BA/MAA = 25/75/2.5, pH = 3.5, SDS = 0.8 phm, CTA = 0.6 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.6	0.32	0.68	0.92	0.23	38443.3	146563.3	3.81	74.4	0.216
180	3.5	0.32	0.68	0.94	0.58	32972.0	122469.6	3.71	48.6	0.148
300	3.5	0.32	0.68	0.92	0.82	26987.4	102873.9	3.81	64.1	0.079
360	3.5	0.32	0.68	0.93	0.93	26317.9	102511.7	3.90	72.1	0.109
420	3.4	0.29	0.71	1	1	26847.0	97279.1	3.62	73.4	0.099

Table A3-1 Recipe – Run I-5 St/BA/MAA = 25/75/2.5, pH = 5.5, SDS = 0.8 phm, CTA = 0.2 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	83.25	25.0	0.1	0.8	0.28
	BA	249.5	75.0	0.29	1.9	0.68
	MAA	8.6	2.5	0.01	0.1	0.04
CTA	Dodecanethiol	0.7	0.2	0.001	0.003	
Medium	Water	513.3	154.3	0.60		
Emulsifier	SDS	2.6481	0.8	0.003	0.01	
Initiator	KPS	2.235	0.7	0.003	0.008	
Buffer	NaHCO ₃	1.16	0.35	0.001	0.014	
Total		861.3931				
Initial charges	Water+SDS+KPS+NaHCO ₃	519.3431	25.0	0.1	0.8	
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	342.05	0.95			

Table A3-2 Raw Data - Run I-5 St/BA/MAA = 25/75/2.5, pH = 5.5, SDS = 0.8 phm, CTA = 0.2 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	5.4	0.32	0.68	0.89	0.22	12548.7	118195.9	9.42	74.4	60.1
180	5.7	0.32	0.68	0.91	0.57	23245.9	29491.9	12.7	48.6	56.8
245	5.6	0.32	0.68	0.91	0.71	27384.2	222440.9	8.12	64.1	72.5
300	5.6	0.32	0.68	0.92	0.82	28546.3	260375.9	9.12	72.1	80.3
420	5.7	0.31	0.69	1	1	67020	29401.2	4.39	73.4	79.1

Table A4-1 Recipe – Run I-13 St/BA/MAA = 25/75/2.5, pH = 5.5, SDS = 1.5 phm, CTA = 0.6 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	84.8	25.0	0.1	0.8	0.28
	BA	253.8	75.0	0.30	2.0	0.68
	MAA	9.4	2.8	0.01	0.1	0.04
CTA	Dodecanethiol	2	0.6	0.002	0.01	
Medium	Water	490.7	144.9	0.58		
Emulsifier	SDS	5.1	1.50	0.006	0.02	
Initiator	KPS	1.65	0.49	0.002	0.006	
Buffer	NaHCO ₃	1.48	0.44	0.002	0.02	
Total		848.93				
Initial charges	Water+SDS+KPS+NaHCO ₃	498.93	25.0	0.1	0.81	
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	350	0.97			

Table A4-2 Raw Data - Run I-13 St/BA/MAA = 25/75/2.5, pH = 5.5, SDS = 1.5 phm, CTA = 0.6 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	6.4	0.31	0.69	0.96	0.24	31393.2	297010.8	9.46	25.6	0.167
180	5.6	0.31	0.69	0.94	0.59	28432.2	144589.5	5.09		
280	5.6	0.31	0.69	0.93	0.80	31020.5	140030.0	4.51	61.7	0.084
360	5.6	0.31	0.69	0.93	0.93	28853.9	168987.6	5.86	67.4	0.126
420	5.9	0.29	0.71	1	1	27517.9	142882.0	5.19	60.8	0.13

Table A5-1 Recipe – Run I-3 St/BA/MAA = 25/75/5.0, pH = 3.5, SDS = 0.8 phm, CTA = 0.2 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	79.15	25.0	0.09	0.76	0.27
	BA	237.4	75.0	0.28	1.9	0.66
	MAA	15.8	5.0	0.02	0.18	0.07
CTA	Dodecanethiol	0.626	0.2	0.0007	0.003	
Medium	Water	517.1	163.4	0.60		
Emulsifier	SDS	2.5627	0.8	0.003	0.009	
Initiator	KPS	1.6954	0.54	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		854.3341				
Initial charges	Water+SDS+KPS+NaHCO ₃	521.3581	25.0	0.09	0.76	
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	332.976	0.925			

Table A5-2 Raw Data - Run I-3 St/BA/MAA = 25/75/5.0, pH = 3.5, SDS = 0.8 phm, CTA = 0.2 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.5	0.31	0.69	0.85	0.21	64595.6	338833.3	5.25	125.4	0.242
180	3.4	0.30	0.70	0.91	0.57	44903.7	237288.1	5.28	56	0.194
290	3.6	0.30	0.70	0.92	0.80	42700.9	244286.8	5.72	63.2	0.12
320	3.9	0.30	0.70	0.92	0.85	49377.1	278666.9	5.64	70	0.083
420	3.7	0.29	0.71	1	1	68833.0	319107	4.64	76.4	0.121

Table A6-1 Recipe – Run I-11 St/BA/MAA = 25/75/5.0, pH = 3.5, SDS = 1.5 phm, CTA = 0.6 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	85.6	25.1	0.1	0.8	0.27
	BA	255	74.9	0.3	2.0	0.66
	MAA	17.4	5.1	0.02	0.2	0.07
CTA	Dodecanethiol	2.08	0.6	0.002	0.01	
Medium	Water	499	146.5	0.58		
Emulsifier	SDS	5.1049	1.5	0.006	0.02	
Initiator	KPS	2.022	0.6	0.002	0.0075	
Buffer	NaHCO ₃	0	0	0	0	
Total		866.2069				
Initial charges	Water+SDS+KPS+NaHCO ₃	506.1269				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	360.08	1.00			

Table A6-2 Raw Data - Run I-11 St/BA/MAA = 25/75/5.0, pH = 3.5, SDS = 1.5 phm, CTA = 0.6 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.4	0.33	0.67	0.86	0.22	71712.5	162145.9	2.26	71.3	0.164
180	3.6	0.32	0.68	0.92	0.58	48781.8	143450	2.94	79.5	0.114
280	3.5	0.31	0.69	0.93	0.72	34920.7	116146.2	3.33	44.5	0.174
360	3.3	0.30	0.70	0.88	0.88	30491.3	97185.01	3.19	57.9	0.137
420	3.3	0.30	0.70	0.96	0.96	26064.0	85496	3.28	55.8	0.177

Table A7-1 Recipe – Run I-15 St/BA/MAA = 25/75/5.0, pH = 5.5, SDS = 1.5 phm, CTA = 0.2 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	82.8	25	0.1	0.8	0.27
	BA	248.4	75	0.29	1.94	0.66
	MAA	16.9	5.1	0.02	0.2	0.07
CTA	Dodecanethiol	0.665	0.2	0.0008	0.003	
Medium	Water	511.1	154.3	0.59		
Emulsifier	SDS	4.95	1.5	0.006	0.02	
Initiator	KPS	1.482	0.4	0.002	0.0055	
Buffer	NaHCO ₃	1.58	0.5	0.002	0.02	
Total		867.877				
Initial charges	Water+SDS+KPS+NaHCO ₃	519.112				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	348.765	0.97			

Table A7-2 Raw Data - Run I-15 St/BA/MAA = 25/75/5.0, pH = 5.5, SDS = 1.5 phm, CTA = 0.2 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	5.4	0.30	0.70	0.88	0.22	34038.9	431153.6	12.67	51.7	0.237
180	5.3	0.30	0.70	0.92	0.58	78910.1	475698.7	6.03	51	0.155
300	5.3	0.31	0.69	0.92	0.82	21660.1	373180.8	17.2	67	0.074
360	5.6	0.31	0.69	0.94	0.94	38870.7	379867.6	9.77	73.3	0.087
420	5.8	0.29	0.71	1	1	91485	378924	4.14	71.7	0.085

Table A8-1 Recipe – Run I-7 St/BA/MAA = 25/75/5.0, pH = 5.5, SDS = 0.8 phm, CTA = 0.6 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	83	25.1	0.095	0.8	0.27
	BA	248.1	74.9	0.28	1.9	0.66
	MAA	17.1	5.2	0.02	0.2	0.07
CTA	Dodecanethiol	2.08	0.6	0.002	0.01	
Medium	Water	517.6	156.3	0.6		
Emulsifier	SDS	2.643	0.8	0.003	0.009	
Initiator	KPS	1.9837	0.6	0.002	0.007	
Buffer	NaHCO ₃	1.562	0.5	0.002	0.019	
Total		874.0687				
Initial charges	Water+SDS+KPS+NaHCO ₃	523.7887				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	350.28	0.97			

Table A8-2 Raw Data - Run I-7 St/BA/MAA = 25/75/5.0, pH = 5.5, SDS = 0.8 phm, CTA = 0.6 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	5.6	0.31	0.69	0.88	0.22	34158.4	282243.4	8.26	105.3	0.287
180	5.3	0.31	0.69	0.91	0.57	38376.3	223700.1	5.83	67.9	0.094
240	5.3	0.31	0.69	0.92	0.70	35229.9	169030	4.80	79.2	0.076
360	5.6	0.31	0.69	0.90	0.90	26962.6	152942.7	5.67	97.4	0.062
420	5.8	0.29	0.71	1	1	30646.9	131035.5	4.28	97.3	0.073

Table A9-1 Recipe – Run I-2 St/BA/MAA = 35/65/2.5, pH = 3.5, SDS = 0.8 phm, CTA = 0.2 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	112.6	35.0	0.14	1.1	0.39
	BA	208.6	65.0	0.25	1.6	0.58
	MAA	8.23	2.5	0.01	0.1	0.03
CTA	Dodecanethiol	0.66	0.20	0.0008	0.003	
Medium	Water	492.1	153.2	0.6		
Emulsifier	SDS	2.56	0.8	0.003	0.009	
Initiator	KPS	1.6	0.5	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		826.35				
Initial charges	Water+SDS+KPS+NaHCO ₃	496.26				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+MAA+CTA	330.09	0.92			

Table A9-2 Raw Data - Run I-2 St/BA/MAA = 35/65/2.5, pH = 3.5, SDS = 0.8 phm, CTA = 0.2 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.2	0.43	0.57	0.84	0.21	61614.3	286094.2	4.64	62.4	0.182
180	3.3	0.42	0.58	0.93	0.58	48286.2	258151.7	5.35	52.5	0.167
240	3.3	0.42	0.58	0.94	0.72	46730.5	319098.3	6.83	56	0.097
360	3.4	0.41	0.59	0.94	0.94	58710.2	313573.4	5.34	71.4	0.182
420	3.4	0.41	0.59	1	1	50702.0	308867.9	6.09	70.1	0.137

Table A10-1 Recipe – Run I-10 St/BA/MAA = 35/65/2.5, pH = 3.5, SDS = 1.5 phm, CTA = 0.6 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	112	35.0	0.14	1.08	0.38
	BA	207.9	65.0	0.25	1.62	0.58
	MAA	8.76	2.7	0.01	0.10	0.04
CTA	Dodecanethiol	2.05	0.6	0.003	0.01	
Medium	Water	478.3	149.5	0.59		
Emulsifier	SDS	4.8	1.5	0.006	0.02	
Initiator	KPS	1.6	0.5	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		815.41				
Initial charges	Water+SDS+KPS+NaHCO ₃	484.7				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+MAA+CTA	330.71	0.92			

Table A10-2 Raw Data - Run I-10 St/BA/MAA = 35/65/2.5, pH = 3.5, SDS = 1.5 phm, CTA = 0.6 phm

Time (min)	PH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.6	0.43	0.57	0.90	0.23	37434.7	149549	3.99	25.6	0.216
180	3.5	0.41	0.59	0.95	0.59	30007.8	108420.4	3.61	37.9	0.184
280	3.4	0.41	0.59	0.94	0.81	28431.3	100937.1	3.55	41.6	0.144
360	3.4	0.41	0.59	0.93	0.93	25815.5	93486.12	3.62	52	0.166
420	3.3	0.41	0.59	0.99	0.99	32778.3	102938.7	3.14	55.9	0.131

Table A11-1 Recipe – Run I-14 St/BA/MAA = 35/65/2.5, pH = 5.5, SDS = 1.5 phm, CTA = 0.2 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	112	35.0	0.14	1.1	0.38
	BA	207.9	65.0	0.25	1.6	0.58
	MAA	8.76	2.7	0.01	0.1	0.04
CTA	Dodecanethiol	2.05	0.6	0.0025	0.01	
Medium	Water	478.3	149.5	0.59		
Emulsifier	SDS	4.8	1.5	0.006	0.02	
Initiator	KPS	1.6	0.5	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		815.41				
Initial charges	Water+SDS+KPS+NaHCO ₃	484.7				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+MAA+CTA	330.71	0.92			

Table A11-2 Raw Data - Run I-14 St/BA/MAA = 35/65/2.5, pH = 5.5, SDS = 1.5 phm, CTA = 0.2 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	5.4	0.41	0.59	0.88	0.22	139467.0	494906.5	3.55	35.3	0.205
185	5.4	0.39	0.61	0.93	0.59	44093.5	314474.8	7.13	40.4	0.153
240	5.4	0.40	0.60	0.94	0.72	100556.9	336286.5	3.34	45.9	0.172
360	5.4	0.41	0.59	0.95	0.95	103540.3	378848	3.66	58	0.1
420	5.8	0.40	0.60	1	1	84490.5	342981	4.06	46.9	0.15

Table A12-1 Recipe – Run I-6 St/BA/MAA = 35/65/2.5, pH = 5.5, SDS = 0.8 phm, CTA = 0.6 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	111.43	36.6	0.14	1.1	0.40
	BA	192.75	63.4	0.24	1.5	0.57
	MAA	7.38	2.4	0.009	0.09	0.03
CTA	Dodecanethiol	1.85	0.6	0.002	0.01	
Medium	Water	490.4	161.2	0.6		
Emulsifier	SDS	2.5646	0.8	0.003	0.009	
Initiator	KPS	1.6	0.5	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		807.9746				
Initial charges	Water+SDS+KPS+NaHCO ₃	494.5646				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+MAA+CTA	313.41	0.87			

Table A12-2 Raw Data - Run I-6 St/BA/MAA = 35/65/2.5, pH = 5.5, SDS = 0.8 phm, CTA = 0.6 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	5.9	0.43	0.57	0.97	0.25	52525.3	244664.8	4.66	33.6	0.21
180	4.4	0.43	0.57	0.89	0.57	33941.7	187780.8	5.56	72.1	0.194
280	4.8	0.43	0.57	0.88	0.77	38355.8	148401.3	3.87	105.7	0.113
360	5.4	0.44	0.56	0.87	0.90	26024.6	213611.5	8.21	118.3	0.079
420	5.4	0.43	0.57	0.95	0.98	31032.5	138231.1	4.45	103	0.115

Table A13-1 Recipe – Run I-12 St/BA/MAA = 35/65/5.0, pH = 3.5, SDS = 1.5 phm, CTA = 0.2 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	111.9	35.0	0.13	1.07	0.37
	BA	207.9	65.0	0.24	1.62	0.56
	MAA	16.67	5.2	0.02	0.2	0.07
CTA	Dodecanethiol	0.678	0.2	0.0008	0.003	
Medium	Water	514.5	160.9	0.6		
Emulsifier	SDS	4.8082	1.5	0.006	0.02	
Initiator	KPS	1.752	0.55	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		858.2082				
Initial charges	Water+SDS+KPS+NaHCO ₃	521.0602				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	337.148	0.936			

Table A13-2 Raw Data - Run I-12 St/BA/MAA = 35/65/5.0, pH = 3.5, SDS = 1.5 phm, CTA = 0.2 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
65	3.2	0.41	0.59	0.92	0.23	45414.1	196906.7	4.33	103.7	0.227
180	3.4	0.41	0.59	0.96	0.61	40535.4	197292.1	4.87	48	0.168
280	3.5	0.41	0.59	0.96	0.82	57489.8	252516.6	4.39	48.8	0.158
360	3.4	0.41	0.59	0.97	0.97	48335.3	249867.2	5.17	56.6	0.102
420	3.4	0.40	0.60	1	1	49611.8	251111.6	5.06	62.9	0.139

Table A14-1 Recipe – Run I-4 St/BA/MAA = 35/65/5.0, pH = 3.5, SDS = 0.8 phm, CTA = 0.6 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	113.1	35.1	0.13	1.09	0.37
	BA	208.7	64.9	0.24	1.63	0.56
	MAA	16.2	5.0	0.02	0.19	0.06
CTA	Dodecanethiol	1.95	0.6	0.002	0.01	
Medium	Water	525.6	163.3	0.60		
Emulsifier	SDS	2.56	0.8	0.003	0.009	
Initiator	KPS	1.437	0.4	0.002	0.005	
Buffer	NaHCO ₃	0	0	0	0	
Total		869.547				
Initial charges	Water+SDS+KPS+NaHCO ₃	529.597				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	339.95	0.944			

Table A14-2 Raw Data - Run I-4 St/BA/MAA = 35/65/5.0, pH = 3.5, SDS = 0.8 phm, CTA = 0.6 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
75	3.2	0.43	0.57	0.82	0.25	39974.5	157257.8	3.93	105.6	0.286
185	3.2	0.42	0.58	0.92	0.57	34382.0	160980.5	4.68	50.6	0.206
280	3.2	0.42	0.58	0.93	0.80	30386.2	126946.7	4.18	56.7	0.14
360	3.4	0.42	0.58	0.94	0.94	28027.3	106929.8	3.82	69.2	0.125
420	3.4	0.40	0.60	0.96	0.96	27594.7	107757.1	3.90	68.2	0.143

Table A15-1 Recipe – Run I-8 St/BA/MAA = 35/65/5.0, pH = 5.5, SDS = 0.8 phm, CTA = 0.2 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	114.6	35.0	0.13	1.10	0.37
	BA	212.6	65.0	0.24	1.66	0.56
	MAA	16.9	5.2	0.02	0.2	0.07
CTA	Dodecanethiol	0.76	0.2	0.001	0.004	
Medium	Water	521.4	159.3	0.6		
Emulsifier	SDS	2.5819	0.79	0.003	0.009	
Initiator	KPS	1.8597	0.57	0.002	0.007	
Buffer	NaHCO ₃	1.784	0.55	0.002	0.02	
Total		872.4856				
Initial charges	Water+SDS+KPS+NaHCO ₃	527.6256				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	344.86	0.958			

Table A15-2 Raw Data - Run I-8 St/BA/MAA = 35/65/5.0, pH = 5.5, SDS = 0.8 phm, CTA = 0.2 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	5.5	0.42	0.58	0.85	0.21	102132.1	343979.4	3.37	45	0.227
185	5.3	0.42	0.58	0.90	0.57	102726.0	369838.7	3.6	64.5	0.058
300	5.3	0.41	0.59	0.89	0.80	90985.7	315099.2	3.46	85.4	0.04
360	5.3	0.41	0.59	0.92	0.92	90131.6	292953.2	3.25	88.6	0.08
420	5.5	0.40	0.60	1	1	88425.0	281445.4	3.18	88.5	0.081

Table A16-1 Recipe – Run I-16 St/BA/MAA = 35/65/5.0, pH = 5.5, SDS = 1.5 phm, CTA = 0.6 phm

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	115.9	35.0	0.13	1.11	0.37
	BA	215.5	65.0	0.25	1.68	0.56
	MAA	17	5.1	0.02	0.2	0.07
CTA	Dodecanethiol	2.05	0.6	0.002	0.01	
Medium	Water	520.17	157.0	0.6		
Emulsifier	SDS	4.9857	1.50	0.006	0.02	
Initiator	KPS	2.058	0.6	0.002	0.008	
Buffer	NaHCO ₃	1.448	0.4	0.002	0.02	
Total		879.1117				
Initial charges	Water+SDS+KPS+NaHCO ₃	528.6617				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	350.45	0.973			

Table A16-2 Raw Data - Run I-16 St/BA/MAA = 35/65/5.0, pH = 5.5, SDS = 1.5 phm, CTA = 0.6 phm

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	5.1	0.42	0.58	0.92	0.23	40444.4	214454.5	5.30	56.2	0.266
185	5.3	0.41	0.59	0.95	0.60	31851.9	153571.7	4.82	53.3	0.093
245	5.3	0.41	0.59	0.95	0.74	30340.7	142982.9	4.71	60.5	0.078
360	5.3	0.41	0.59	0.95	0.95	30432.8	148991.5	4.90	77.7	0.08
420	5.6	0.39	0.61	1	1	31140.2	124491.4	4.00	69.4	0.086

Table A17-1 Recipe – Run II-1 St/BA/MAA = 20/80/2.5, pH = Med

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	62.71	20.0	0.08	0.60	0.23
	BA	250.22	80.0	0.30	1.95	0.74
	MAA	7.88	2.5	0.01	0.09	0.03
CTA	Dodecanethiol	1.88	0.6	0.002	0.01	
Medium	Water	493.8	157.8	0.6		
Emulsifier	SDS	4.7093	1.50	0.006	0.02	
Initiator	KPS	1.662	0.53	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		822.8613				
Initial charges	Water+SDS+KPS+NaHCO ₃	500.1713				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	322.69	0.896			

Table A17-2 Raw Data - Run II-1 St/BA/MAA = 20/80/2.5, pH = Med

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.9	0.41	0.59	0.96	0.24	38288.2	135849.4	3.55	642.0	0.402
180	4.0	0.37	0.63	0.97	0.60	31639.1	95774.7	3.03		
280	4.0	0.40	0.60	0.93	0.79	31767.7	91942.1	2.90	119.4	0.226
360	3.9	0.42	0.58	0.93	0.93	30273.7	92553.6	3.06		
420	4.4	0.42	0.59	0.95	0.95	29009.1	95067.2	3.28	42.2	0.196

Table A18-1 Recipe – Run II-5 St/BA/MAA = 20/80/5.0, pH = Low

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	62.75	20.0	0.08	0.60	0.22
	BA	249.66	80.0	0.30	1.95	0.71
	MAA	15.6	5.0	0.02	0.18	0.07
CTA	Dodecanethiol	1.89	0.6	0.002	0.009	
Medium	Water	492.3	157.6	0.59		
Emulsifier	SDS	4.7546	1.5	0.006	0.016	
Initiator	KPS	1.698	0.54	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		828.6526				
Initial charges	Water+SDS+KPS+NaHCO ₃	498.7526				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	329.9	0.916			

Table A18-2 Raw Data – Run II-5 St/BA/MAA = 20/80/5.0, pH = Low

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.5	0.23	0.77	0.87	0.22	33414.1	102909.0	3.08	400.9	0.43
180	3.7	0.22	0.78	0.94	0.58	25293.0	74530.2	2.95		
280	3.7	0.23	0.77	0.95	0.81	24456.2	69867.1	2.86	46.9	0.20
360	3.8	0.22	0.78	0.94	0.94	22498.1	71727.4	3.19		
420	3.8	0.22	0.78	0.99	0.99	27200.9	74233.1	2.73	47.3	0.23

Table A19-1 Recipe – Run II-7 St/BA/MAA = 20/80/5.0, pH = High

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	62.47	20.0	0.07	0.60	0.22
	BA	250	80.0	0.28	1.95	0.71
	MAA	15.64	5.0	0.02	0.18	0.07
CTA	Dodecanethiol	1.9	0.6	0.002	0.009	
Medium	Water	546.7	175.0	0.6		
Emulsifier	SDS	4.7	1.50	0.005	0.016	
Initiator	KPS	1.568	0.50	0.002	0.006	
Buffer	NaHCO ₃	5.452	1.74	0.006	0.065	
Total		888.43				
Initial charges	Water+SDS+KPS+NaHCO ₃	558.42				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	330.01	0.917			

Table A19-2 Raw Data - Run II-7 St/BA/MAA = 20/80/5.0, pH = High

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
70	5.9	0.24	0.76	0.95	0.26	29031.7	122009.6	4.20	49.2	0.16
180	5.7	0.24	0.76	0.92	0.57	19448.6	96616.4	4.97		
280	5.7	0.24	0.76	0.89	0.75	26750.0	119037.7	4.45	103.4	0.087
360	5.8	0.24	0.76	0.86	0.86	15782.6	89554.0	5.67		
420	5.8	0.23	0.77	0.95	0.95	17333.7	155401.7	8.97	115.6	0.161

Table A20-1 Recipe – Run II-3 St/BA/MAA = 20/80/7.5, pH = Med

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	55.74	20.0	0.07	0.54	0.21
	BA	222.98	80.0	0.28	1.74	0.69
	MAA	20.9	7.5	0.07	0.24	0.10
CTA	Dodecanethiol	1.672	0.6	0.002	0.008	
Medium	Water	490.72	176.1	0.62		
Emulsifier	SDS	4.1913	1.50	0.005	0.015	
Initiator	KPS	1.513	0.54	0.002	0.006	
Buffer	NaHCO ₃	0.184	0.07	0.0002	0.002	
Total		797.9003				
Initial charges	Water+SDS+KPS+NaHCO ₃	496.6083				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
300	St+BA+CTA	301.292	1.00			

Table A20-2 Raw Data - Run II-3 St/BA/MAA = 20/80/7.5, pH = Med

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
50	4.5	0.23	0.77	0.87	0.21	39262.2	161608.7	4.11	76.4	0.218
120	4.5	0.24	0.76	0.95	0.49	32635.0	140019.5	4.29	35.8	0.173
210	4.5	0.23	0.77	0.97	0.77	32231.7	141934.9	4.40	39	0.208
300	4.5	0.22	0.78	0.99	0.99	23928.5	99630.8	4.16	50.5	0.153
330	4.5	0.23	0.77	1	1	20809.2	95260.3	4.58	53.7	0.175

Table A21-1 Recipe – Run II-9 St/BA/MAA = 35/65/2.5, pH = Low

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	112.41	35.1	0.14	1.08	0.39
	BA	207.76	64.9	0.25	1.62	0.58
	MAA	7.95	2.5	0.01	0.09	0.03
CTA	Dodecanethiol	1.99	0.6	0.002	0.01	
Medium	Water	489.9	153.0	0.59		
Emulsifier	SDS	4.636	1.4	0.006	0.02	
Initiator	KPS	1.638	0.5	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		826.284				
Initial charges	Water+SDS+KPS+NaHCO ₃	496.174				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+MAA+CTA	330.11	0.917			

Table A21-1 Raw Data - Run II-9 St/BA/MAA = 35/65/2.5, pH = Low

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.6	0.42	0.58	0.90	0.22	29185.5	112815.7	3.87	240.6	0.284
180	3.8	0.40	0.60	0.95	0.59	28082.7	85316.6	3.04	109.1	0.242
280	3.8	0.40	0.60	0.96	0.82	25640.8	78512.9	3.06	62.1	0.219
375	3.8	0.40	0.60	0.95	0.95	24102.7	79143.2	3.28	58.5	0.261
420	3.8	0.40	0.60	0.97	0.97	18889.5	75025.8	3.97	52.2	0.253

Table A22-1 Recipe – Run II-11 St/BA/MAA = 35/65/2.5, pH = High

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	103.5	35.0	0.125	0.99	0.37
	BA	191.42	64.9	0.232	1.49	0.56
	MAA	14.75	5.0	0.018	0.17	0.06
CTA	Dodecanethiol	1.83	0.6	0.002	0.01	
Medium	Water	507.2	172.0	0.615		
Emulsifier	SDS	4.5	1.5	0.005	0.016	
Initiator	KPS	1.37	0.5	0.002	0.005	
Buffer	NaHCO ₃	0.126	0.04	0.0001	0.0015	
Total		824.696				
Initial charges	Water+SDS+KPS+NaHCO ₃	513.196				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	311.5	0.865			

Table A22-2 Raw Data - Run II-11 St/BA/MAA = 35/65/2.5, pH = High

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.1	0.45	0.55	0.92	0.23	39420.6	139406.2	3.54	26.3	0.121
180	3.2	0.44	0.56	0.95	0.59	30439.5	112145.3	3.68	32.7	0.176
240	3.2	0.44	0.56	0.96	0.81	25058.0	83835.1	3.35	44	0.164
360	3.2	0.44	0.56	0.96	0.96	22261.9	81968.8	3.68	54.2	0.133
420	3.4	0.43	0.57	1	1	23435.5	86007.4	3.67	44.9	0.164

Table A23-1 Recipe – Run II-13 St/BA/MAA = 35/65/5.0, pH = Med

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	103.5	35.0	0.125	0.99	0.37
	BA	191.42	64.9	0.232	1.49	0.56
	MAA	14.75	5.0	0.018	0.17	0.06
CTA	Dodecanethiol	1.83	0.6	0.002	0.01	
Medium	Water	507.2	172.0	0.615		
Emulsifier	SDS	4.5	1.5	0.005	0.016	
Initiator	KPS	1.37	0.5	0.002	0.005	
Buffer	NaHCO ₃	0.126	0.04	0.0001	0.0015	
Total		824.696				
Initial charges	Water+SDS+KPS+NaHCO ₃	513.196				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	311.5	0.865			

Table A23-2 Raw Data - Run II-13 St/BA/MAA = 35/65/5.0, pH = Med

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	4.0	0.42	0.58	0.89	0.22	22243.2	80398.5	3.61	171.7	0.394
180	4.0	0.40	0.60	0.94	0.59	20136.6	71719.0	3.56	62.2	0.189
280	4.5	0.40	0.60	0.96	0.83	17784.7	58948.4	3.31	38.9	0.252
360	4.5	0.40	0.60	0.97	0.97	17353.9	58876.3	3.39	36.5	0.208
420	4.6	0.38	0.61	0.97	0.97	17373.6	62416.0	3.59	40.8	0.203

Table A24-1 Recipe – Run II-14 St/BA/MAA = 35/65/5.0, pH = Med

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	108.95	34.7	0.13	1.05	0.369
	BA	205.06	65.3	0.25	1.6	0.565
	MAA	16.09	5.1	0.02	0.2	0.066
CTA	Dodecanethiol	1.899	0.60	0.002	0.009	
Medium	Water	494.1	157.4	0.6		
Emulsifier	SDS	4.7042	1.5	0.006	0.016	
Initiator	KPS	1.674	0.53	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		832.4772				
Initial charges	Water+SDS+KPS+NaHCO ₃	500.4782				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	331.999	0.922			

Table A24-2 Raw Data - Run II-14 St/BA/MAA = 35/65/5.0, pH = Med

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	4.5	0.40	0.60	0.92	0.23	32964.0	92929.4	2.82	51.7	0.177
185	4.5	0.41	0.59	0.96	0.61	26680.4	82918.3	3.11		
280	4.7	0.42	0.58	0.96	0.82	34502.9	100727.0	2.92	35.7	0.194
360	4.8	0.42	0.58	0.97	0.97	32945.1	100227.0	3.04		
420	4.7	0.42	0.58	1	1	26410.3	91498.0	3.46	35.7	0.194

Table A25-1 Recipe – Run II-15 St/BA/MAA = 35/65/5.0, pH = Med

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	108.45	34.7	0.13	1.04	0.37
	BA	204.34	65.3	0.24	1.6	0.57
	MAA	15.9	5.0	0.02	0.18	0.06
CTA	Dodecanethiol	1.898	0.6	0.002	0.01	
Medium	Water	502.3	160.6	0.60		
Emulsifier	SDS	4.7539	1.5	0.006	0.016	
Initiator	KPS	1.6275	0.5	0.002	0.006	
Buffer	NaHCO ₃	0.221	0.07	0.0003	0.003	
Total		839.4904				
Initial charges	Water+SDS+KPS+NaHCO ₃	508.9024				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	330.588	0.918			

Table A25-2 Raw Data - Run II-15 St/BA/MAA = 35/65/5.0, pH = Med

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
70	4.4	0.39	0.61	0.92	0.26	12522.0	101522.3	8.11	86.6	0.307
180	4.6	0.39	0.61	0.96	0.60	20588.3	80042.3	3.89	35.8	0.213
240	4.6	0.38	0.62	0.96	0.82	10591.3	62731.2	5.93	44.3	0.185
360	4.8	0.40	0.60	0.98	0.98	20543.4	67287.9	3.28	44.2	0.174
420	4.8	0.38	0.62	1	1	18170.9	65645.6	3.61	44.8	0.19

Table A26-1 Recipe – Run II-10 St/BA/MAA = 35/65/7.5, pH = Low

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	105.2	35.0	0.13	1.01	0.36
	BA	195.34	65.0	0.24	1.52	0.55
	MAA	22.56	7.50	0.03	0.26	0.09
CTA	Dodecanethiol	1.805	0.60	0.002	0.01	
Medium	Water	495.6	164.9	0.60		
Emulsifier	SDS	4.5011	1.5.0	0.005	0.02	
Initiator	KPS	1.643	0.55	0.002	0.01	
Buffer	NaHCO ₃	0	0	0	0	
Total		826.6491				
Initial charges	Water+SDS+KPS+NaHCO ₃	501.7441				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+MAA+CTA	324.905	0.903			

Table A26-2 Raw Data - Run II-10 St/BA/MAA = 35/65/7.5, pH = Low

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.7	0.41	0.59	0.92	0.23	27904.2	119577.7	4.29	83	0.211
182	3.6	0.42	0.58	0.97	0.61	26441.9	84850.1	3.21	29.3	0.197
280	3.7	0.39	0.60	0.98	0.84	25329.6	78872.7	3.11	37.9	0.168
360	3.3	0.41	0.59	0.97	0.97	27342.1	82691.0	3.02	44.7	0.14
420	3.3	0.38	0.62	0.99	0.99	21982.0	75746.0	3.44	62.6	0.259

Table A27-1 Recipe – Run II-12 St/BA/MAA = 35/65/7.5, pH = High

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	105.2	35.0	0.12	1.01	0.36
	BA	195.8	65.0	0.22	1.53	0.55
	MAA	22.5	7.5	0.03	0.26	0.09
CTA	Dodecanethiol	1.8	0.6	0.002	0.009	
Medium	Water	552.9	183.7	0.62		
Emulsifier	SDS	4.4968	1.5	0.005	0.02	
Initiator	KPS	1.613	0.5	0.002	0.006	
Buffer	NaHCO ₃	5.025	1.7	0.006	0.06	
Total		889.3348				
Initial charges	Water+SDS+KPS+NaHCO ₃	564.0348				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+MAA+CTA	325.3	0.904			

Table A27-2 Raw Data - Run II-12 St/BA/MAA = 35/65/7.5, pH = High

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	6.0	0.42	0.58	0.99	0.24	38109.6	156983.1	4.12	32	0.214
180	5.3	0.37	0.63	0.93	0.57	35117.8	190052.1	5.41		
240	5.4	0.41	0.59	0.90	0.76	18844.1	119756.9	6.36	99	0.066
360	5.3	0.43	0.57	0.89	0.89	20983.2	144722.1	6.90		
420	5.5	0.41	0.59	1	1	20049.5	108177.2	5.40	109.4	0.129

Table A28-1 Recipe – Run II-2 St/BA/MAA = 50/50/2.5, pH = Med

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	160.05	50.0	0.19	1.54	0.53
	BA	160.05	50.0	0.19	1.25	0.43
	MAA	7.975	2.5	0.01	0.09	0.03
CTA	Dodecanethiol	1.925	0.6	0.002	0.01	
Medium	Water	509.87	159.3	0.60		
Emulsifier	SDS	4.806	1.50	0.006	0.02	
Initiator	KPS	1.545	0.5	0.002	0.006	
Buffer	NaHCO ₃	0.132	0.04	0.0002	0.002	
Total		846.353				
Initial charges	Water+SDS+KPS+NaHCO ₃	516.353				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	330	0.917			

Table A28-2 Raw Data - Run II-2 St/BA/MAA = 50/50/2.5, pH = Med

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.8	0.42	0.55	0.45	0.23	24193.0	106268.4	4.39	198.2	0.331
180	4.4	0.37	0.55	0.45	0.61	8657.4	67266.5	7.77	92.8	0.262
285	4.6	0.41	0.55	0.45	0.84	10898.6	66399.2	6.09	51.4	0.233
360	4.8	0.43	0.55	0.45	0.97	11083.2	68582.6	6.19	39.3	0.221
420	4.8	0.41	0.55	0.45	1	11653.0	67291.9	5.77	31.4	0.207

Table A29-1 Recipe – Run II-6 St/BA/MAA = 50/50/5.0, pH = Low

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	156.24	50	0.18	1.50	0.52
	BA	156.24	50	0.18	1.22	0.42
	MAA	15.57	5.0	0.02	0.18	0.06
CTA	Dodecanethiol	1.832	0.6	0.002	0.01	
Medium	Water	518	165.8	0.60		
Emulsifier	SDS	4.65	1.5	0.005	0.02	
Initiator	KPS	1.4778	0.5	0.002	0.005	
Buffer	NaHCO ₃	0	0	0	0	
Total		854.0098				
Initial charges	Water+SDS+KPS+NaHCO ₃	524.1278				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	329.882	0.916			

Table A29-2 Raw Data - Run II-6 St/BA/MAA = 50/50/5.0, pH = Low

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	3.4	0.55	0.45	0.86	0.21	20973.5	96281.1	4.59	62	0.271
180	4.1	0.56	0.44	0.95	0.59	11709.2	65270.6	5.57	26.1	0.218
280	4.1	0.55	0.45	0.98	0.83	10930.6	59856.7	5.48	35.1	0.188
360	3.5	0.54	0.46	0.96	0.96	9631.5	58319.0	6.06	39.5	0.147
420	3.6	0.54	0.46	0.99	0.99	10438.6	59669.5	5.72	43	0.155

Table A30-1 Recipe – Run II-8 St/BA/MAA = 50/50/5.0, pH = High

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	156.37	50.0	0.16	1.50	0.52
	BA	156.19	50.0	0.16	1.22	0.42
	MAA	15.64	5.0	0.02	0.2	0.06
CTA	Dodecanethiol	1.898	0.60	0.002	0.01	
Medium	Water	614.9	196.7	0.64		
Emulsifier	SDS	4.7	1.50	0.005	0.02	
Initiator	KPS	1.62	0.5	0.002	0.006	
Buffer	NaHCO ₃	6.169	2.0	0.006	0.07	
Total		957.487				
Initial charges	Water+SDS+KPS+NaHCO ₃	627.389				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	330.098	0.917			

Table A30-2 Raw Data - Run II-8 St/BA/MAA = 50/50/5.0, pH = High

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac.)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	6.3	0.56	0.44	0.97	0.23	7168.7	102644.7	14.31	198.2	0.331
180	5.6	0.58	0.42	0.96	0.58	13159.4	84155.8	6.40	92.8	0.262
280	5.2	0.56	0.44	0.931	0.78	20771.3	86109.0	4.15	51.4	0.233
360	5.5	0.56	0.44	0.92	0.92	15316.0	73485.2	4.80	39.3	0.221
420	5.6	0.55	0.45	1	1	10128.1	84088.2	8.30	31.4	0.207

Table A31-1 Recipe – Run II-4 St/BA/MAA = 50/50/7.5, pH = Med

	Ingredients	Mass (g)	phm	wt. frac.	N (mol)	mol. frac.
Monomer	St	149.15	50	0.18	1.43	0.50
	BA	149.15	50	0.18	1.16	0.41
	MAA	22.84	7.6	0.03	0.27	0.09
CTA	Dodecanethiol	1.86	0.6	0.002	0.01	
Medium	Water	496.3	166.4	0.60		
Emulsifier	SDS	4.5155	1.5	0.005	0.02	
Initiator	KPS	1.6158	0.5	0.002	0.006	
Buffer	NaHCO ₃	0	0	0	0	
Total		825.4313				
Initial charges	Water+SDS+KPS+NaHCO ₃	502.4313				
Feeding time (min)		Feeding mass (g)	Mass feed rate (g/min)			
360	St+BA+CTA	323	0.897			

Table A31-2 Raw Data - Run II-4 St/BA/MAA = 50/50/7.5, pH = Med

Time (min)	pH	St mol. Frac.	BA mol. Frac.	Inst. Conversion (wt. frac.)	Overall Conversion (wt. frac)	M _n	M _w	M _w /M _n	PS (nm)	PS Polydispersity
60	4.1	0.55	0.45	0.90	0.22	20284	97436.3	4.80	29.7	0.231
180	4.4	0.54	0.46	0.96	0.43	17380.4	68672.4	3.95	30.5	0.217
240	4.5	0.55	0.45	1	0.78	17584.6	66712.1	3.80	29.9	0.222
360	4.6	0.55	0.45	0.99	0.99	34703.8	115560.3	3.33	45.2	0.136
420	4.8	0.55	0.45	1	1	20605.7	68482.0	3.32	45.8	0.185

APPENDIX B 2^{5-1}_V Fractional Factorial Design of Experiments

– Estimated Effects and Coefficients

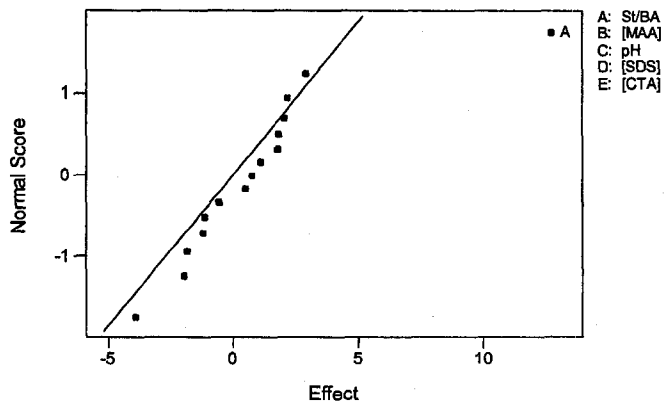
Estimated effects and coefficients for T_g (coded units)

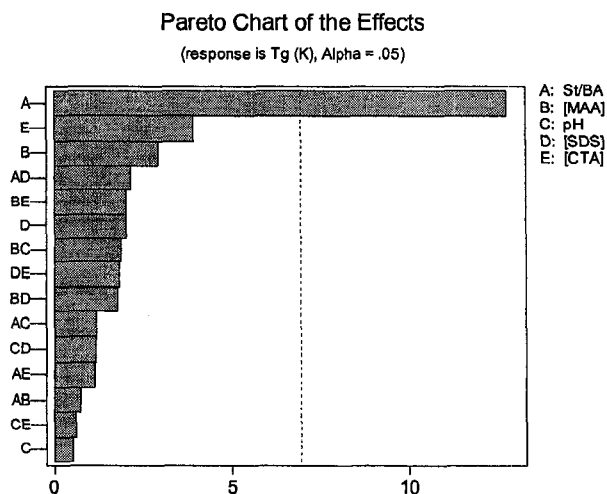
Term	Effect	Coef
Constant		270.420
St/BA	12.737	6.369
[MAA]	2.910	1.455
pH	0.497	0.249
[SDS]	-2.002	-1.001
[CTA]	-3.922	-1.961
St/BA*[MAA]	0.748	0.374
St/BA*pH	-1.185	-0.593
St/BA*[SDS]	2.140	1.070
St/BA*[CTA]	1.125	0.562
[MAA]*pH	-1.872	-0.936
[MAA]*[SDS]	1.773	0.886
[MAA]*[CTA]	2.012	1.006
pH*[SDS]	-1.160	-0.580
pH*[CTA]	-0.605	-0.302
[SDS]*[CTA]	1.825	0.912

Analysis of Variance for T_g (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	5	761.42	761.42	152.284	*	*
2-Way Interactions	10	94.19	94.19	9.419	*	*
Residual Error	0	0.00	0.00	0.000		
Total	15	855.62				

Normal Probability Plot of the Effects
(response is T_g (K), Alpha = .05)



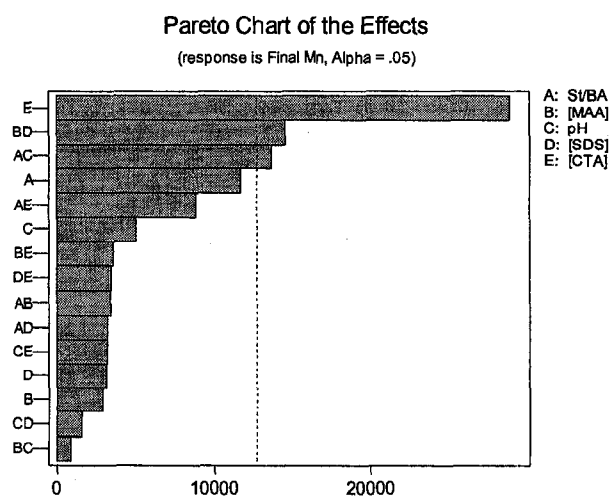
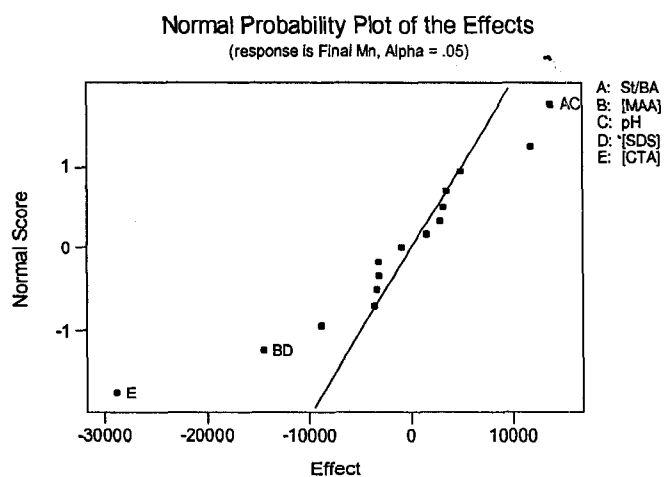


Estimated Effects and Coefficients for M_n (coded units)

Term	Effect	Coef
Constant		43627
St/BA	11690	5845
[MAA]	2847	1424
pH	4931	2466
[SDS]	-3117	-1558
[CTA]	-28848	-14424
St/BA* [MAA]	-3405	-1702
St/BA*pH	13669	6834
St/BA* [SDS]	3183	1592
St/BA* [CTA]	-8823	-4411
[MAA] *pH	-883	-441
[MAA] * [SDS]	-14532	-7266
[MAA] * [CTA]	-3530	-1765
pH* [SDS]	1550	775
pH* [CTA]	-3168	-1584
[SDS] * [CTA]	3462	1731

Analysis of Variance for Final (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	5	4044055671	4044055671	808811134	*	*
2-Way Interactions	10	2141033210	2141033210	214103321	*	*
Residual Error	0	0	0	0		
Total	15	6185088881				



Estimated Effects and Coefficients for M_w (coded units)

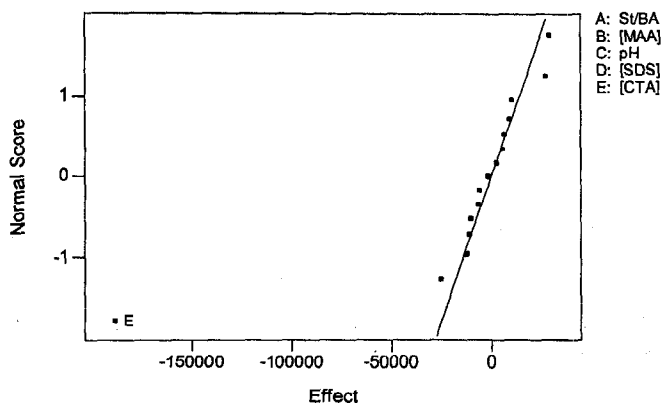
Term	Effect	Coef
Constant		210310
St/BA	-6164	-3082
[MAA]	-6641	-3321
pH	26824	13412
[SDS]	6380	3190
[CTA]	-188093	-94046
St/BA* [MAA]	-25412	-12706
St/BA*pH	2294	1147
St/BA* [SDS]	-10074	-5037
St/BA* [CTA]	10346	5173
[MAA] * pH	5419	2710
[MAA] * [SDS]	-12073	-6036
[MAA] * [CTA]	-1497	-748
pH* [SDS]	29089	14545
pH* [CTA]	8968	4484
[SDS] * [CTA]	-11003	-5502

Analysis of Variance for M_w (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	5	1.44885E+11	1.4488E+11	2.8977E+10	*	*
2-Way Interactions	10	8338563855	8338563855	833856385	*	*
Residual Error	0	0	0	0		
Total	15	1.53223E+11				

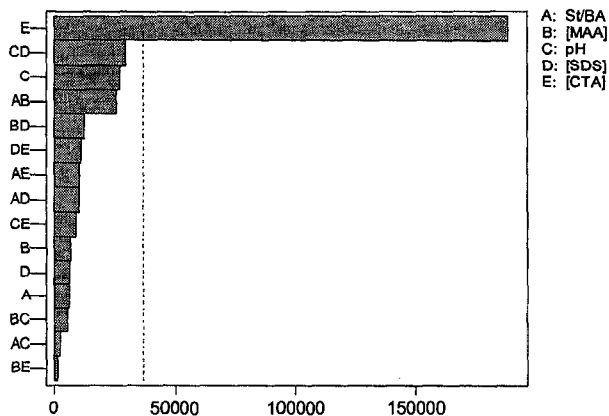
Normal Probability Plot of the Effects

(response is Final Mw, Alpha = .05)



Pareto Chart of the Effects

(response is Final Mw, Alpha = .05)



Estimated Effects and Coefficients for M_w/M_n (coded units)

Term	Effect	Coef
Constant		4.8749
St/BA	-1.2765	-0.6383
[MAA]	-0.3317	-0.1659
pH	0.7006	0.3503

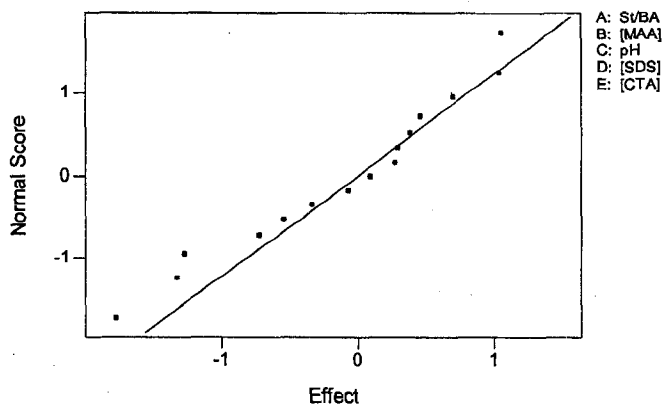
[SDS]	0.3811	0.1905
[CTA]	-1.7825	-0.8912
St/BA*[MAA]	-0.0680	-0.0340
St/BA*pH	-1.3267	-0.6633
St/BA*[SDS]	-0.7248	-0.3624
St/BA*[CTA]	1.0580	0.5290
[MAA]*pH	0.2761	0.1381
[MAA]*[SDS]	1.0373	0.5186
[MAA]*[CTA]	0.0937	0.0469
pH*[SDS]	0.4599	0.2300
pH*[CTA]	0.2922	0.1461
[SDS]*[CTA]	-0.5430	-0.2715

Analysis of Variance for MWD (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	5	22.21	22.21	4.442	*	*
2-Way Interactions	10	20.65	20.65	2.065	*	*
Residual Error	0	0.00	0.00	0.000		
Total	15	42.86				

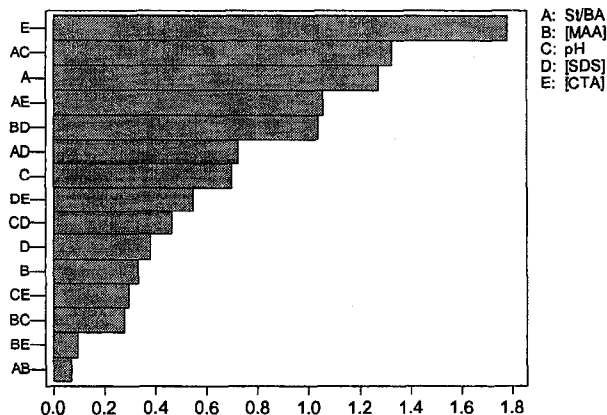
Normal Probability Plot of the Effects

(response is MWD, Alpha = .05)



Pareto Chart of the Effects

(response is MWD, Alpha = .05)



Estimated Effects and Coefficients for pull-off adhesion (coded units)

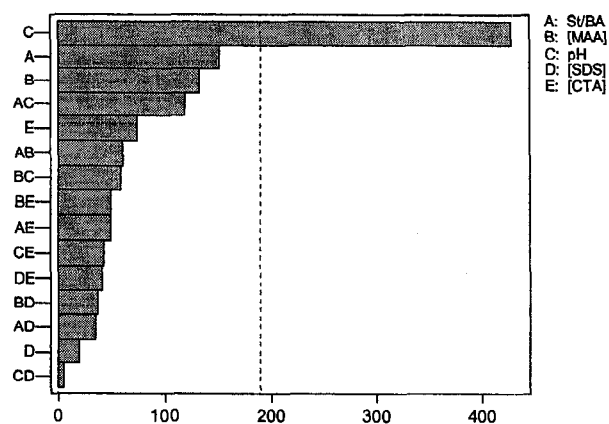
Term	Effect	Coef
Constant		385.61
St/BA	150.44	75.22
[MAA]	132.69	66.34
pH	426.71	213.36
[SDS]	-19.24	-9.62
[CTA]	-74.39	-37.19
St/BA*[MAA]	-61.04	-30.52
St/BA*pH	119.54	59.77
St/BA*[SDS]	-35.11	-17.56
St/BA*[CTA]	49.14	24.57
[MAA]*pH	58.69	29.34
[MAA]*[SDS]	36.89	18.44
[MAA]*[CTA]	-49.46	-24.73
pH*[SDS]	5.61	2.81
pH*[CTA]	-42.64	-21.32
[SDS]*[CTA]	-40.84	-20.42

Analysis of Variance for adhesion (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	5	912898	912898	182580	*	*
2-Way Interactions	10	129723	129723	12972	*	*
Residual Error	0	0	0	0		
Total	15	1042621				

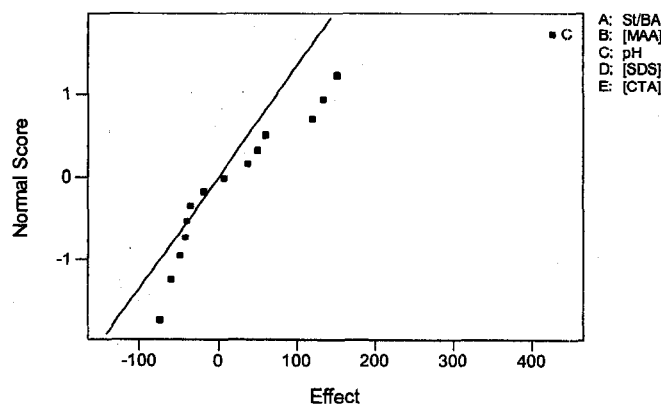
Pareto Chart of the Effects

(response is adhesion, Alpha = .05)



Normal Probability Plot of the Effects

(response is adhesion, Alpha = .05)



APPENDIX C Box-Behnken Design of Experiments – Regression Analysis

Estimated Regression Coefficients for $T_g(K)$

Term	Coef	StDev	T	P
Constant	276.613	1.5785	175.243	0.000
St/BA	21.593	0.9666	22.339	0.000
[MAA]	3.720	0.9666	3.849	0.012
pH	-1.323	0.9666	-1.368	0.230
St/BA*St/BA	-0.768	1.4228	-0.540	0.613
[MAA] * [MAA]	2.442	1.4228	1.716	0.147
pH*pH	-0.373	1.4228	-0.262	0.804
St/BA*[MAA]	0.067	1.3670	0.049	0.963
St/BA*pH	-1.218	1.3670	-0.891	0.414
[MAA] *pH	-1.892	1.3670	-1.384	0.225

S = 2.734 R-Sq = 99.1% R-Sq(adj) = 97.3%

Analysis of Variance for $T_g(K)$

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	3901.18	3901.18	433.46	57.99	0.000
Linear	3	3854.59	3854.59	1284.86	171.90	0.000
Square	3	26.32	26.32	8.77	1.17	0.407
Interaction	3	20.27	20.27	6.76	0.90	0.501
Residual Error	5	37.37	37.37	7.47		
Lack-of-Fit	3	33.09	33.09	11.03	5.15	0.167
Pure Error	2	4.28	4.28	2.14		
Total	14	3938.55				

Estimated Regression Coefficients for $T_g(K)$

Term	Coef	StDev	T	P
Constant	277.307	0.7377	375.906	0.000
St/BA	21.593	1.0101	21.376	0.000
[MAA]	3.720	1.0101	3.683	0.003

S = 2.857 R-Sq = 97.5% R-Sq(adj) = 97.1%

Analysis of Variance for $T_g(K)$

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	2	3840.60	3840.60	1920.30	235.24	0.000
Linear	2	3840.60	3840.60	1920.30	235.24	0.000
Residual Error	12	97.96	97.96	8.16		
Lack-of-Fit	6	53.92	53.92	8.99	1.22	0.406
Pure Error	6	44.04	44.04	7.34		
Total	14	3938.55				

Unusual Observations for $T_g(K)$

Observation	$T_g(K)$	Fit	StDev Fit	Residual	St Resid
8	293.510	298.900	1.251	-5.390	-2.10R

R denotes an observation with a large standardized residual

Estimated Regression Coefficients for particle size D_p

Term	Coef	StDev	T	P
Constant	41.133	8.446	4.870	0.005
St/BA	-5.988	5.172	-1.158	0.299
[MAA]	12.600	5.172	2.436	0.059
pH	19.437	5.172	3.758	0.013
St/BA*St/BA	4.508	7.613	0.592	0.580
[MAA] * [MAA]	-2.367	7.613	-0.311	0.768
pH*pH	28.508	7.613	3.744	0.013
St/BA*[MAA]	0.725	7.315	0.099	0.925
St/BA*pH	-5.150	7.315	-0.704	0.513
[MAA] *pH	13.525	7.315	1.849	0.124

S = 14.63 R-Sq = 88.8% R-Sq(adj) = 68.8%

Analysis of Variance for particle

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	8523.40	8523.40	947.04	4.43	0.058
Linear	3	4579.41	4579.41	1526.47	7.13	0.030
Square	3	3104.09	3104.09	1034.70	4.83	0.061
Interaction	3	839.89	839.89	279.96	1.31	0.369
Residual Error	5	1070.10	1070.10	214.02		
Lack-of-Fit	3	1045.44	1045.44	348.48	28.26	0.034
Pure Error	2	24.67	24.67	12.33		
Total	14	9593.50				

Unusual Observations for particle

Observation	particle	Fit	StDev Fit	Residual	St Resid
10	62.600	46.913	12.669	15.687	2.14R
11	44.900	60.587	12.669	-15.687	-2.14R

R denotes an observation with a large standardized residual

Estimated Regression Coefficients for particle size D_p

Term	Coef	StDev	T	P
Constant	42.36	5.464	7.751	0.000
[MAA]	12.60	5.111	2.465	0.031
pH	19.44	5.111	3.803	0.003
pH*pH	28.36	7.482	3.790	0.003

S = 14.46 R-Sq = 76.0% R-Sq(adj) = 69.5%

Analysis of Variance for particle

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	3	7294.3	7294.3	2431.44	11.63	0.001
Linear	2	4292.6	4292.6	2146.31	10.27	0.003
Square	1	3001.7	3001.7	3001.70	14.36	0.003
Residual Error	11	2299.2	2299.2	209.02		

Lack-of-Fit	5	1865.8	1865.8	373.15	5.17	0.035
Pure Error	6	433.4	433.4	72.24		
Total	14	9593.5				

Unusual Observations for particle

Observation	particle	Fit	StDev Fit	Residual	St Resid
7	115.600	90.150	7.229	25.450	2.03R
11	44.900	77.550	8.853	-32.650	-2.86R

R denotes an observation with a large standardized residual

Estimated Regression Coefficients for Mn

Term	Coef	StDev	T	P
Constant	20652	2248	9.188	0.000
St/BA	-5191	1376	-3.771	0.013
[MAA]	57	1376	0.042	0.968
pH	-946	1376	-0.687	0.523
St/BA*St/BA	-2473	2026	-1.221	0.277
[MAA] * [MAA]	2341	2026	1.155	0.300
pH*pH	-1903	2026	-0.939	0.391
St/BA*[MAA]	4288	1947	2.203	0.079
St/BA*pH	2389	1947	1.227	0.274
[MAA]*pH	-1620	1947	-0.832	0.443

S = 3893 R-Sq = 83.7% R-Sq(adj) = 54.4%

Analysis of Variance for Mn

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	389387589	389387589	43265288	2.85	0.130
Linear	3	222745167	222745167	74248389	4.90	0.060
Square	3	59764131	59764131	19921377	1.31	0.367
Interaction	3	106878291	106878291	35626097	2.35	0.189
Residual Error	5	75783763	75783763	15156753		
Lack-of-Fit	3	25721981	25721981	8573994	0.34	0.802
Pure Error	2	50061782	50061782	25030891		
Total	14	465171352				

Estimated Regression Coefficients for Mn

Term	Coef	StDev	T	P
Constant	18151	1463	12.410	0.000
St/BA	-5191	1368	-3.794	0.004
[MAA]	57	1368	0.042	0.967
[MAA] * [MAA]	2653	2003	1.325	0.215
St/BA*[MAA]	4288	1935	2.216	0.051

S = 3870 R-Sq = 67.8% R-Sq(adj) = 54.9%

Analysis of Variance for Mn

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	4	315428937	315428937	78857234	5.27	0.015
Linear	2	215593027	215593027	107796513	7.20	0.012
Square	1	26282988	26282988	26282988	1.76	0.215
Interaction	1	73552922	73552922	73552922	4.91	0.051

Residual Error	10	149742416	149742416	14974242		
Lack-of-Fit	4	38751274	38751274	9687819	0.52	0.723
Pure Error	6	110991141	110991141	18498524		
Total	14	465171352				

Unusual Observations for Mn

Observation	Mn	Fit	StDev Fit	Residual	St Resid
14	26410.300	18150.871	1462.593	8259.429	2.31R

R denotes an observation with a large standardized residual

Estimated Regression Coefficients for Mn

Term	Coef	StDev	T	P
Constant	19566	1033	18.943	0.000
St/BA	-5191	1414	-3.670	0.004
[MAA]	57	1414	0.041	0.968
St/BA*[MAA]	4288	2000	2.144	0.055

S = 4000 R-Sq = 62.2% R-Sq(adj) = 51.8%

Analysis of Variance for Mn

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	3	289145948	289145948	96381983	6.02	0.011
Linear	2	215593027	215593027	107796513	6.74	0.012
Interaction	1	73552922	73552922	73552922	4.60	0.055
Residual Error	11	176025404	176025404	16002309		
Lack-of-Fit	5	65034263	65034263	13006853	0.70	0.642
Pure Error	6	110991141	110991141	18498524		
Total	14	465171352				

Unusual Observations for Mn

Observation	Mn	Fit	StDev Fit	Residual	St Resid
7	17333.700	24756.911	1751.316	-7423.211	-2.06R

R denotes an observation with a large standardized residual

Estimated Regression Coefficients for Mw

Term	Coef	StDev	T	P
Constant	73187	8839	8.280	0.000
St/BA	-17554	5413	-3.243	0.023
[MAA]	3034	5413	0.561	0.599
pH	18625	5413	3.441	0.018
St/BA*St/BA	7724	7967	0.969	0.377
[MAA] * [MAA]	615	7967	0.077	0.941
pH*pH	12438	7967	1.561	0.179
St/BA*[MAA]	249	7655	0.033	0.975
St/BA*pH	-14188	7655	-1.853	0.123
[MAA]*pH	5363	7655	0.701	0.515

S = 15309 R-Sq = 85.6% R-Sq(adj) = 59.7%

Analysis of Variance for Mw

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	6978072979	6978072979	775341442	3.31	0.100
Linear	3	5313808179	5313808179	1771269393	7.56	0.026
Square	3	743821673	743821673	247940558	1.06	0.445
Interaction	3	920443127	920443128	306814376	1.31	0.369
Residual Error	5	1171858174	1171858174	234371635		
Lack-of-Fit	3	663684331	663684331	221228110	0.87	0.574
Pure Error	2	508173843	508173843	254086921		
Total	14	8149931153				

Estimated Regression Coefficients for Mw

Term	Coef	StDev	T	P
Constant	84267	4021	20.959	0.000
St/BA	-17554	5505	-3.188	0.008
pH	18625	5505	3.383	0.005

S = 15572 R-Sq = 64.3% R-Sq(adj) = 58.3%

Analysis of Variance for Mw

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	2	5240160863	5240160863	2620080431	10.81	0.002
Linear	2	5240160863	5240160863	2620080431	10.81	0.002
Residual Error	12	2909770291	2909770291	242480858		
Lack-of-Fit	6	2154856124	2154856124	359142687	2.85	0.114
Pure Error	6	754914167	754914167	125819028		
Total	14	8149931153				

Unusual Observations for Mw

Observation	Mw	Fit	StDev Fit	Residual	St Resid
7	155402.000	120445.958	8762.740	34956.042	2.72R

R denotes an observation with a large standardized residual

Estimated Regression Coefficients for Mw/Mn

Term	Coef	StDev	T	P
Constant	3.5566	0.6968	5.104	0.004
St/BA	0.4459	0.4267	1.045	0.344
[MAA]	0.0061	0.4267	0.014	0.989
pH	1.3088	0.4267	3.067	0.028
St/BA*St/BA	1.4946	0.6281	2.379	0.063
[MAA] * [MAA]	-0.8129	0.6281	-1.294	0.252
pH*pH	1.3771	0.6281	2.192	0.080
St/BA*[MAA]	-0.9380	0.6035	-1.554	0.181
St/BA*pH	-0.9125	0.6035	-1.512	0.191
[MAA]*pH	0.5629	0.6035	0.933	0.394

S = 1.207 R-Sq = 85.1% R-Sq(adj) = 58.1%

Analysis of Variance for Mw/Mn

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	41.4454	41.4454	4.60505	3.16	0.109
Linear	3	15.2945	15.2945	5.09816	3.50	0.106
Square	3	18.0339	18.0339	6.01129	4.13	0.081
Interaction	3	8.1171	8.1171	2.70570	1.86	0.254
Residual Error	5	7.2838	7.2838	1.45676		
Lack-of-Fit	3	7.2709	7.2709	2.42362	375.01	0.003
Pure Error	2	0.0129	0.0129	0.00646		
Total	14	48.7292				

Estimated Regression Coefficients for Mw/Mn

Term	Coef	StDev	T	P
Constant	3.946	0.5818	6.782	0.000
pH	1.309	0.5443	2.405	0.033
pH*pH	1.328	0.7967	1.667	0.121

S = 1.539

R-Sq = 41.6%

R-Sq(adj) = 31.9%

Analysis of Variance for polydisp

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	2	20.2915	20.2915	10.1458	4.28	0.040
Linear	1	13.7033	13.7033	13.7033	5.78	0.033
Square	1	6.5882	6.5882	6.5882	2.78	0.121
Residual Error	12	28.4377	28.4377	2.3698		
Pure Error	12	28.4377	28.4377	2.3698		
Total	14	48.7292				

Unusual Observations for polydisp

Observation	polydisp	Fit	StDev Fit	Residual	St Resid
11	3.670	6.583	0.770	-2.913	-2.19R

R denotes an observation with a large standardized residual

Estimated Regression Coefficients for pull-off adhesion

Term	Coef	StDev	T	P
Constant	278.233	35.19	7.906	0.001
St/BA	170.425	21.55	7.908	0.001
[MAA]	95.900	21.55	4.450	0.007
pH	184.825	21.55	8.576	0.000
St/BA*St/BA	4.096	31.72	0.129	0.902
[MAA]*[MAA]	40.096	31.72	1.264	0.262
pH*pH	150.346	31.72	4.739	0.005
St/BA*[MAA]	38.325	30.48	1.257	0.264
St/BA*pH	67.325	30.48	2.209	0.078
[MAA]*pH	33.475	30.48	1.098	0.322
S = 60.96	R-Sq = 97.4%	R-Sq(adj) = 92.7%		

Analysis of Variance for pull-off

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	694524	694524	77169	20.77	0.002
Linear	3	579214	579214	193071	51.96	0.000
Square	3	86821	86821	28940	7.79	0.025
Interaction	3	28488	28488	9496	2.56	0.169
Residual Error	5	18578	18578	3716		
Lack-of-Fit	3	17358	17358	5786	9.49	0.097
Pure Error	2	1220	1220	610		
Total	14	713102				

Unusual Observations for pull-off

Observation	pull-off	Fit	StDev Fit	Residual	St Resid
10	284.400	346.275	52.789	-61.875	-2.03R
11	586.000	524.125	52.789	61.875	2.03R

R denotes an observation with a large standardized residual

Estimated Regression Coefficients for pull-off adhesion

Term	Coef	StDev	T	P
Constant	303.49	27.52	11.029	0.000
St/BA	170.43	25.74	6.621	0.000
[MAA]	95.90	25.74	3.726	0.004
pH	184.82	25.74	7.180	0.000
pH*pH	147.19	37.68	3.906	0.003

S = 72.81 R-Sq = 92.6% R-Sq(adj) = 89.6%

Analysis of Variance for pull-off

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	4	660096	660096	165024	31.13	0.000
Linear	3	579214	579214	193071	36.42	0.000
Square	1	80881	80881	80881	15.26	0.003
Residual Error	10	53006	53006	5301		
Lack-of-Fit	8	51786	51786	6473	10.61	0.089
Pure Error	2	1220	1220	610		
Total	14	713102				

Unusual Observations for pull-off

Observation	pull-off	Fit	StDev Fit	Residual	St Resid
7	331.300	465.075	44.584	-133.775	-2.32R

R denotes an observation with a large standardized residual