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POLYMERIZATION MONITORING USING AN IN-LINE INFRARED SENSOR

by

Hong Hua

A thesis submitted to the Faculty of Graduate and Postdoctoral Studies in partial
fulfillment of the requirements for the degree of

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Abstract

The development of comprehensive methods to control polymer quality in terms of polymer reactor operation and polymer property trajectory monitoring during a polymerization reaction is key to the efficient production of tailored, high quality polymers and the improvement of plant operability and economics. To this end, an in-line mid-IR probe manufactured by ASI Applied Systems was used to monitor single and multicomponent solution and emulsion polymerization processes. The probe, which employs Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR), is capable of collecting information on the state and behaviour of polymerization reactions in a chemically aggressive and highly viscous reactor environment.

In this study, the disappearance of monomer was monitored using the probe by following the changes of characteristic infrared absorbance peaks of monomers. Experimental procedures were designed to ensure the proper use of the ATR-FTIR spectroscopy technique to perform off-line and in-line monitoring of multicomponent polymerization systems.

In the first part of this study, bench scale solution polymerizations of butyl acrylate (BA), methyl methacrylate (MMA), and vinyl acetate (VAc) homopolymers as well as BA/MMA and MMA/VAc copolymers were run. The probe was used off-line to analyze the monomer/polymer mixtures. A major contribution of this work was the identification of the characteristic IR absorbance peaks for each monomer. Results were compared to data from gravimetry and ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR) spectrometry to evaluate the capabilities and limitations of this probe. Good agreement

was observed for the conversion and polymer composition results between the different techniques.

In the second part of this thesis, batch emulsion polymerization experiments were conducted in a 5L stainless steel pilot scale reactor. Using the probe, spectral measurements were performed directly in the reaction vessel, with no sample handling required, to provide both real time reaction pathway and kinetic information; i.e. monomer conversion and polymer composition. Favorable agreement between the ATR-FTIR probe and gravimetric and ^{1}H-NMR measurements was achieved.

Finally, the approach used for the homo- and copolymerizations was repeated for BA/MMA/VAc solution and emulsion terpolymerizations. The sensor was used off-line for the identification of characteristic IR absorbances and solution terpolymerization monitoring. This was followed by the use of the probe to monitor the emulsion terpolymerizations in-line. Results obtained from the ReactIR™ 1000 reaction analysis system agreed well with those determined by traditional gravimetry and ^{1}H-NMR spectroscopy.

Due to the wealth of kinetic data generated in this thesis, a parallel study concerning the evaluation of a previously developed multicomponent solution polymerization model was performed. For this study, molecular weight measurements were performed on selected samples in each solution polymerization run. Solvent effects on the rate parameters of BA and VAc monomers were applied to predict monomer conversion, polymer composition and molecular weight averages. Comparisons between experimental data and model predictions showed that the model was effective for

predicting solution homo-, co- and terpolymerization behaviour of the BA/MMA/VAc system.

This thesis has demonstrated that off-line and in-line monitoring of monomer conversion and polymer composition for BA/MMA/VAc homo-, co-, and terpolymerizations is possible using ATR-FTIR spectroscopy. These results may lead to the development of accurate and robust control strategies for the production of polymers with pre-specified properties.

Résumé

Le développement de méthodes compréhensives pour le contrôle de la qualité des polymères du point de vue de l'opération des réacteurs ainsi que de la surveillance continue des propriétés des polymères lors des réactions de polymérisation est la clé pour la production efficace de polymères sur mesure de haute qualité, et pour l'amélioration des procédés industriels en terme d'opération. A cette fin, une sonde mi-infrarouge fabriquée par ASI Applied Systems à été utilisée afin d'accomplir la surveillance continue de polymérisations en solution et en émulsions à composants simples et multiples. Cette sonde, qui utilise le facteur de réflexion total atténué - spectroscopie infrarouge de la tansformation Fourier (ATR-FTIR), est capable d'acquérir des données sur l'état et le comportement des réactions de polymérisation dans des environements chimiques agressifs et très visceux.

Dans cette étude, la disparition des monomères ainsi que la formation des polymères furent suivient en utilisant la sonde en suivant les changements des bandes infrarouges charactéristiques associées aux monomères. La procédure expérimentale fût développée afin d'assurer l'utilisation adéquate de la technique de spectroscopie ATR-FTIR pour accomplir la surveillance différée et continue de systèmes de polymérisation à composants multiples.

En première partie de cette étude, des ploymérisations en solution, à petite échelle, d'acrylate de butyle (BA), de méthacrylate de méthyle (MMA) et d'acétate de vinyle (VAc) ont été effectuées ainsi que la co-polymérisation des systèmes BA/MMA et MMA/VAc. La sonde fût utilisée en situation différée pour analyser les mélanges de monomères/polymères. La plus grande contribution de ce travail fût l'identification des

bandes IR charactéristiques pour chacun des monomères. Les résultats ont été comparés à ceux obtenus par analyse gravimétrique et par résonance magnétique nucléaire (^{1}H-NMR) pour évaluer la capacité et les limites de cette sonde. Une bonne concordance fût observée pour la conversion et la composition des polymères entre les différentes techniques.

En seconde partie de cette étude, des polymérisations en émulsion furent exécutées dans un réacteur en acier inoxidable de 5L (échelle pilote). En utilisant la sonde, des mesures spectrales furent prises directement du réacteur, sans avoir recours à la manipulation d'échantillons, dans le but d'acquérir des données en temps réel pour obtenir la conversion des monomères et la composition des polymères. Une bonne concordance entre les résultats obtenus par la sonde, par analyse gravimétrique et par ^{1}H-NMR fût observée.

Finalement, l'approche utilisée pour la polymérisation à composants simples et pour la co-polymérisation fût répétée pour la terpolymérisation en solution et en émulsion du système BA/MMA/VAc. La sonde fût utilisée en situation différée pour l'identification des bandes infrarouges charactéristiques et pour la surveillance de la terpolymérisation en solution. Ceci fut suivi par l'utilisation de la sonde pour la surveillance continue de la terpolymérisation en émulsion. Les résultats obtenus par le système d'analyse ReactIR^{TM} 1000 sont en bon accord avec ceux obtenus par l'analyse gravimétrique traditionelle et par ^{1}H-NMR.

Etant donné la quantité de données cinétiques générées par cette étude, une étude parallèle concernant l'évaluation d'un modèle de polymérisation en solution avec composants multiples déjà développé fut accomplie. Pour cette étude, des mesures de masse moléculaire furent obtenues sur des échantillons sélectionnés de chacune des expériences de polymérisation en solution. L'effet du solvent sur les paramètres des monomères BA et VAc fût appliqué pour prédire la conversion des monomères, la composition des polymères et les masses moléculaires moyennes. La comparaison entre les données expérimentales et les prédictions par le modèle démontre que le modèle est efficace pour prédire les polymérisations, les co-polymérisations et les terpolymérisation.

Cette thèse a démontré que la surveillance différée et continue de la conversion des monomères et de la composition des polymères pour les polymérisations, les co-polymérisations et les terpolymérisation des systèmes BA/MMA/VAc est possible en utilisant la spectroscopie ATR-FTIR. Ces résultats peuvent mener au développement de stratégies de contrôle rigides pour la production de polymères ayant des propriétés pré-définies.

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CHAPTER 1

INTRODUCTION

Introduction

1 Introduction to polymerization monitoring techniques

Polymers are macromolecules built up by linking together large numbers of much smaller unit molecules, called monomers. Polymerizations consist of initiation, propagation, termination, and chain transfer reactions. Polymers find application in the building, construction, packaging, transportation, electronic industries, amongst others. They have many uses due to the unique properties they exhibit compared to small molecules.

The molecular, structural and morphological properties of a polymer material - such as molecular weight and molecular weight distribution, polymer composition, chain sequence distribution, degree of branching, and stereoregularity - strongly influence its physical, chemical, thermal, rheological, and mechanical properties as well as its end-use applications. Changes in polymerization reaction conditions can greatly alter those critical polymer properties. Therefore, product quality is a much more complex issue in polymerization than in more conventional small molecule reactions.

As the polymer industry becomes more competitive, polymer manufacturers face increasing pressures for production cost reductions and more stringent polymer quality requirements.[1] Therefore, the development of comprehensive methods to control the polymer quality in terms of polymer reactor operation and polymer property trajectory monitoring during a polymer reaction is key to the efficient production of tailored, high quality polymers and the improvement of plant operability and economics.

Traditional polymerization monitoring is carried out by sampling and off-line characterization of polymer quality that is done in a laboratory on discrete samples taken from a process flow line. For example, gravimetry and gas chromatography (GC) are used to measure monomer conversion. Nuclear magnetic resonance (NMR) spectroscopy can be used to obtain cumulative composition, sequence length, and other structural information about the polymer produced in multicomponent polymerizations. Gel permeation chromatography (GPC) is used with a variety of detectors to obtain molecular weight information of the produced polymers. Multi-angle laser light scattering instruments provide precise weight-average molecular weights while osmometry gives number-average molecular weights of polymer samples. The list of off-line measurement devices is extensive.

- Monomer conversion:
    - Gravimetry
    - Gas chromatography
- Copolymer composition:
    - Elemental analysis
    - Gas chromatography
    - NMR spectroscopy
    - Infrared spectroscopy
- Molecular weight and molecular weight distribution:
    - Viscometry
    - Gel permeation (size exclusion) chromatography
    - Light scattering
    - Osmometry

Nowadays, the increasing demand for the production of polymers with prespecified properties and high quality places more emphasis on the development of accurate and robust analytical instrumentation and sensors for the on-line monitoring of polymerization reactions. Many of the problems encountered in polymerization reactor control can be attributed to the lack of on-line measurements of the reaction evolution.[2] For polymer reactions, on-line monitoring devices adapted to industrial processes must have satisfactory analysis and response time behavior to be able to measure continuously. In addition, they have to supply correct results over long periods of time in environments inherent to polymer reaction processes that are often physically and chemically aggressive. Different techniques available now can be classified as direct and indirect methods. The former methods involve monitoring of either the residual monomer content in the reactor, while the latter measure a property change of the polymerization system that can be related to the mass of monomer or formed polymer. The term *on-line* mentioned here means the device for analysis is connected to the process stream via a side-loop or sample thief while the term *in-line* means the device obtains the measurement directly in the process stream.[3] A brief survey of these methods is discussed next. The following list presents the major on-line methods for monomer conversion and polymer composition monitoring.

- Densimetry
- Refractive index measurements
- Calorimetry/reactor energy balances
- Gas chromatography
- Ultrasound measurements

- Fluorescence spectroscopy

By utilizing the density difference between the unreacted monomer and the formed polymer, the reaction conversion can be calculated by measuring the density of the reactor contents with on-line industrial densitometers and knowing the amount of monomer and other components fed to the reactor. Fevotte et al.[4] reported that they assessed monomer conversions within emulsion and solution polymerization reactors by monitoring the density variation of the reactor contents through external sampling circuits. Together with gravimetry data of the copolymerization reaction, they also estimated individual monomer conversions for use in estimating instantaneous and global copolymer compositions. This combined use of on-line data successfully follows the evolution of a polymerization reaction though difficulties are encountered due to noise, false signals, and especially fouling.

Monomer concentration changes during polymerization can, in principle, be followed by measuring the corresponding changes in the refractive index or dielectric constant of the reacting mixture. Crowley et al.[5] used a low-frequency dielectric sensor to conduct successful in-line monitoring of monomer conversion during solution polymerization of methyl methacrylate in a laboratory-scale batch reactor.

On-line calorimetry has been one of the most widely investigated techniques for monitoring conversion.[1] Since polymerization reactions are exothermic, it is an appropriate technique for on line measurements of polymerizations. The measurement is non-invasive and rapid and it is based on the real-time measurement of the instantaneous heat release from the polymerization. Both Gugliotta et al.[6] and Saenz de Buruaga et al.[7] reported their work on individual monomer conversion estimation in unseeded emulsion copolymerization of butyl acrylate and vinyl acetate from calculation of the instantaneous heat release rate by combining polymerization reactor temperature and flow rate measurements with a set of dynamic energy balance equations for the reactor and its cooling jacket. Kammona et al.[1] mentions that this technique suffers from problems associated with the propagation of errors due to noise in the calorimetric measurements and possible unpredictable variations of the heat transfer coefficient through the reactor wall due to fouling.

On-line gas chromatography (GC) can be employed to infer copolymer composition on line based on the residual monomer composition in combination with a material balance in the reactor. Nöel et al.[8] used a GC equipped with an extra on-line sample injection system to determine individual conversions of both monomers for monitoring and controlling composition drift in emulsion copolymerization of methyl acrylate and vinyl acetate in combination with on-line densimetry measurements. It gave satisfactory estimation of the individual monomer conversion, agreeing with the off-line results and theoretical predictions. However, reaction mixture flocculation in the sampling system was often problemic.

The estimation of monomer conversion through measurements of ultrasound propagation velocity is a potential alternative to the densimetry, calorimetry and GC techniques because the probe can be directly plugged into the process without the need for a sampling system.[1] Gendron et al.[9] performed in-line ultrasonic measurements on polystyrene, polyethylene, and polypropylene blends of different compositions during an extrusion process and found an approximately linear relation between the ultrasonic properties and variations in composition.

Fluorescence spectroscopy is based on the emission of electromagnetic radiation when an electronically excited species at one state returns to its ground state. Serrano et al.[10] used a fluorimeter coupled with a fiber optic system to monitor polymerization reactions of cyclohexyl methacrylate and 2-ethylhexyl acrylate by following the changes in probe fluorescence properties throughout the reaction. The extrinsic probes were present in such small quantities that they did not interfere with the polymerization and were sensitive to changes in local microenvironments.

The majority of the techniques mentioned above are often complicated by the heterogeneous and/or viscous nature of polymerization systems, which may give rise to operational difficulties encountered in handling the reaction mixture and cause significant measurement delays. In addition, many of the techniques typically require an external circulation loop to draw sample from the process flow and thus suffer from problems of polymer buildup and fouling, as well as from temperature control difficulties. Actually, most of these available conversion-monitoring techniques were not originally designed for continuous monitoring. The operating conditions of these hardware sensors have to be properly tuned to minimize the analysis and response time with respect to the characteristic time of the reaction, thus providing a practically continuous signal in time. Fevotte et al.[4] also mentioned that other problems associated with on-line data treatment in polymerization system include the relatively high signal to noise ratio of sensors due to weak signals from calorimeters and problems with gas bubbles. Additionally, the stability of polymer emulsions may be compromised when using sampling loops.

An additional difficulty to be overcome pertains to systems that involve more than one monomer species since the basic property measured may depend on polymer composition. The lack of a one-to-one relationship between the monitored quantity and polymer conversion requires the implementation of additional on-line sensors for determining the conversion of each species or copolymer composition. Thus, the development of non-invasive in-line sensors to conduct continuous measurements is required to provide correct real-time information on the state and behavior of the polymerization process for the implementation of high-level process and polymer quality optimization.

2 Infrared spectroscopy for polymer and polymerization analysis

Infrared (IR) spectroscopy is one of the most often used spectroscopic tools for the study of polymers.[11] The IR method is rapid, sensitive, and employs sampling techniques that are easy to use. In addition, the instrumentation is inexpensive, operation of the equipment is simple, and service and maintenance of the equipment are not difficult. Finally, interpreting the spectra is not particularly difficult and can be learned easily.

The energy of infrared (IR) radiation is comparable in magnitude to the vibrational energy of chemical bonds. Resonant absorption occurs when the energy of an IR photon matches the energy required to excite a molecule from its lowest vibrational level to a higher vibrational level. IR spectroscopy measures the vibrational energy levels of molecules. It uses the information from the electromagnetic spectrum that covers the wavelength range from 0.7 to 1000 μm. Because the vibrational energy levels are distinctive for each molecule and its isomers, an IR spectrum has often been called the fingerprint of a molecule.[11] It consists of peaks whose frequencies are characteristic of the chemical bonds present in the sample. By matching band positions to those of known compounds, IR spectra can be used to determine the presence or absence of certain functional groups.

These characteristic group frequencies can also be used as structural probes for chemical groups in polymer chains because they are relatively unaffected by the chemical nature of the rest of the molecule and have nearly the same vibrational energy regardless of the attached molecular skeleton. They will generally appear in the same spectral region for polymers as for other molecules.[12] Sometimes, specific couplings can occur with regularly ordered chemical functional groups in polymers, and this condition shifts the group frequencies and leads to valuable microstructural information about polymers. Careful cataloging of the IR spectra reveals correlations between the presence of certain chemical groups in the polymer chain and the appearance of specific IR absorbance frequencies.

Absorbance of IR radiation is often used for quantitative analysis by applying the Beer-Lambert Law; that is, the absorbance intensity at a certain frequency is proportional to the concentration of the component that absorbs at that frequency.

2.1 Fourier transform infrared (FTIR) spectroscopy

Infrared (IR) instrumentation has changed a great deal since it became important for materials characterization. The following IR instrumentation is being utilized currently:

- dispersive instruments,
- multichannel dispersive instruments,
- multiplex instruments,
- multichannel/multiplex instruments.

Originally, IR spectra were measured using a dispersive method that was highly limited in sensitivity. The accuracy and reproducibility of the frequencies were also very low.

A multiplex spectrometer is one that can measure spectral information about the intensities at individual frequencies while measuring the intensities of all frequencies simultaneously with a single detector. The sensitivity of IR spectroscopy has improved with multiplex optical devices such as interferometers due to the continuous detection of all transmitted frequencies simultaneously. Fourier Transform Infrared (FTIR) spectroscopy uses the Michelson interferometer as the multiplex optical device that has several advantages compared to dispersive IR instrumentation including:

- higher signal-to-noise ratio due to improved detector irradiance,
- signal-to-noise ratio can be improved by signal averaging,
- higher energy throughtput because no slits are required,
- accurate wavelength measurement due to calibration with an internal laser,
- high speed as interferometers can be more rapidly scanned than monochromators.

FTIR instrumentation has high-energy throughput and the multiplex advantage coupled with computerized signal enhancement by signal averaging. With the rapid-scanning capability of FTIR spectroscopy, the time-dependent intensity changes of absorbance bands characteristic of polymerization reactants and reaction products can be monitored.

2.2 Sampling methods for IR spectroscopy

FTIR instrumentation allows the use of a number of additional sampling techniques for polymers compared to the traditional dispersion instrumentation. IR sampling techniques currently in use include:

- transmission,
- specular reflection,
- diffuse reflection,
- reflection-absorbance.

Transmission spectroscopy is the traditional sampling method for qualitative analysis for the purposes of polymer identification. The spectrum is generally recorded in a cell constructed with windows made of an IR-transmitting material and the IR beam passes directly through samples. It is useful for quantitative measurements only when uniform thin films of polymeric samples are available.

Internal reflection spectroscopy (often called attenuated total reflection or ATR) is a widely used technique for the analysis of samples with low transmission.[13] It is a contacting sampling method involving a crystal, used as an internal reflection element, with high refractive index and low IR absorption in the IR region of interest. When the IR beam enters the internal reflection element below an angle that exceeds the critical angle for total internal reflection, an evanescent wave is set up which penetrates a small distance beyond the crystal surface into space. A sample brought into contact with the crystal can interact with the evanescent wave, absorb infrared radiation, and have its infrared spectrum detected. The evanescent wave is attenuated by the sample's absorbance. Thus, intimate contact between the sample and crystal is critical to ensure the evanescent wave penetrates into the sample.

The depth of penetration, analogous to the idea of path length in transmission sampling techniques, depends on several factors such as the IR light frequency, the angle of incidence and refractive index, but is approximately equal to the wavelength of the IR light. Because the penetration depth is sample independent, the ATR technique is well suited to quantitative analysis.

ZnSe and CdTe can be used as ATR crystal elements. Diamond, cubic zirconia and silicon can be used for systems requiring chemical resistance.

2.3 Near-infrared (NIR) and mid-infrared (MIR) spectral regions

NIR spectroscopy encompasses the frequency range of 14,000 to 4,000 cm^{-1}. This spectral region received much early attention for the development of on-line analyzers since it does not require complicated hardware or sampling techniques.[14] However, it suffers from nonspecificity of the absorbance peaks and possible nonlinearity associated with light scattering in heterogeneous systems. In this region of the spectrum, absorbances are mainly due to third overtone and combinations of the fundamental infrared bands originating from -CH, -NH, and -OH stretches. Most NIR absorptions are typically weaker than their corresponding fundamental transitions, which make it impossible to be unambiguously assigned and used for minor component analysis. Consequently, this necessitates the use of very sophisticated statistical methods to correlate observed spectra with the process variables of interest (i.e. concentration or composition), which are very powerful but are quite capable of producing spurious results.[15-17]

The MIR range extending from about 4,000 to 400 cm^{-1} includes the frequencies corresponding to the fundamental vibrations of virtually all of the functional groups of organic molecules. These spectral lines are typically narrow and distinct, and are easy to identify. As a result, quantitative analyses performed in the MIR are usually straightforward and robust, being largely independent of effects such as source variations, changes in overall sample transmission or scattering. Ironically, another problem arises from the fact that most molecular vibrations fall in the MIR region. It is difficult to find proper optics materials for the equipment to transmit the IR radiation in this region with little absorption.[18]

2.4 IR monitoring of polymer reactions

Very few comprehensive studies have been done on IR monitoring for only a limited number of polymerization systems. In this thesis, an MIR spectroscopy technique will be used for in-line polymerization monitoring due to its wealth of qualitative and quantitative information. The IR transmitting problem is solved by using the light conduit technology of a ReactIR™ 1000 (ASI applied systems Inc.) reaction analysis system.

In Table 1.1 are listed some references to work performed using near infrared spectroscopy as an on-line technique. While many of the references listed refer to polymer processing monitoring, three of these refer to polymer reaction monitoring. Long et al.[19] monitored anionic solution polymerizations while Wu et al.[20,21] tracked the emulsion polymerization of styrene. Dallin et al.[3] monitored some polyesterification reactions at elevated temperatures. These were all successful but required the use of a calibration curve and sophisticated statistical methods to interpret their data.

In Table 1.2 are listed various attempts at monitoring polymerizations with MIR probes. Doyle et al.[22] used what appears to be the precursor to the ReactIR™1000 to monitor styrene and methyl methacrylate solution homo- and copolymerizations. Users of the ReactIR™ 1000 reaction analysis system (ASI applied systems, Millersville, MD)

Table 1.1: Polymer reaction monitoring studies using NIR spectroscopy

Reference	Instrumentation	Process conditions	Monitored variables
McPeters et al. (1992)	NIR spectrophotometer coupled with fiber optic cables and optical probes inside the extruder	Methacrylate/styrene/acrylate terpolymer with different composition extrusion, 260-300°C	-OH absorbance for composition measurement
Long et al. (1993)	NIR spectrophotometer equipped with a fiber probe and fiber optic cables	Styrene and isoprene anionic solution homo- and copolymerization (10-20% solids) system	Monomer conversion through the absorbance change of vinyl proton to methylene proton
Khettry et al. (1996)	NIR spectrophotometer coupled with fiber optic probes installed in the flow cell	Poly (ethylene vinyl acetate) copolymer extrusion with vinyl acetate varying in the 0-40wt% range, 200°C	Variation of vinyl acetate concentration
Wu et al. (1996 a,b)	NIR spectroscopy with an in-line fiber-optical diffuse reflectance probe	Styrene emulsion polymerization	Polymer percentage in th reaction mixture through the absorbance change at 880 nm
Dallin et al. (1997)	Interactance immersion NIR probe with fiber optic	polyesterification reactions, 200-300°C	Acid value Hydroxyl number Viscosity
	Same as above	PET polymerization	Degree of polymerization
	NIR spectrophotometer coupled with fiber optic cables and optical probes inside the extruder	Polypropylene blending/drying/extrusion, 100-300°C, >1000psig	Xylene extractable parameter
Vedula et al. (1998)	NIR spectrophotometer equipped with fiber optic cables and transmission probe attached to a single-screw extruder	Poly (ethylene vinyl acetate) (EVA) extrusion, 200°C	Linear viscoelastic properties of molten EVA copolymers through the absorbance change of C-H vibration stretch, first overtone, wavelength region 1620-1840 nm

Table 1.2: Polymer reaction monitoring studies using MIR spectroscopy

Reference	Instrumentation	Process conditions	Monitored variables
Doyle et al. (1990)	A process FTIR spectrometer coupled with an ATR probe immersed in a laboratory scale reactor	Styrene and methyl methacrylate solution polymerization for both homo- and copolymer system	Individual monomer conversions through absorbance changes of 1600cm^{-1} for styrene and 1730 cm^{-1} for methyl methacrylate
Mijovic et al. (1996)	FTIR spectrometer equipped with gold coated waveguides and disposable reaction vessels	Cure of a multifunctional epoxy/amine formulation composed of diglycidylether of bisphenol-F and 4,4'-methylene dianiline.	The extent of reaction through characteristic peak changes at 915 cm^{-1} for epoxy and 3360 cm^{-1} for amine
Chatzi et al. (1997)	FTIR spectrometer equipped with chalcogenide optical fibers and an ATR probe immersed in a laboratory scale reactor	2-ethylhexyl acrylate/styrene emulsion copolymerization at the azeotropic composition	Individual monomer conversions through absorbance changes of 1600cm^{-1} for styrene and 1155 cm^{-1} for 2-ethylhexyl acrylate
Puskas et al. (1998)	FTIR spectrometer equipped with a fiber optic ATR probe immersed in a laboratory scale reactor	Carbocationic polymerization of isobutylene and styrene	Monomer conversions through absorbance changes of 1630cm^{-1} for styrene and 1655 cm^{-1} for isobutylene
Storey et al. (1998)	ReactIR™ 1000 equipped with a light conduit an ATR insertion probe	Carbocationic polymerization of isobutylene	Monomer conversions through absorbance changes of 887 cm^{-1} for isobutylene
Pasquale et al. (1999)	ReactIR™ 1000 equipped with a light conduit an ATR insertion probe	Stable free radical polymerization of styrene	Styrene conversion through absorbance changes of 907 and 1628 cm^{-1}

include Storey et al.[23] and Pasquale et al.[24] The former monitored the solution polymerization of styrene while the latter followed the carbocationic polymerization of isobutylene. The other authors used fiber optic techniques to monitor their polymerizations. Of note is the successful monitoring of the emulsion copolymerization of styrene/2-ethylhexyl acrylate by Chatzi et al.[25]

3 Thesis objectives

The objective of this thesis was to evaluate the capability of the ReactIR™1000 reaction analysis system to monitor polymerization systems that include butyl acrylate/ methyl methacrylate/ vinyl acetate (BA/MMA/VAc) terpolymers, and its associated homo- and copolymers.

The first step was to use this instrument for off-line analysis of samples from solution polymerizations to see if it could distinguish the monomer/polymer spectra from the solvent background, identify characteristic peaks to follow the reaction, and give reliable estimation of polymerization conversion and polymer composition from spectral changes.

The second step was to use the characteristic absorbance information obtained from the off-line measurements to perform in-line monitoring of emulsion polymerizations.

The collected information should help one evaluate the capability of the ReactIR™ 1000 reaction analysis system for further polymerization kinetics and process control studies.

4 Thesis outline

This thesis is composed of three manuscripts that either have been or will be submitted for publication in refereed journals.

Chapter 2 (paper 1) describes the off-line analysis for bulk and solution polymerization of all systems except for terpolymers of BA/MMA/VAc. It has been submitted to *Polymer*.

Chapter 3 (paper 2) presents the in-line analysis for the emulsion polymerization of all systems except for terpolymers of BA/MMA/VAc. It will be submitted to *Macromolecules*.

Chapter 4 (paper 3) presents both off-line and in-line analysis for solution and emulsion terpolymerization of the BA/MMA/VAc system. It will be submitted to *Journal of Polymer Science*.

The final section lists conclusions and recommendations based upon the results. The appendix section includes sample calculations of polymerization conversion and polymer composition results from gravimetry and ^{1}H-NMR methods and from ATR-FTIR spectroscopy.

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CHAPTER 2

(PAPER 1)

Off-line Monitoring of Butyl Acrylate, Methyl Methacrylate and Vinyl Acetate Homo- and Copolymerizations in Toluene Using ATR-FTIR Spectroscopy

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Abstract

Butyl acrylate, methyl methacrylate, and vinyl acetate solution homo- and copolymerizations were monitored using ATR-FTIR spectroscopy with conduit and diamond-composite sensor technology. Monomer conversion and copolymer composition changes as a function of time were calculated by monitoring the peak height of characteristic absorbances of monomers. Results obtained from the ReactIR™ 1000 reaction analysis system agreed well with those determined by traditional gravimetry and ^{1}H-NMR spectroscopy. Improved models developed previously to incorporate solvent effects on solution polymerizations of butyl acrylate and vinyl acetate monomers were applied to predict monomer conversion, copolymer composition and molecular weight averages. Comparisons between experimental data and model predictions are presented in this study.

Keywords: butyl acrylate, methyl methacrylate, vinyl acetate, IR spectroscopy, solution polymerization, copolymerization kinetics, toluene

Introduction

As the polymer industry becomes more competitive, polymer manufacturers face increasing pressures for production cost reductions and more stringent polymer quality requirements.[1] Therefore, the development of comprehensive methods to control polymer quality (in terms of polymer reactor operation and polymer property trajectory monitoring) during a polymerization is key to the efficient production of tailored, high quality polymers and the improvement of plant operability and economics.

Traditional polymerization monitoring is carried out by sampling and off-line characterization of polymer quality that is done in a laboratory on discrete samples taken from a process flow line. For example: gravimetry and gas chromatography (GC) are used to measure monomer conversion; nuclear magnetic resonance (NMR) spectroscopy can be used to obtain cumulative composition, sequence length, and other structural information about the polymer produced in multicomponent polymerizations; and gel permeation chromatography (GPC) is used with a variety of detectors to obtain molecular weight information of the produced polymers.

Nowadays, the increasing demand for the production of polymers of high quality with prespecified properties places more emphasis on the development of accurate and robust analytical instrumentation and sensors for the on-line monitoring of polymerization reactions. Many of the problems encountered in polymerization reactor control can be attributed to the lack of on-line measurements of the reaction evolution.[2] For polymer reactions, on-line monitoring devices adapted to industrial processes must have satisfactory analysis and response time behavior to be able to measure continuously. In addition, they have to supply correct results over long periods of time in environments inherent to polymer reaction processes that are often physically and chemically aggressive. Different techniques now available can be classified as direct and indirect. The former methods involve monitoring of the residual monomer content in the reactor, while the latter methods measure a property change of the polymerization system that can be related to the mass of monomer or formed polymer. The term *on-line* mentioned here refers to a device for analysis that is connected to the process stream via a side-loop or sample thief while the term *in-line* refers to a device that obtains the measurement directly in the process stream.[3]

To improve the control of polymer properties such as copolymer composition, one must be able to follow the advancement of a polymerization reaction first, i.e. follow key measurements such as the individual monomer conversions and polymer composition during the process. By using the on-line sensed information, the task to control the system parameters and guide the process along an optimum path can be successfully accomplished. Thus, real-time monitoring of the polymerization reaction is of crucial importance in efforts to optimise polymerization processes and polymer product qualities.

Among various densimetry, calorimetry, gas chromatography and spectroscopy monitoring techniques, mid-infrared (MIR) spectroscopy has significant potential. Compared to near infrared (NIR), the MIR range, extending from 4000 to 400 cm^{-1}, is the preferred choice owing to the unmatched wealth of molecular level information contained in the infrared portion of the electromagnetic spectrum.[4] In-situ Fourier transform infrared (FTIR) spectroscopy is a state-of-the-art monitoring technique that is well suited to obtain real-time structural and kinetic information on a polymerization process. In addition, when using FTIR, reactions can be analyzed without expensive reactor modifications, complicated sampling methods, and difficult experimental operation.

Mijovic et al.[5] described an inexpensive remote MIR-FTIR spectroscopy set-up utilizing gold-coated hollow waveguides instead of fibre optics to investigate the cure of a multifunctional epoxy/amine formulation. They monitored the change of characteristic absorption band intensities. The evaluated reaction kinetic data agreed with the data from NIR spectroscopy in the range extending from 14000 to 4000 cm^{-1}, up to about 60% conversion. Doyle[6] described an MIR-FTIR spectroscopy set-up to investigate free radical copolymerization of styrene and methyl methacrylate (MMA) in toluene on-line. An attenuated total reflection (ATR) immersion probe was designed and connected with an FTIR instrument through metallic hollow waveguides. The toluene spectrum was easily subtracted from the spectra of the reaction mixture. A convenient set of spectral bands for both monomers was selected for quantitative analysis using a computer program to solve simultaneous equations for estimating individual monomer conversions. The probe was shown to yield an intimate view of a polymerization reaction with continuous on-line data, making it possible to optimise its parameters and to terminate the reaction at any desired degree of completion. Puskas et al.[7,8] described an example of in-situ monitoring of cationic polymerization of isobutylene and styrene by using a fibre optic ATR probe in conjunction with an FTIR instrument in the MIR region. The results compared favourably with a developed kinetic model. Storey et al.[9-11] have reported their use of a ReactIR™1000 reaction analysis system (ASI Applied Systems, Metter-Toledo Corp.) equipped with a light conduit and DiComp (diamond-composite) insertion probe. Their efforts focused on the development of a method for experimentally determining kinetics of the cationic polymerization of isobutylene through in-situ, real-time reaction monitoring by utilizing MIR-FTIR spectroscopy. Pasquale et al.[12] also used the same instrument to study the kinetics of stable free radical polymerizations of styrene.

Butyl acrylate/methyl methacrylate/vinyl acetate (BA/MMA/VAc) terpolymers, and their corresponding homo- and copolymers are commercially important components in many paints, adhesives, and binders. Dubé and Penlidis[13-15] described in detail a systematic approach to the study of multicomponent batch polymerization kinetics of this system in bulk, solution, and emulsion. All the analyses were done off-line. Gravimetric analysis of monomer consumption was used to estimate conversion, proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy was used to measure the polymer composition and GPC was used to measure molecular weight averages. Due to the widely differing monomer reactivity ratios in the batch polymerizations containing VAc, polymer composition drift was significant during the process. The acrylic monomer was preferentially consumed during the early stages of the reaction resulting in copolymers containing only small amounts of VAc at the beginning of the reaction. As the reaction proceeded, the acrylic monomer was completely depleted and the remaining unreacted VAc monomer was polymerized. Thus, the final product contained polymers with a distribution of compositions and microstructures. In order to produce polymers with homogeneous properties, semi-batch policies to control the monomer feed, coupled with on-line monitoring based on analysis of the overall monomer concentrations, are often used.[16] However, traditional off-line methods are unable to monitor the polymerization in an adequate time frame when violent composition drifts occur during the process. Some current sensing techniques such as on-line GC also pose sampling difficulties.[17]

In this paper, we report the results of a solution homopolymerization of MMA and solution copolymerizations of BA/MMA and MMA/VAc initiated with 2,2'-

azobisisobutyronitrile (AIBN), and conducted in toluene (50 wt.%) at 60 °C. The ReactIR^{TM}1000 reaction analysis system was used for off-line analysis of our samples to identify characteristic peaks, to follow the reaction kinetics and to evaluate its ability to estimate monomer conversion and polymer composition from spectral changes. Kinetic data obtained through IR analysis were compared to results from the traditional gravimetric and ^{1}H-NMR methods. Results were also compared to predictions from a mechanistic model.

Experimental section

Materials

Purification of reagents was performed by classical methods.[13] The monomers butyl acrylate and methyl methacrylate (Aldrich Chemical Co. Inc.) were washed three times with a 10% sodium hydroxide solution to remove the inhibitor and subsequently washed three times with distilled water. Calcium chloride ($CaCl_2$) was added to remove any residual water. These monomers were freshly distilled under vacuum at most 24hrs before use. The monomer vinyl acetate (Aldrich Chemical Co. Inc.) was also distilled under vacuum at most 24hrs before use. The first 20-50 ml of distillate were discarded (distillate bottoms). All purified monomers were stored at −10 °C when not in use. The initiator 2,2'-azobisisobutyronitrile (AIBN) (Polysciences Inc.) was recrystallized three times from absolute methanol. The chain transfer agent 1-dodecanethiol (Acros Organics) was used as received. All of the solvents used in these experiments and for characterization of the copolymers (toluene, ethanol, deuterated chloroform, tetrahydrofuran (THF)) were also used as packaged.

Instrumentation

A ReactIR™ 1000 reaction analysis system equipped with a light conduit and DiComp (diamond composite) insertion probe was used to collect mid-FTIR spectra of the polymerization components. These spectra were used to calculate monomer conversion and, for the case of copolymerization, polymer composition. Resulting polymer compositions were also obtained through ^{1}H-NMR spectra taken by a Bruker AMX500 Fourier-transform ^{1}H-NMR spectrometer. 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, thermostated to 30°C, and a Waters 410 differential refractometer thermostated to 38°C. THF was used as the mobile phase and was delivered at 0.3 mL/min.

Procedures

High conversion solution polymerizations of MMA homopolymer and two copolymer pairs, BA/MMA and MMA/VAc, were run at 60°C in a 50 wt% toluene solution. Further details of the reaction conditions are shown in Table 2.1.

Table 2.1: Reaction conditions (all monomer values in mole fraction)

Ingredient	M1	BM1	BM2	MV1	MV2	MV3	MV4
BA	-	0.5	0.4	-	-	-	-
MMA	1.0	0.5	0.6	0.5	0.4	0.5	0.4
VAc	-	-	-	0.5	0.6	0.5	0.6
AIBN (mol/L)	0.05	0.1	0.1	0.05	0.05	0.1	0.1
CTA (mol/L)	0.05	0.025	0.025	0.025	0.05	0.025	0.025

Polymerizations were carried out in glass ampoules of length 20 cm and outer diameter 0.8 cm. The monomers and initiators, together with solvent and chain transfer agent (CTA), were weighed into a flask to prepare the initial feed and an amount of about 2.7 mL was then pipetted into several numbered ampoules. Next, the ampoules were degassed through several vacuum freeze-thaw cycles and subsequently submerged in a water bath for a recorded time interval with the temperature controlled at 60°C. Two ampoules were taken out at the same time, one for traditional polymer analysis and the other for IR spectroscopy analysis, and submerged in liquid nitrogen to quench the reaction.

For the traditional analysis, the content of one ampoule was poured into a 10-fold excess of ethanol. Mass conversion based on the total polymer in the reaction mixture was measured using gravimetry. In the case of copolymers, the resulting isolated polymers were analyzed for cumulative polymer composition by ^{1}H-NMR spectroscopy. Analysis was carried out at room temperature in deuterated chloroform (~2% (w/v) solutions), which was used as both the solvent and the reference. Acquisition time was 4.6 seconds, and 16 scans were performed per readout (for averaging). The relative amounts of monomer bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. All spectra exhibited good peak separations for a straightforward interpretation of the results. For BA/MMA copolymers, the spectral peaks for the $-OCH_2$ group in BA were located at ~4.0 ppm and those for the $-OCH_3$ group in MMA were at ~3.6 ppm. The MMA/VAc copolymers exhibited peaks for the α-hydrogen in VAc at ~4.9 ppm and the $-OCH_3$ group in MMA at ~3.6 ppm. The individual conversion profile for each monomer was obtained by combining results from the overall conversions through gravimetry and each monomer's corresponding mole fraction in the copolymer chain through ^{1}H-NMR spectroscopy.

The resulting polymer molecular-weight averages and molecular-weight distributions were determined by GPC. THF (HPLC grade) was used as the carrier fluid and 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 μm filters to remove any high molecular weight gel. 200μL 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 shown in Table 2.2.[18-20] K and α values for the copolymers were obtained using weighted averages based on the cumulative copolymer composition data.

Table 2.2: Mark-Houwink parameters determined in THF

Polymer	K (× 10^3 mL/g)	α
Polystyrene[18]	16	0.700
Polybutyl acrylate[19]	11	0.708
Polymethyl methacrylate[18]	12.8	0.690
Polyvinyl acetate[20]	15.6	0.708

The contents in each duplicate ampoule were poured into 5-dram vials and were analyzed using the ATR-FTIR insertion probe. The standard acquisition mode of the ReactIR™ 1000 was used to collect the IR spectra. The ATR-FTIR data were comprised of spectra collected from 64, 128, and 1024 scans, over the spectral ranges of 4000 – 700 cm^{-1}, with either 4 or 8 cm^{-1} resolution. At 4 cm^{-1} resolution, the spectral acquisition times associated with those numbers of scans were approximately 21.3, 42.7, and 341.3s, respectively. The insertion probe was put into the vial to record the spectra of the polymerization contents. The spectra were recorded and further analyzed using the ReactIR™ (version 2.2) software.

Monomer conversion monitoring was accomplished by following the change of certain characteristic peaks in the MIR spectra during the polymerization process. It was assumed that the component concentrations were proportional to absorbances measured as the corresponding peak heights. Equations 1 and 2, reported by Chatzi et al.,[21] were used to calculate the conversion, x, of individual monomers:

$$x(mol\%) = 1 - \frac{peak\ height\ at\ time\ t}{peak\ height\ at\ time\ t = 0} \tag{1}$$

and the overall conversion, X, of the copolymerization:

$$X(wt\%) = \frac{w_i}{w_i + w_j} x_i(mol\%) + \frac{w_j}{w_i + w_j} x_j(mol\%) \tag{2}$$

where ${w_i}/{(w_i + w_j)}$ was the weight fraction of monomers i fed into the reactor at time t=0.

Typically, a resolution of 4 to 8 cm^{-1} is adequate for good peak resolution and high signal to noise ratio for most condensed phase samples such as polymer solutions. Using a higher resolution would give noisier spectra and extend the data acquisition time, while there would be no improvement in peak assignment and measurement accuracy compared to the lower resolution spectra.[22] If reaction kinetics are fast, the number of scans should be kept low in order to capture the reaction process. However, more scans would give spectra with a higher signal-to-noise ratio.

Results and discussion

Data acquisition

An FTIR spectrum of a solution polymerization will include absorbances of monomer, produced polymer, and solvent. The solvent absorbance may interfere with the quantitative analysis of monomer and polymer absorbances if it overlaps with them. One way to solve the problem is to subtract the solvent spectrum to show the pure component spectrum of the reaction mixture using the data manipulation software. However, few subtractions yield a clear spectrum with a flat baseline and no solvent bands.[22]

An alternative can be to choose a region without solvent absorbance interference for quantitative analysis, thus rendering the spectral subtraction unnecessary. Toluene was used as the solvent in our solution polymerizations. It exhibited strong absorbances at 1606, 1498, and 1459 cm^{-1} for benzene ring stretching; 1081 and 1031 cm^{-1} for aryl CH bending; and 896, 726, and 695 cm^{-1} for aryl CH wagging. Thus, those wavenumbers were avoided when choosing characteristic absorbances for quantitative analysis of the monomers.

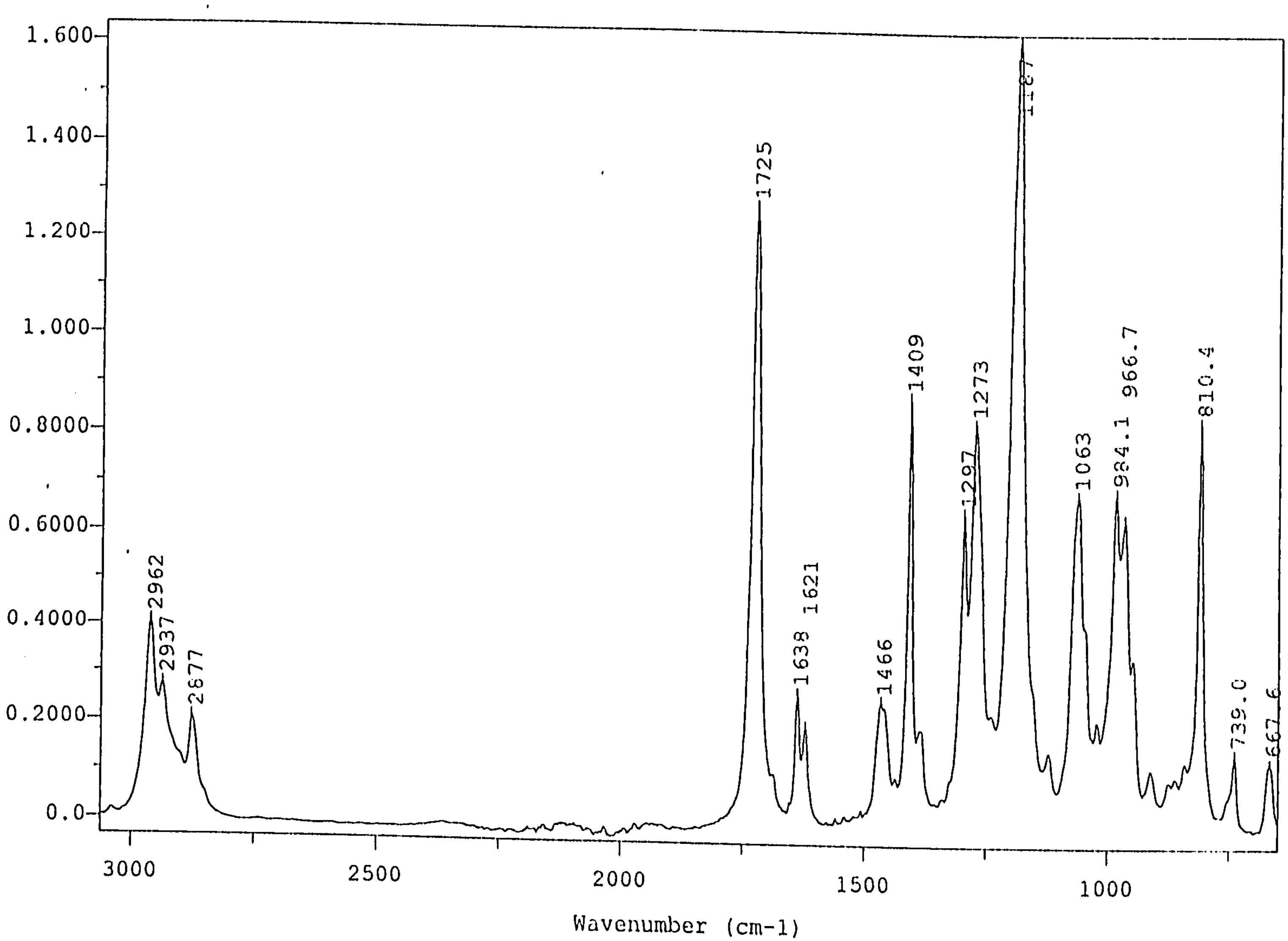
The successful use of an in-line spectroscopic sensor for monitoring polymerization, especially for copolymerization reactions, also presupposes the existence of characteristic absorbance bands for monomers and the individual structural units in the polymer. The characteristic group frequencies will generally appear in the same region for polymers as for monomers, which may also interfere with analysis on monomer bands. While specific couplings can occur with regularly ordered chemical functional groups in polymers, these couplings shift the group frequencies so that those bands can be distinguished from those of the monomers in the spectra. For copolymerization cases, absorbance bands from different monomers chosen for quantitative analysis should not overlap with each other.

Figure 2.1 shows the spectra of pure BA, MMA, VAc and toluene. Tables 2.3 through 2.5 show the characteristic frequencies assigned to each monomer and its corresponding homopolymers. Based on the heuristics mentioned above, 1409 cm^{-1} of CH deformation for BA, 1326 cm^{-1} of C-O-C stretching for MMA, and 876 cm^{-1} of $=CH_2$ wagging for VAc were found to be suitable to follow the copolymerizations.

MMA homopolymerization

One MMA homopolymerization run was conducted in 50 wt% toluene solution (see Table 2.1). Figure 2.2 shows the distinct reaction mixture spectral changes as the consequence of the polymerization reaction. Characteristic absorbance bands for monomer were easily identified such as the C=C stretching at 1640 cm^{-1}, the C-O-C stretching vibration of the aliphatic ester group at 1324 cm^{-1}, and the C=O wag at 652 cm^{-1}, which all diminished with increasing reaction time. Those peaks did not overlap with the peaks from the polymer produced nor from those due to the solvent. Thus, no solvent subtraction was required for the analysis of the overall spectra. A quantitative estimate of the monomer conversion during the reaction was made by calculating the ratio of the absorbances of the 1640, 1324, and 652 cm^{-1} characteristic absorption bands at reaction time t to each of their corresponding peaks at the start of the polymerization reaction (t=0), according to equation 1. The absorbance of each peak was measured as the peak height referenced to a single-point baseline after baseline correction. The absorbance at the start of the reaction was the absorbance of the reaction contents measured prior to polymerization.

Figure 2.1a: ATR-FTIR spectrum of butyl acrylate monomer.



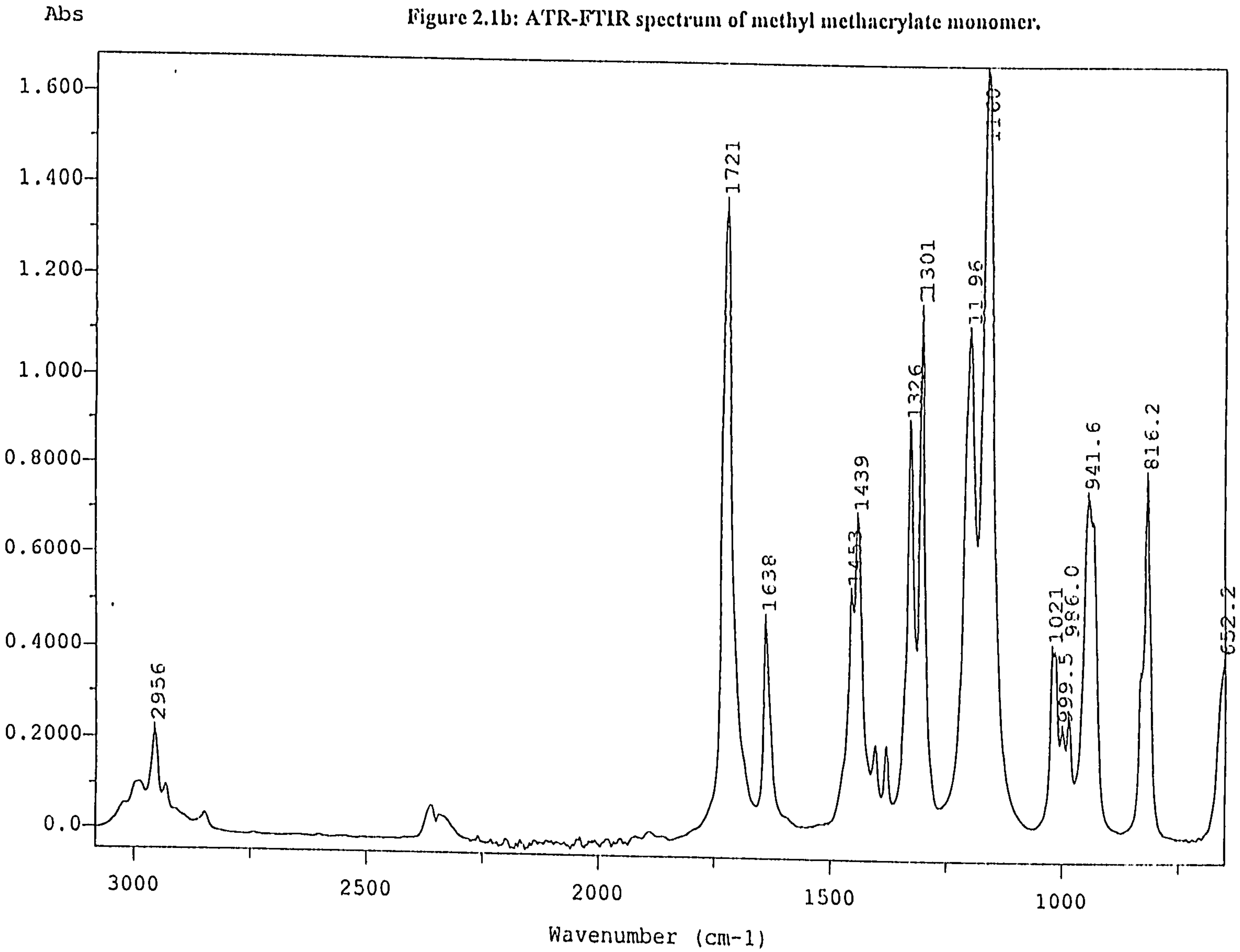


Figure 2.1b: ATR-FTIR spectrum of methyl methacrylate monomer.

Figure 2.1c: ATR-FTIR spectrum of vinyl acetate monomer.

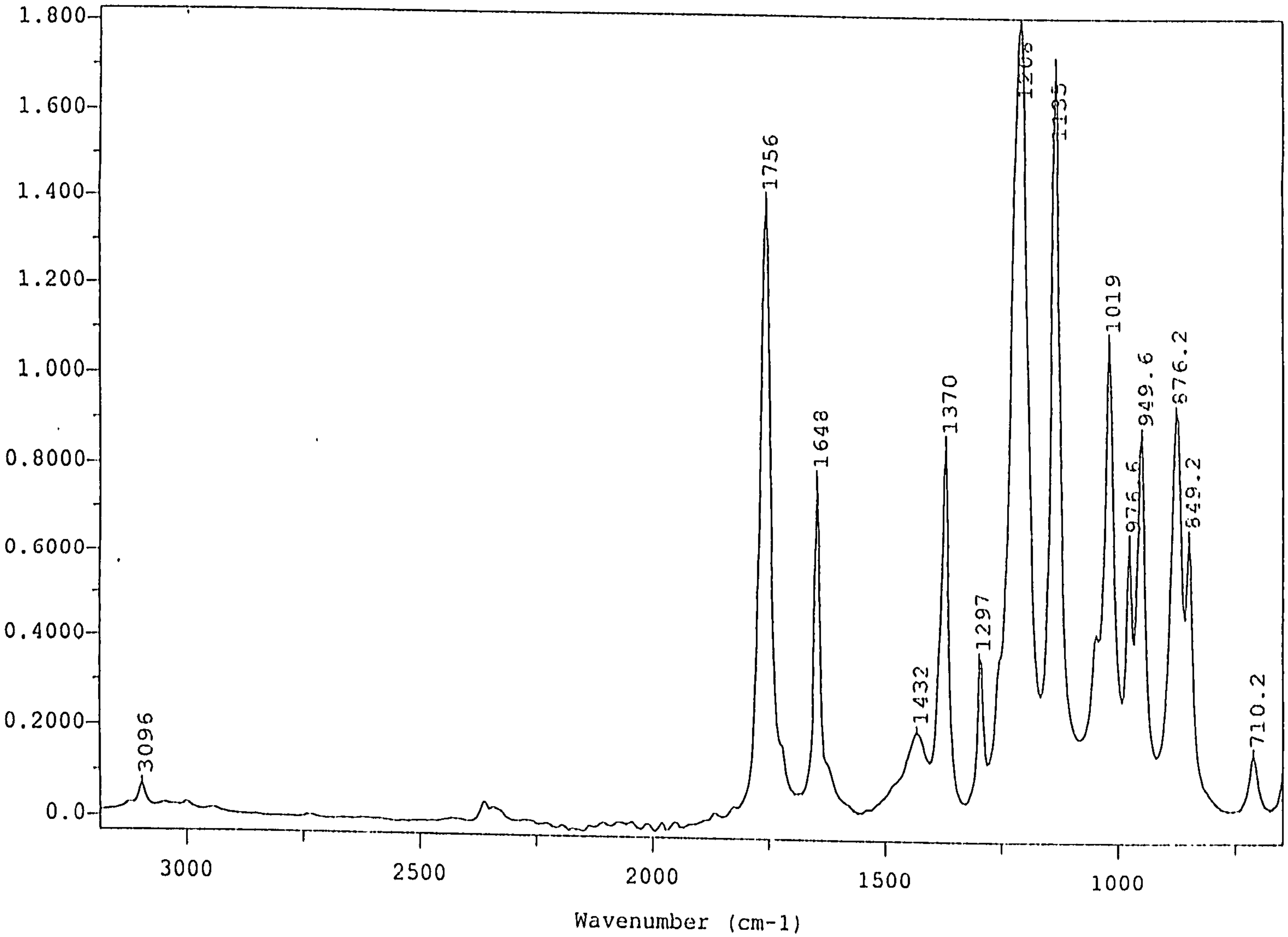


Figure 2.1d: ATR-FTIR spectrum of toluene.

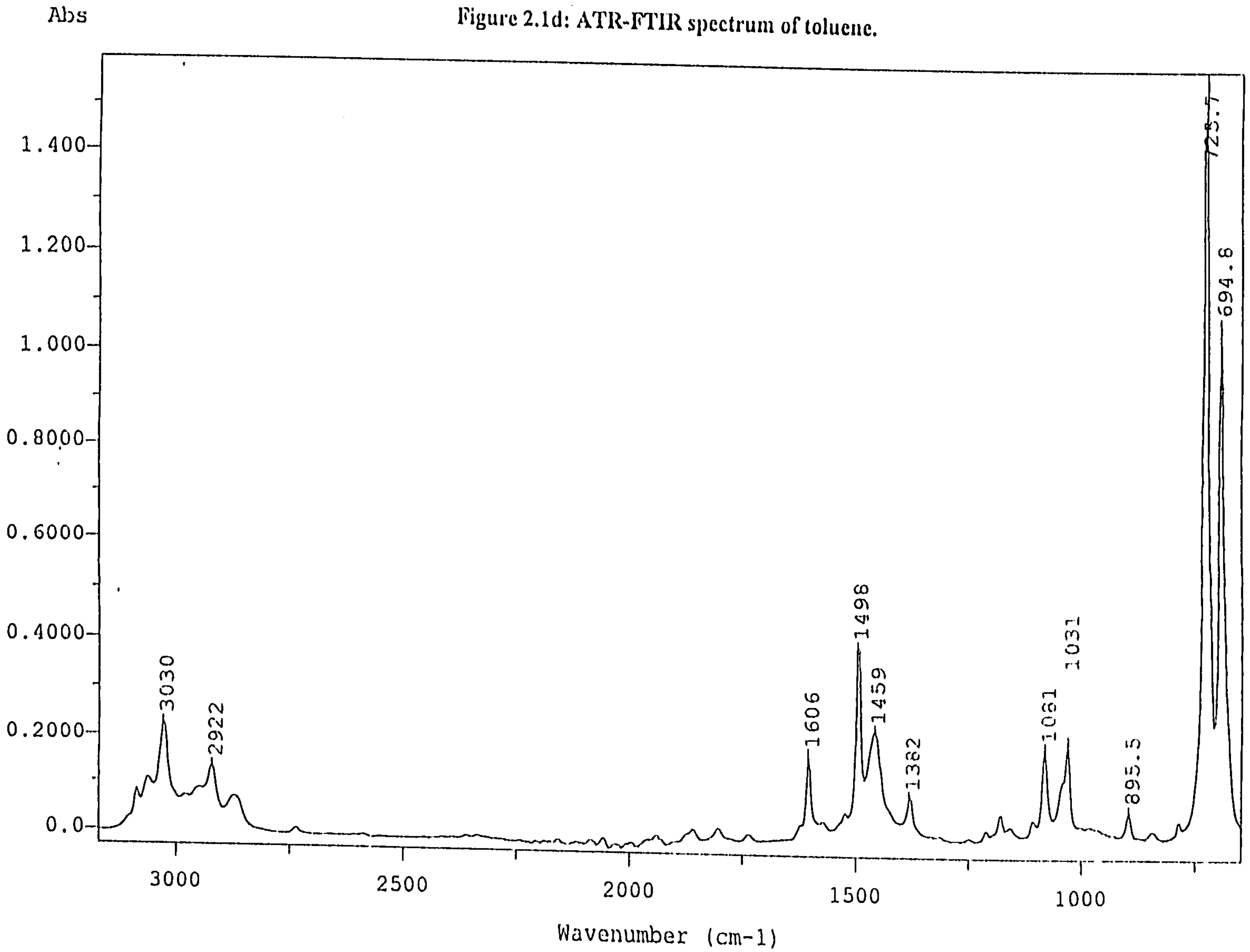


Table 2.3: Peak assignments for BA monomer and homopolymers[23-25]

Butyl Acrylate		Polybutyl Acrylate	
Spectral region	Absorbance assignments	Spectral region	Absorbance assignments
2950-2850 cm^{-1}	Aliphatic C-H stretching	3000-2800 cm^{-1}	Methyl, methylene, and methane C-H stretching
1725 cm^{-1}	C=O stretching	1740 cm^{-1}	C=O stretching
1638 and 1621 cm^{-1}	Acrylate C=C doublet		
1466 cm^{-1}	C-H deformation in methyl and methylene bands	1470 cm^{-1}	C-H deformation in methyl and methylene bands
1409 cm^{-1}	C-H deformation in $=CH_2$		
1273 cm^{-1}	=CH rock	1400-1300 cm^{-1}	C-H deformation in $C-CH_3$ band
1187 cm^{-1}	$=C-(C=O)-O-CH_2-$ stretching of aliphatic ester bands	1270-1150 cm^{-1}	$-C-(C=O)-O-CH_3$ stretching of aliphatic ester bands
1063 cm^{-1}	$=CH_2$ rock		
984 cm^{-1}	Trans =CHR wag		
967 cm^{-1}	$=CH_2$ wag		
810 cm^{-1}	$=CH_2$ twist		
668 cm^{-1}	C=O wag	486	C=O wag

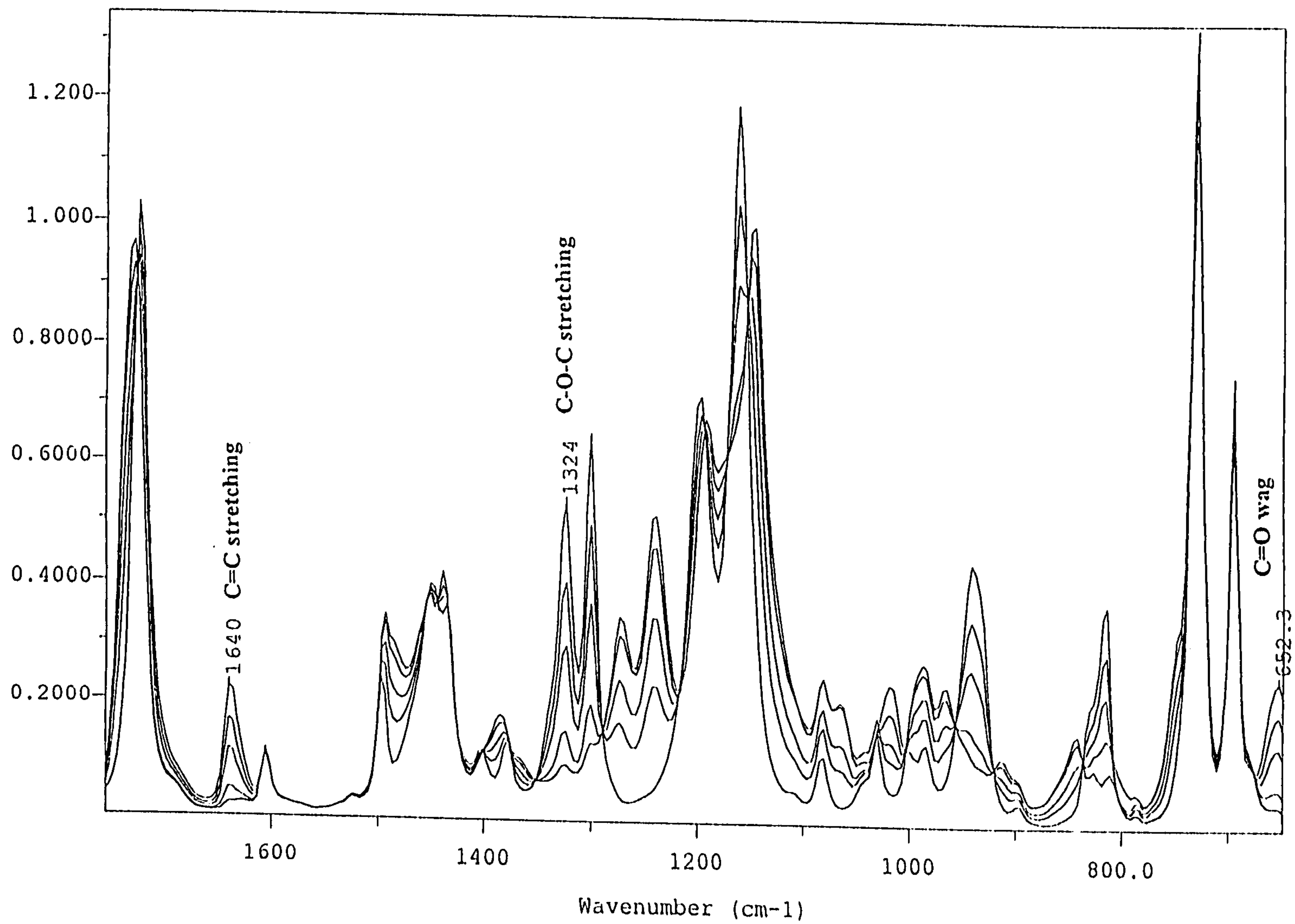
Table 2.4: Peak assignments for MMA monomer and homopolymers[23-25]

Methyl Methacrylate		Polymethyl Methacrylate	
Spectral region	Absorbance assignments	Spectral region	Absorbance assignments
3000 – 2800 cm^{-1}	Aliphatic C-H stretching	2993 and 2947 cm^{-1}	Methyl and methylene C-H stretching
1725 cm^{-1}	C=O stretching	1730 cm^{-1}	C=O stretching
1640 cm^{-1}	C=C stretching		
1440 cm^{-1}	C-H deformation in O-CH_3 band	1443 cm^{-1}	C-H deformation in O-CH_3 band
1378 cm^{-1}	C-H deformation in methyl band hyperconjugated with C=C	1386 cm^{-1}	C-H deformation in C-CH_3 band
1324, 1301, 1197, 1158, and 1021 cm^{-1}	=C-(C=O)-O-CH_3 stretching of aliphatic ester bands	1274, 1239, 1193, 1150, and 987.4 cm^{-1}	-C-(C=O)-O-CH_3 stretching of aliphatic ester bands
984 cm^{-1}	CH_2=CR_2 wag		
942 cm^{-1}	=CH_2 wag		
815 cm^{-1}	=CH_2 twist		
652 cm^{-1}	C=O wag	486 cm^{-1}	C=O wag

Table 2.5: Peak assignments for VAc monomer and homopolymers[23-25]

Vinyl Acetate		Polyvinyl Acetate	
Spectral region	Absorbance assignments	Spectral region	Absorbance assignments
3096 cm^{-1}	C-H in methyl bands stretching	2900-2800 cm^{-1}	Aliphatic C-H stretching
1756 cm^{-1}	C=O stretching	1740 cm^{-1}	C=O stretching
1648 cm^{-1}	C=C stretching		
1432 cm^{-1}	C-H deformation in =CH-	1470 cm^{-1}	C-H deformation in methyl and methylene bands
1370 cm^{-1}	Intensified C-H deformation in (O=C)-CH_3	1400-1300 cm^{-1}	Intensified C-H deformation in (O=C)-CH_3
1297, 1212, 1135, and 1019 cm^{-1}	=C-O-(C=O)-CH_3 stretching of aliphatic ester bands	1240-1020 cm^{-1}	=C-O-(C=O)-CH_3 stretching of aliphatic ester bands
950 cm^{-1}	Trans =CHR wag		
876 cm^{-1}	=CH_2 wag		
849 cm^{-1}	=CH_2 twist		
710 cm^{-1}	Cis- C=C wag		

Figure 2.2: ATR-FTIR spectra of MMA solution polymerization run M1 in toluene (50 wt%).



The monomer conversion estimated from the ATR-FTIR spectra agreed with the conversion values obtained from conventional gravimetric measurements, as shown in Figure 2.3. It is evident that any of these characteristic absorbance bands (i.e. 1640, 1324, and 652 cm^{-1}) can be used for real-time monitoring of MMA homopolymerization. Analysis of error in the characteristic absorbance peak heights indicated that a precision of ±3 wt% conversion is expected with 95% confidence. This is indicated by the confidence intervals in Figure 2.3. These confidence intervals show that there is no difference between the IR and gravimetric data. This applies to all of the systems studied herein.

The monomer conversion data of the polymerization from gravimetric and IR spectral methods were also compared to predictions from a JAVA™-based computer simulation[26] in Figure 2.3. This computer simulation was developed using the mathematical model described by Dubé et al.[27] The model has been validated for a wide range of homopolymerization and copolymerization systems including BA, MMA, and VAc by Gao and Penlidis.[28,29] Model predictions appear to be reasonable in this case.

The kinetics of the homopolymerization of MMA have been studied extensively and are well understood. However, the issue of solvent effects on the propagation and/or termination rate constants is of concern. Fernandez-Garcia et al.[30] showed that the propagation rate constant for MMA polymerized in toluene was not significantly different from that in bulk polymerization, while the termination rate constant was dependent on the polymer chain length. Coote et al.[31] also concluded that solvent effects were small for MMA solution homopolymerization. Thus, the good predictions of our model without modification for solvent effects are supported by these recent publications.

The change of the cumulative number- and weight-average molecular weights with conversion was plotted in Figure 2.4, and compared to model predictions. The products exhibited narrower molecular weight distributions than predicted by the model.

BA/MMA copolymerization

Two BA/MMA copolymerization runs were conducted in a 50 wt% toluene solution (see Table 2.1). Reaction mixture spectra were collected in the same way as for the MMA homopolymerization and distinct changes, as a consequence of the polymerization reaction, were observed (see Figure 2.5). Characteristic absorbance bands for both monomers were easily identified at 1409 cm^{-1} for the BA hyperconjugated –CH deformation and at 1326 cm^{-1} for the MMA C-O-C stretching vibration of the aliphatic ester group, which diminished with increasing reaction time. There was no interference from the polymer nor from the solvent absorbances around these regions. Thus, these two peaks were used for tracking the reaction. The 1640 cm^{-1} C=C stretching and 652 cm^{-1} C=O wagging for MMA were not used because they overlapped with BA's 1638 cm^{-1} C=C doublet and 668 cm^{-1} C=O wagging, which could introduce error into the profile for MMA concentration over time.

A quantitative estimate of the individual conversion of both monomers during the reaction was made by calculating the ratio of the absorbances (peak height referenced to a single-point baseline after baseline correction) of the 1409 and 1326 cm^{-1} characteristic absorption bands, for BA and MMA, respectively, at reaction time t to those corresponding peaks at the start of the polymerization reaction (t=0), according to equation 1. The absorbances at the start of the reaction were the absorbances of the reaction contents measured prior to polymerization. The overall weight percentage conversion was subsequently calculated according to equation 2. Figures 2.6 and 2.7 show good agreement of the overall and individual monomer conversion data obtained between traditional

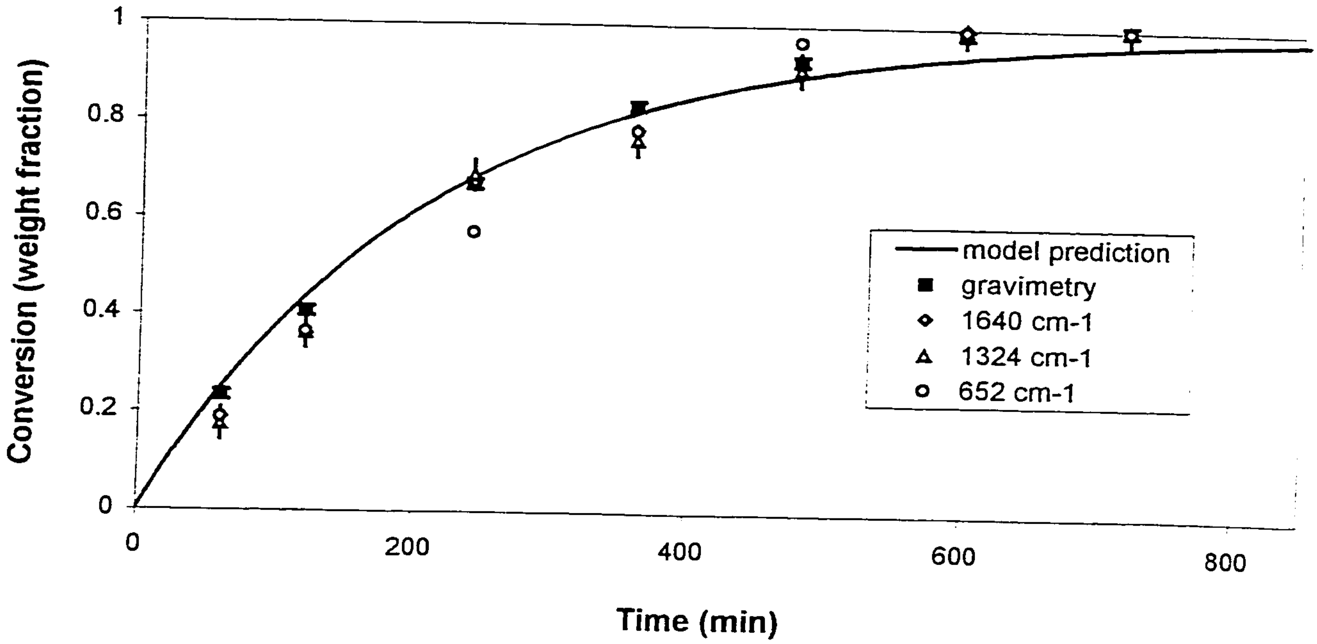


Figure 2.3: MMA homopolymerization run M1: conversion vs. time

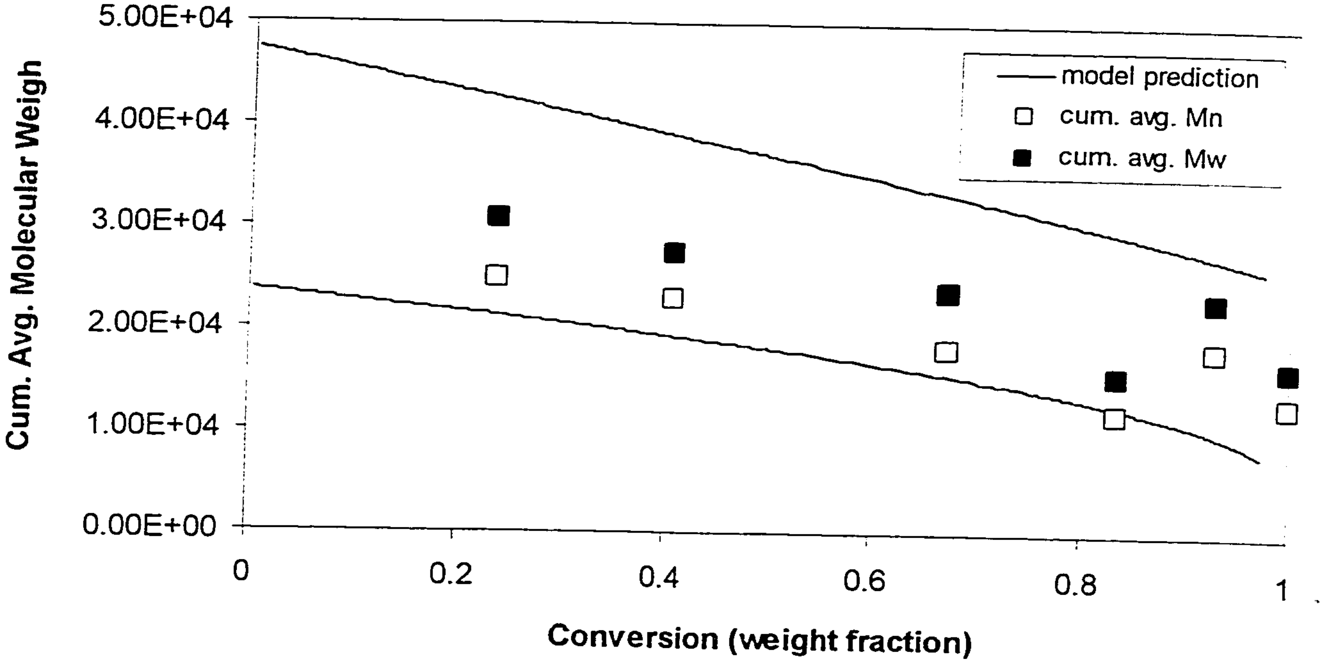


Figure 2.4: MMA homopolymerization run M1: cumulative number- and weight-average molecular weight vs. conversion.

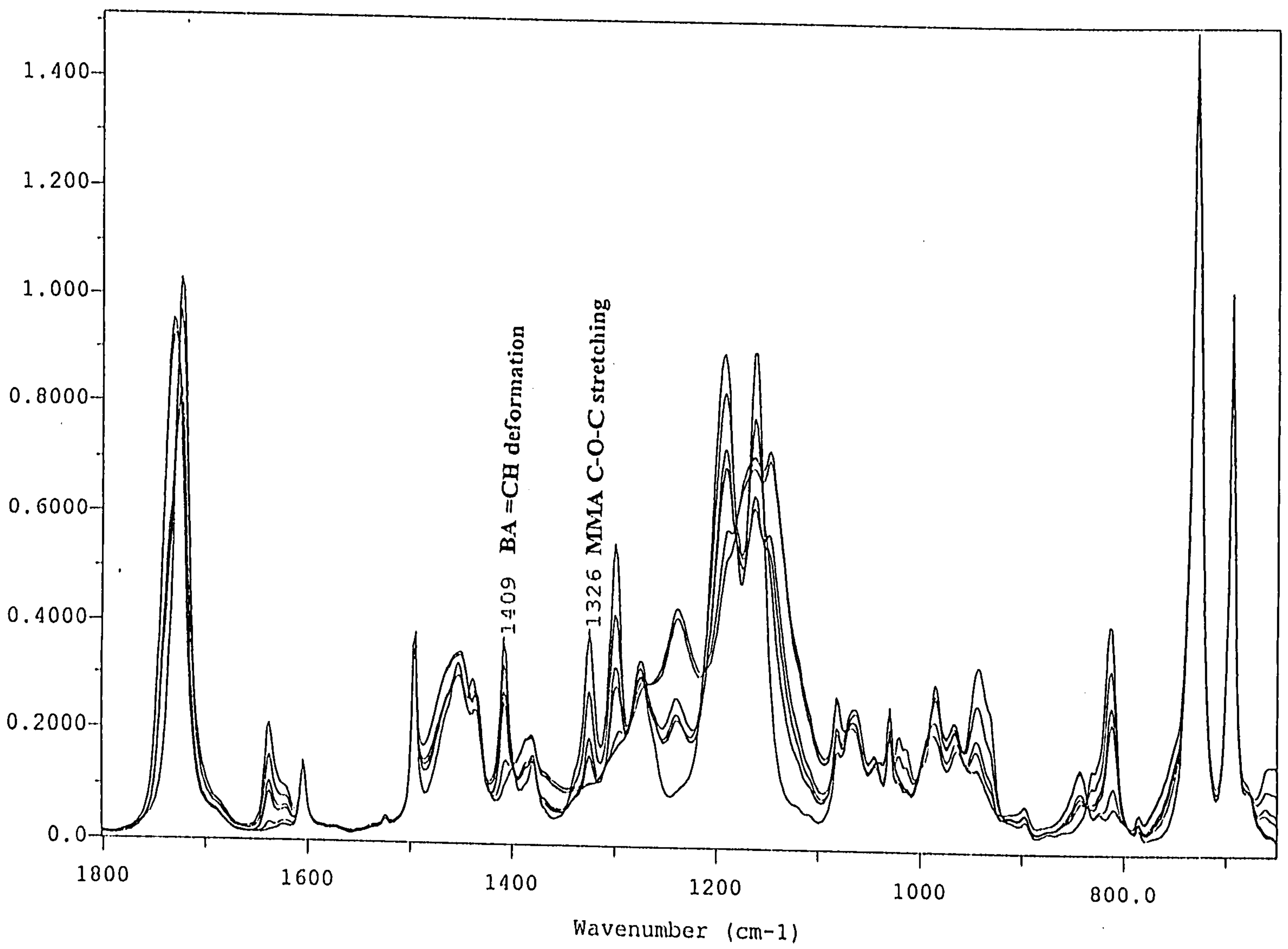
gravimetry and ^{1}H-NMR spectroscopy techniques and ATR-FTIR spectroscopy.

From Figures 2.6 and 2.7, a slightly higher overall copolymerization rate was observed when the MMA mole fraction in the feed was increased from 0.5 to 0.6. Since all the conditions except for monomer feed compositions were the same for both two BA/MMA runs, cumulative copolymer composition vs. conversion plots were combined in Figure 8. In this figure, only minor composition drift can be observed during the polymerization. Since the reactivity ratios are somewhat different in the BA/MMA pair ($r_{BA} = 0.291$ and $r_{MMA} = 1.871$)[32], MMA was slightly more rapidly consumed when copolymerized with BA.

The cumulative number- and weight-average molecular weights for the produced copolymers are shown in Figures 2.9 and 2.10. The use of CTA in the solution polymerizations helped keep the copolymer molecular weights low and the molecular weight distribution narrow and unchanged during the process.

There have been only limited kinetic studies for the BA/MMA solution copolymerization. Hakim et al.[33] studied solvent effects on the BA/MMA reactivity ratios in toluene over an extended temperature range from 60 to 140°C. No significant solvent effects on copolymer composition were detected. Madruga et al.[34] reported on the homo- and copolymerization of BA/MMA in benzene solution. They found that the lumped parameter, $k_p/k_t^{0.5}$ (where k_p is the propagation rate constant and k_t is the termination rate constant), for the BA homopolymerization increased when the monomer concentration in the solution increased while it did not change in the case of MMA. McKenna et al.[19] demonstrated similar phenomena for BA polymerizations in toluene. Thus, model parameters for BA were modified according to Jovanovic and Dubé[35] who modelled the BA/VAc in toluene solution

Figure 2.5: ATR-FTIR spectra of BA/MMA solution copolymerization run BM2 in toluene (50 wt%).



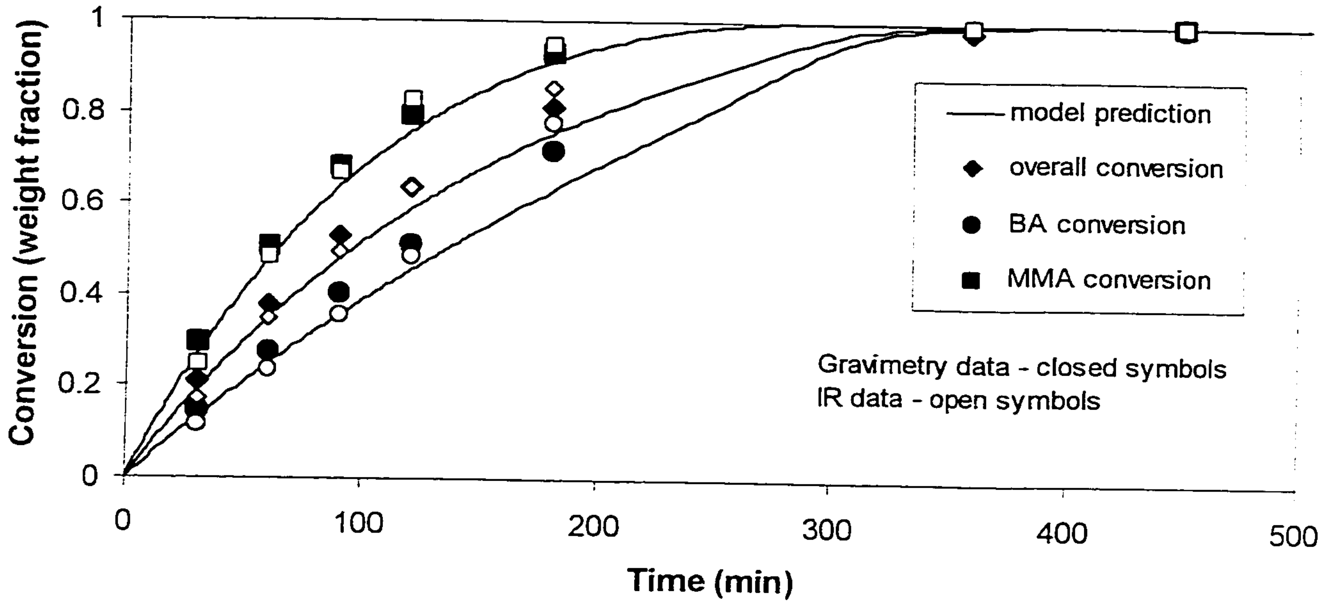


Figure 2.6: BA/MMA solution copolymerization run BM1: conversion vs. time

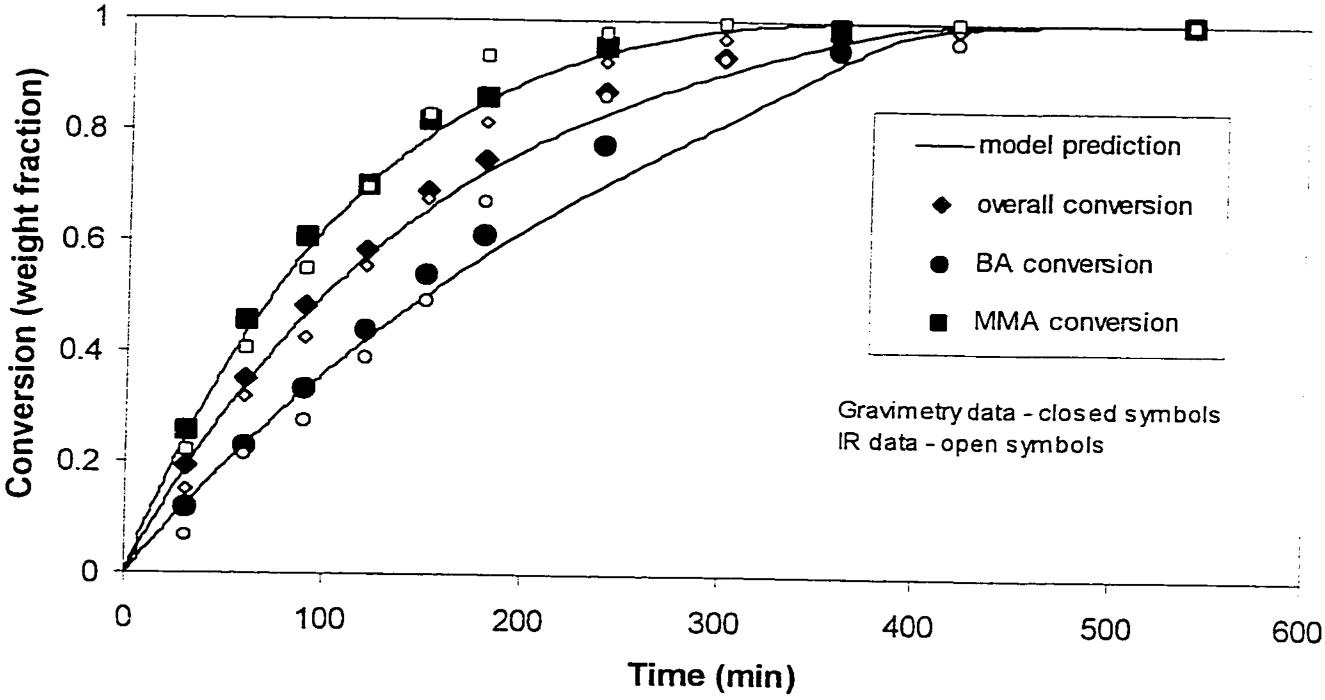


Figure 2.7: BA/MMA solution copolymerization run BM2: conversion vs. time

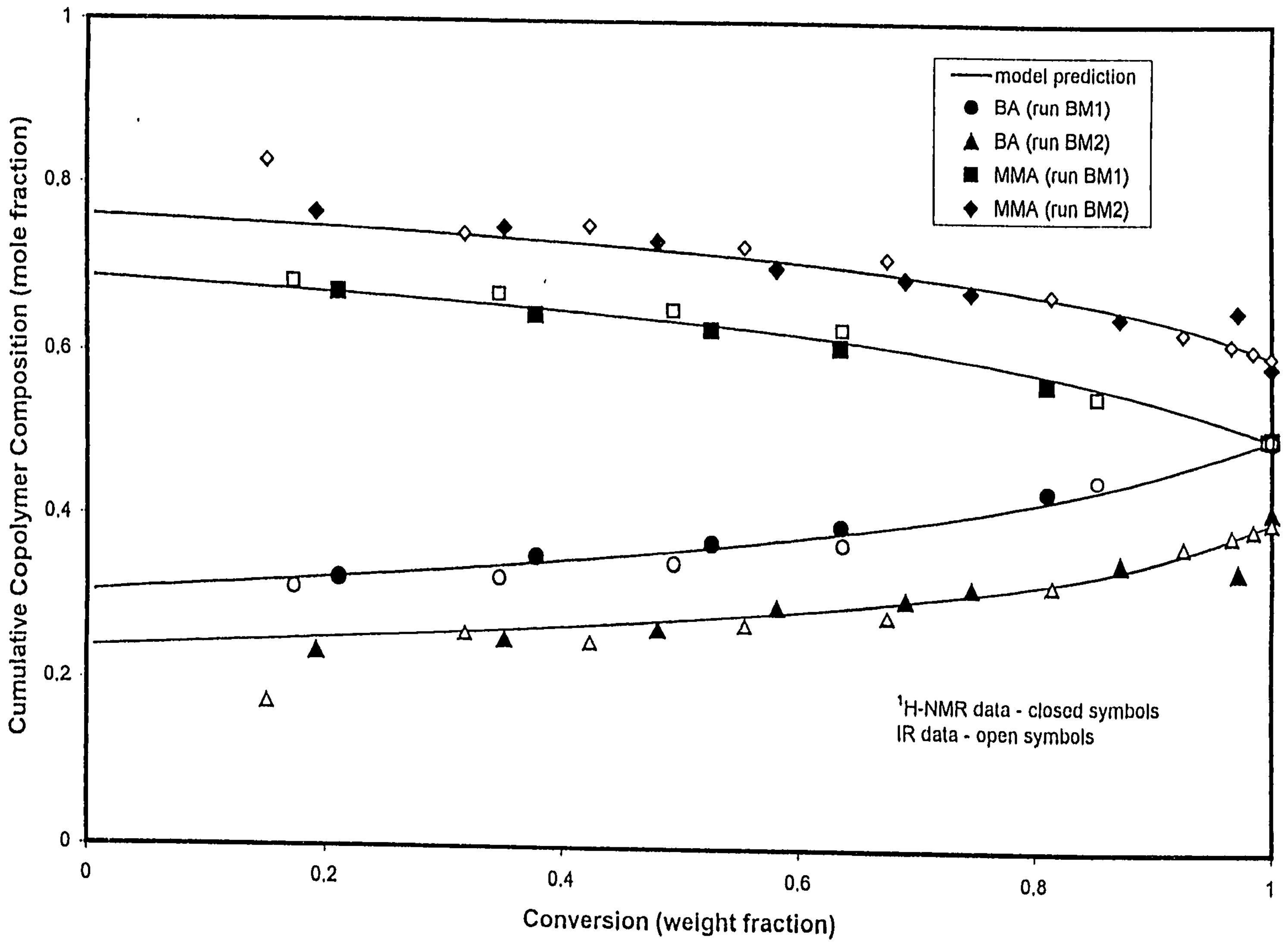


Figure 2.8: BA/MMA solution copolymerization runs BM1 and BM2: cumulative copolymer composition vs. conversion.

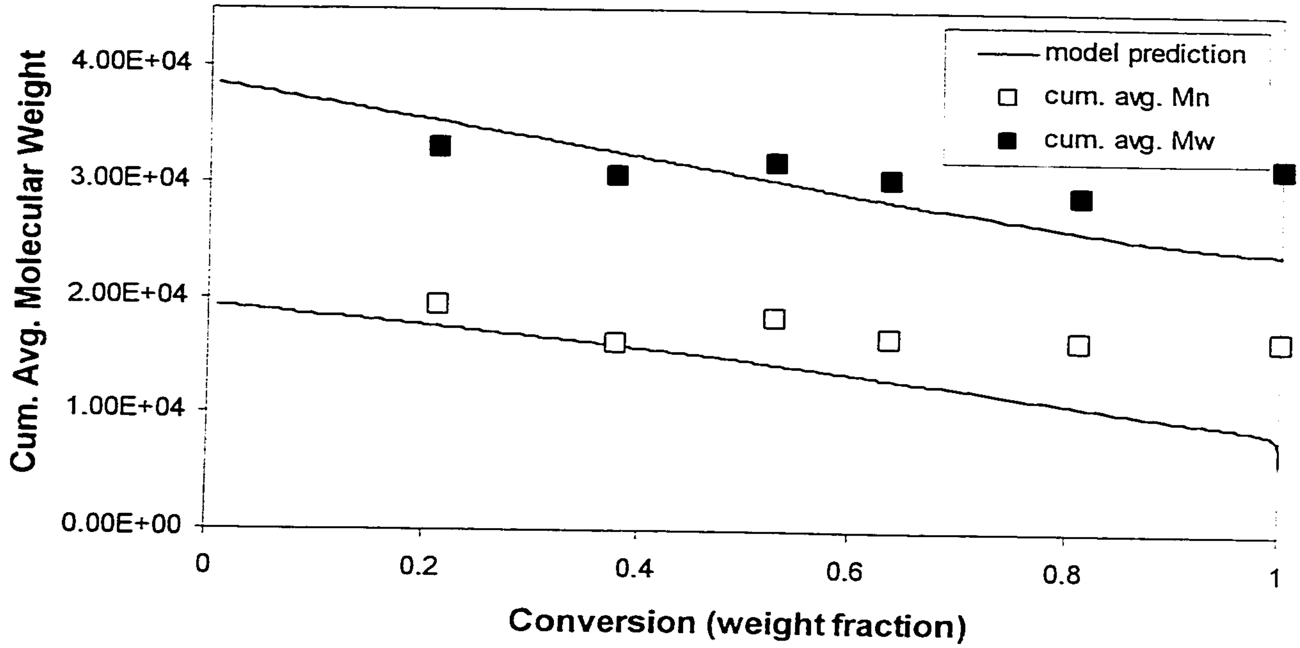


Figure 2.9: BA/MMA solution copolymerization run BM1: cumulative number- and weight-average molecular weight vs. conversion

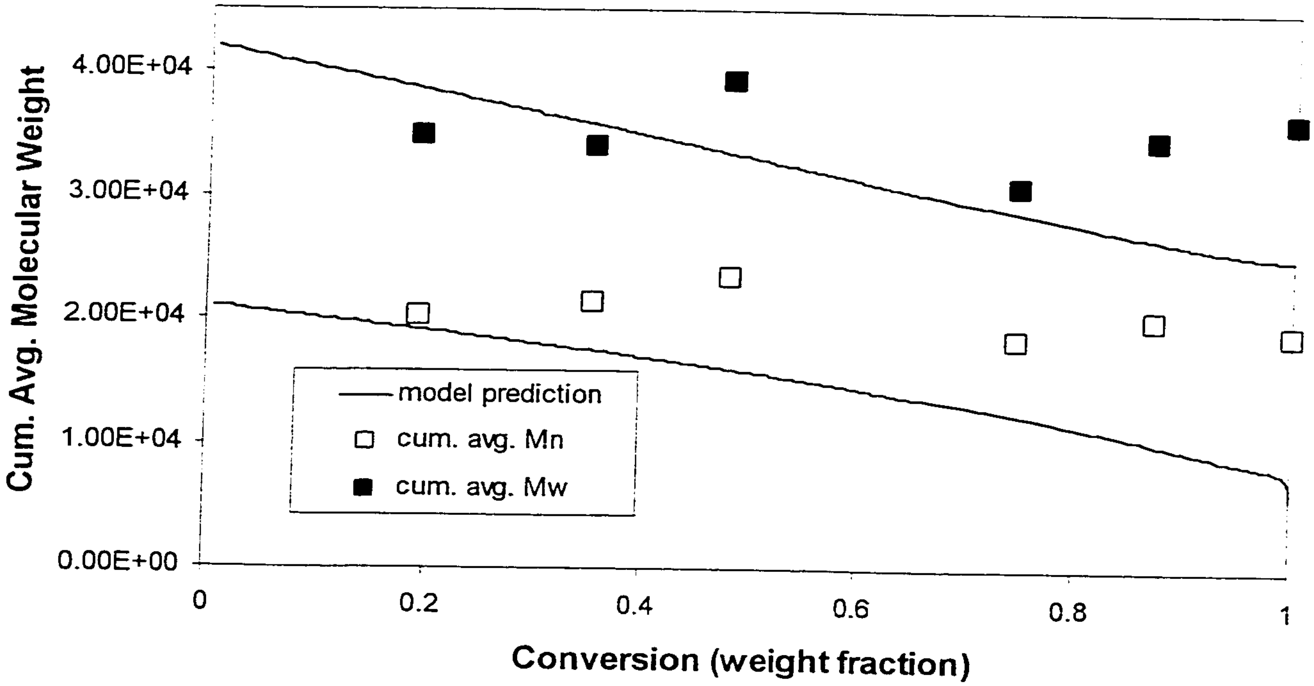


Figure 2.10: BA/MMA solution copolymerization run BM2: cumulative number- and weight-average molecular weight vs. conversion

copolymerization. Model predictions of conversion, composition and molecular weight averages are in agreement with the collected data (see Figures 2.6 through 2.10).

MMA/VAc copolymerization

Four MMA/VAc copolymerization runs were conducted in a 50 wt% toluene solution (see Table 2.1). Reaction mixture spectra were collected the same way as for the other polymerization runs and distinct changes as the consequence of the polymerization reaction were observed (see Figure 11). Characteristic absorbance bands for both monomers were identified at 1326 cm^{-1} for the MMA C-O-C stretching vibration of the aliphatic ester group and at 874 cm^{-1} for the VAc $=CH_2$ wagging, which diminished with increasing reaction time. There was no interference from the polymer nor from the solvent absorbances around these regions. Thus, these two peaks were used for tracking the reaction. Since the 1640 cm^{-1} C=C stretching for MMA overlapped somewhat with VAc's 1648 cm^{-1} C=C stretching, they were not used for the profiles of either monomer's concentration over time.

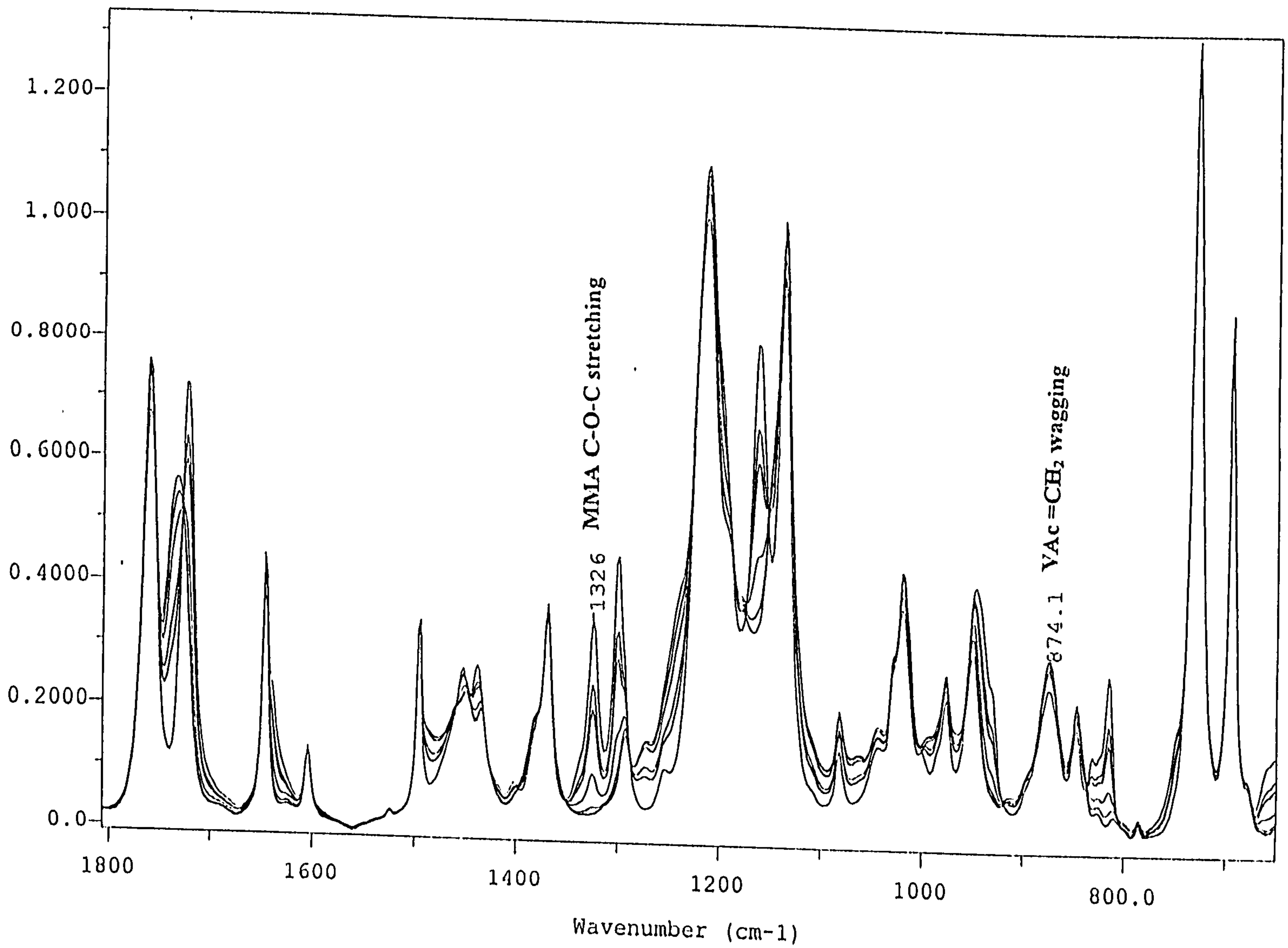
The individual conversions of both MMA and VAc monomers during the reactions were estimated similar to that for the BA/MMA copolymerizations. The overall weight percentage conversion was subsequently calculated according to equation 2. The monomer conversion versus time data obtained from the different measurement techniques are plotted in Figures 2.12 though 2.15. Good agreement was observed for MMA between the ATR-FTIR measurements and the measurements from the gravimetric and ^{1}H-NMR techniques for both the overall and the individual monomer conversions.

Final conversions ranging from 60 to 80 wt.% were achieved in the experiments. They all exhibited a two-stage rate effect as described in Dubé and Penlidis.[13] Since MMA is much more reactive than VAc according to the reactivity ratios (r_{MMA} = 24.025 and r_{VAc} =

0.0261)[36], MMA dominated the beginning of the reaction to form polymer mostly composed of MMA while VAc dominated the polymerization after the MMA was depleted. As shown in Figures 2.12 through 2.15, VAc was not reacting much during the early stages of the copolymerizations and behaved much like a solvent so that the MMA homopolymerization gel effect was dampened by the VAc. During the latter stages of reaction, the polymerization rate was very high, owing to the fact that the VAc homopolymerization exhibited an autoacceleration in the high viscosity environment of the polymer chains. Comparison between Figures 2.12 and 2.13, and Figures 2.14 and 2.15 indicate that, when the MMA mole fraction in the monomer feed was increased from 0.4 to 0.5, the two-stage rate effect was delayed to higher conversions. Higher polymerization rates were also observed during the first stage of the polymerization while the overall polymerization rates did not change very much. The increase in initiator concentration from 0.05 to 0.1 mol/L, as shown in Figures 2.12 and 2.14, and Figures 2.13 and 2.15 also increased the overall rates of polymerization according to classical kinetic theory.

Cumulative copolymer compositions were plotted as a function of conversion and are shown in Figures 2.16 and 2.17. Those plots looked similar because there was no effect from either the initiator or the CTA concentration on copolymer composition. Significant copolymer composition drift was observed at higher conversion levels (above 50%). This coincided with the two-stage rate effect shown in Figures 2.12 through 2.15. Furthermore, when the MMA fraction in the monomer feed was increased, the two-stage rate effect was delayed to higher conversions. Comparing BA/MMA and MMA/VAc runs using the same initiator and CTA concentration conditions (see Figures 2.8 and 2.17), striking differences can be seen. Due to the difference in the reactivity ratios for BA/MMA as compared to

Figure 2.11: ATR-FTIR spectra of MMA/VAc solution copolymerization run MV3 in toluene (50 wt%).



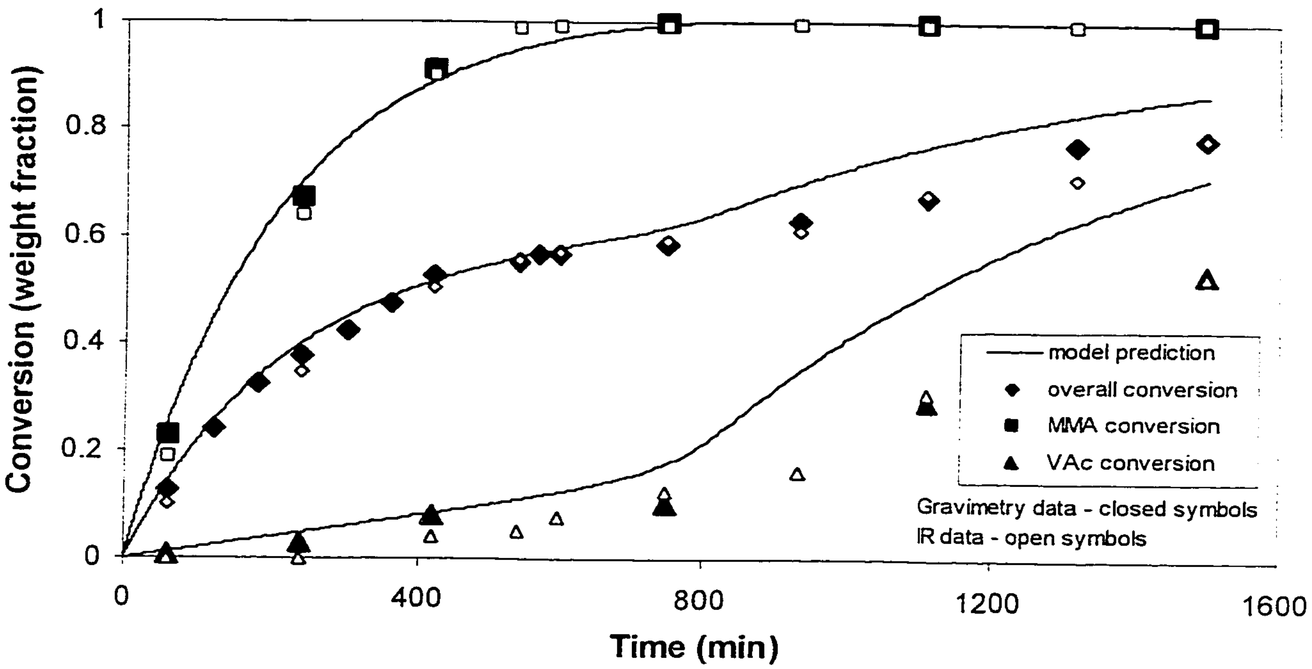


Figure 2.12: MMA/VAc solution copolymerization run MV1: conversion vs. time

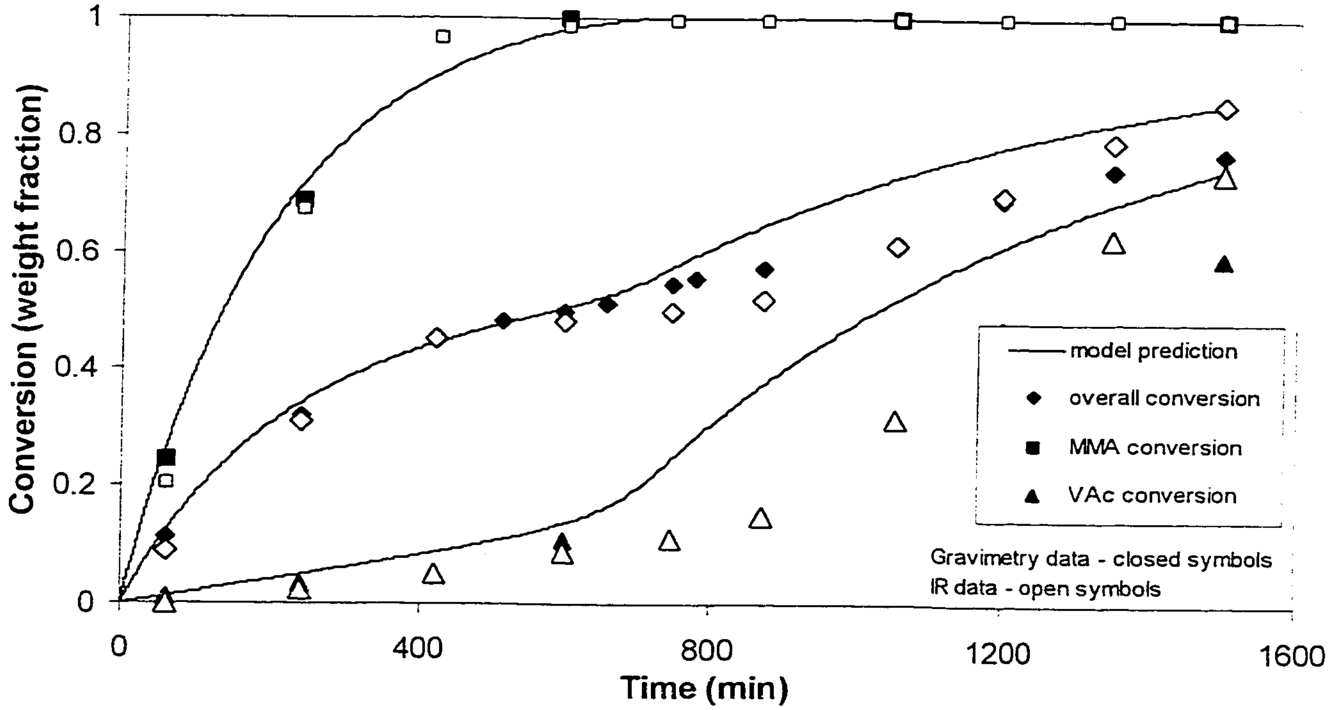


Figure 2.13: MMA/VAc solution copolymerization run MV2: conversion vs. time

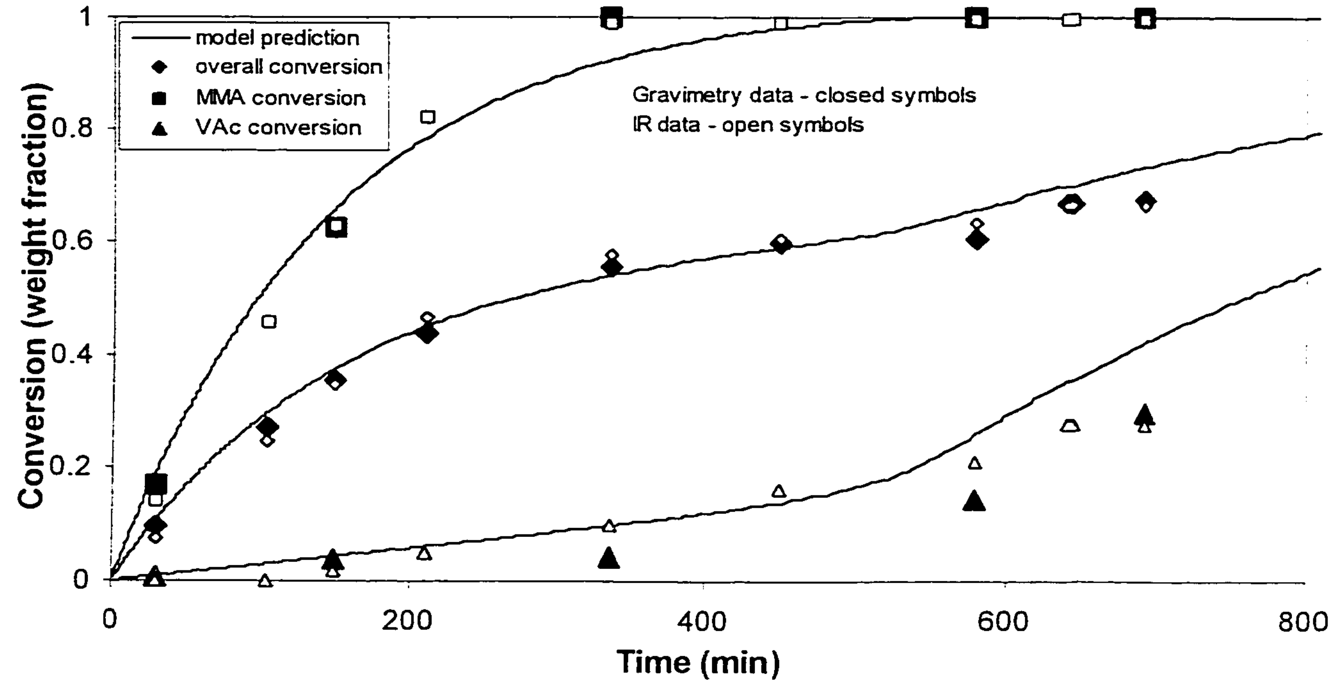


Figure 2.14: MMA/VAc solution copolymerization run MV3: conversion vs. time

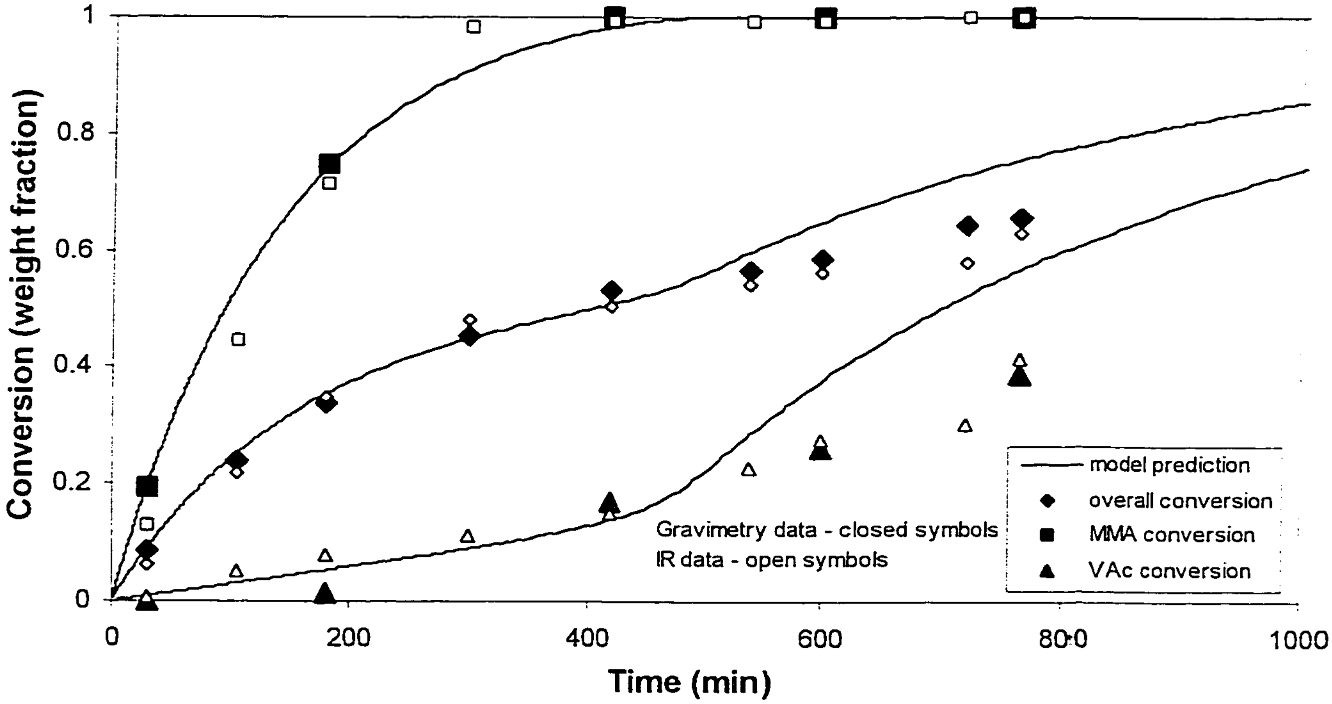


Figure 2.15: MMA/VAc solution copolymerization run MV4: conversion vs. time

MMA/VAc, the latter exhibited a much larger composition drift.

The cumulative number- and weight-average molecular weights vs. conversion data, together with model predictions are plotted in Figures 2.18 through 2.21. As shown in Figures 2.18 and 2.19, and 2.20 and 2.21 respectively, a higher MMA fraction in the monomer feed resulted in slightly faster polymerization rates and thus, higher molecular weight averages. Increasing the CTA concentration by 2 fold significantly decreased the molecular weight averages due to the chain transfer reaction, as observed in Figures 2.18 and 2.19. Comparison between Figures 2.18 and 2.20 indicates that increases in initiator concentration contributed to slightly higher molecular averages. This agreed with the increasing polymerization reaction rate as shown previously in Figures 2.12 and 2.14. Combined effects of increases in initiator concentration and decreases in CTA concentration on the molecular averages were observed in Figures 2.19 and 2.21. Though increases in initiator concentration resulted in slightly higher molecular weight averages, higher CTA concentrations led to lower molecular weight averages and narrower molecular weight distributions.

Solvent effects on VAc rate coefficients can be significant because the toluene acts as a strong retardant for VAc homopolymerization.[31] The modified lumped parameter used to incorporate the solvent effect for VAc polymerization modelling was introduced from similar modelling efforts for BA/VAc solution copolymerizations in toluene.[35] Model predictions for overall conversions, copolymer compositions, and molecular weight averages for the most part, are reasonably good (see Figures 12 through 21). There are some discrepancies between model predictions of VAc conversion and experimental data at high overall conversions. These model predictions were achieved using the homopolymerization

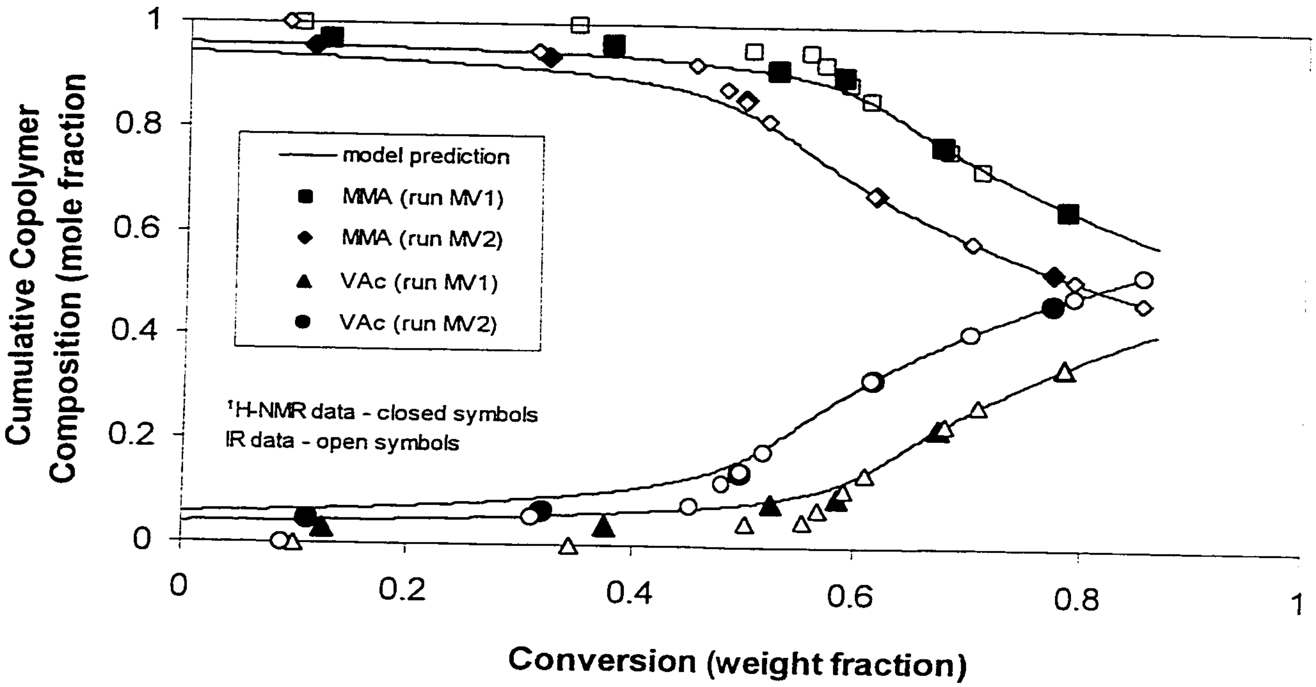


Figure 2.16: MMA/VAc solution copolymerization runs MV1 and MV2: cumulative copolymer composition vs. conversion

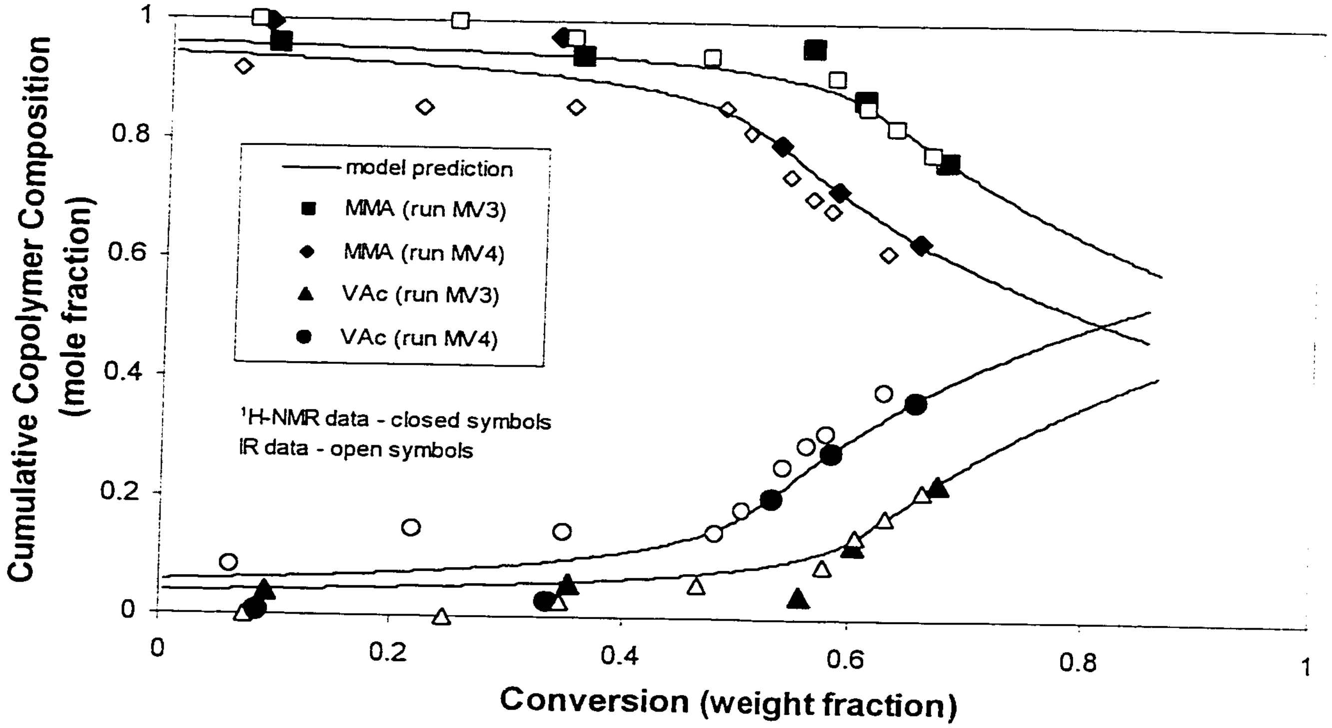


Figure 2.17: MMA/VAc solution copolymerization runs MV3 and MV4: cumulative copolymer composition vs. conversion

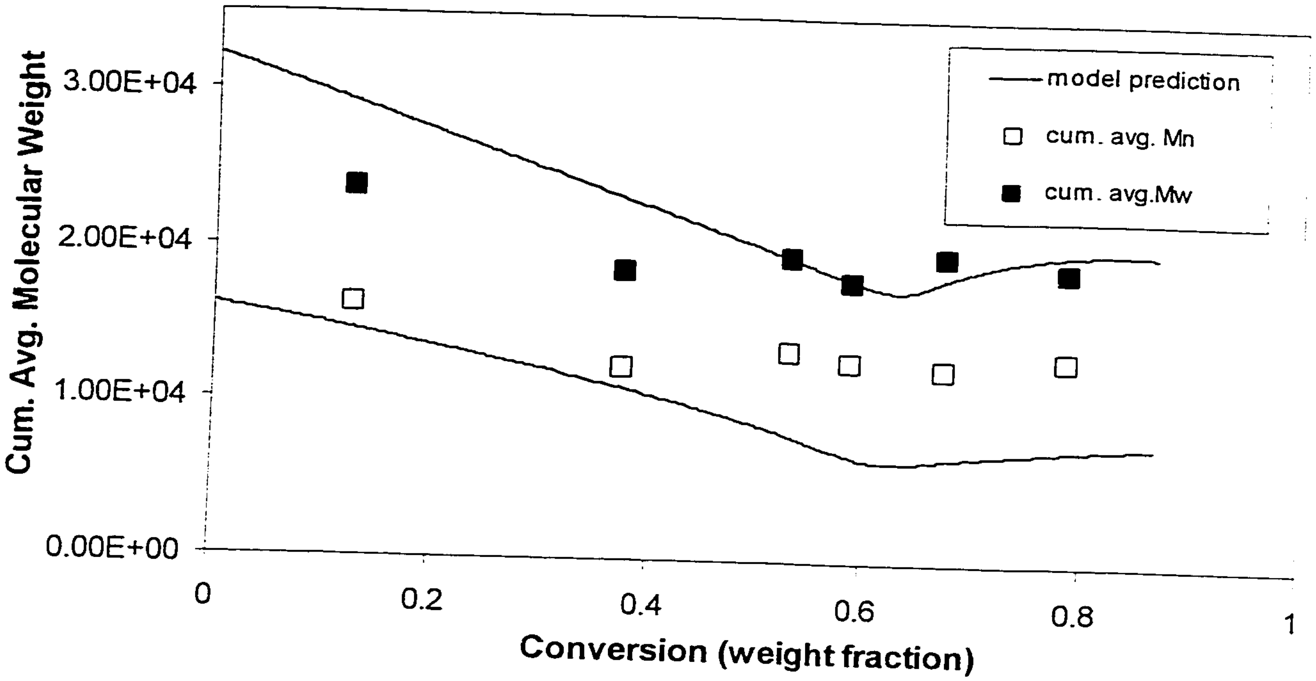


Figure 2.18: MMA/VAc solution copolymerization run MV1: cumulative number- and weight-average molecular weight vs. conversion

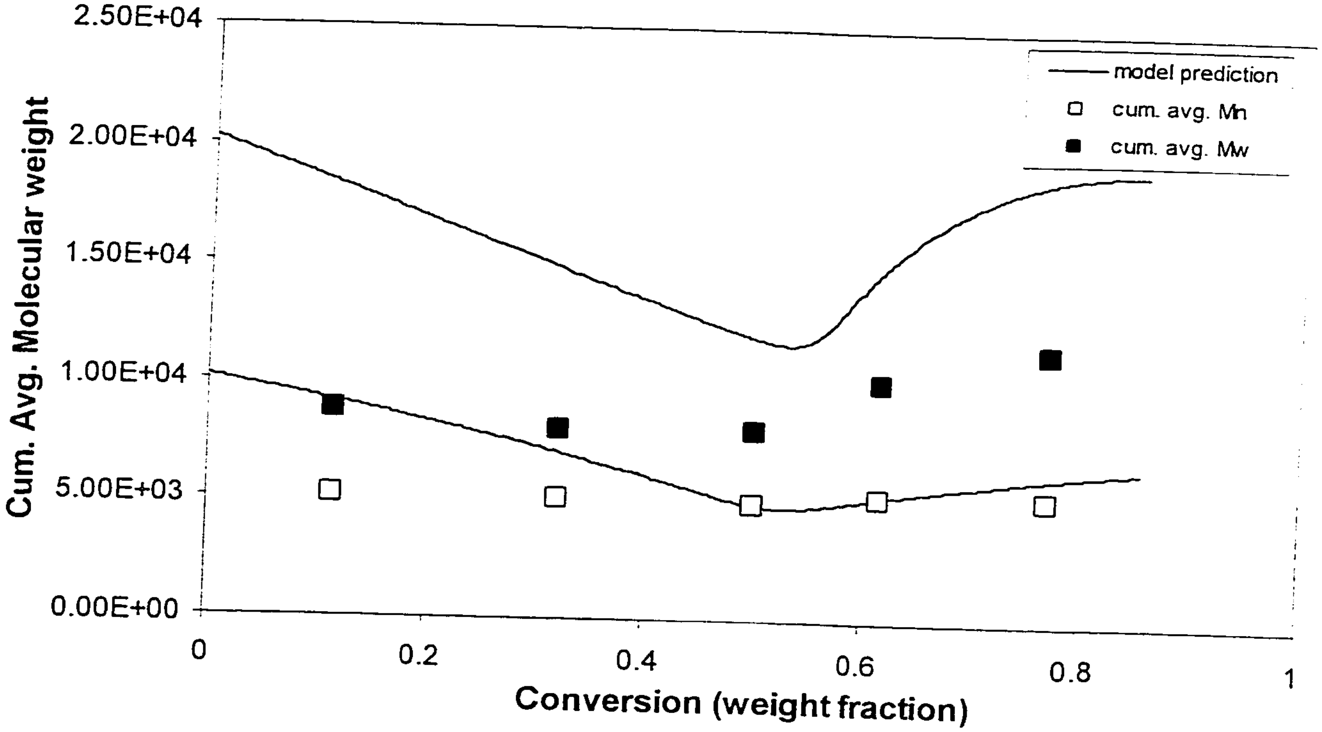


Figure 2.19: MMA/VAc solution copolymerization run MV2: cumulative number- and weight-average molecular weight vs. conversion

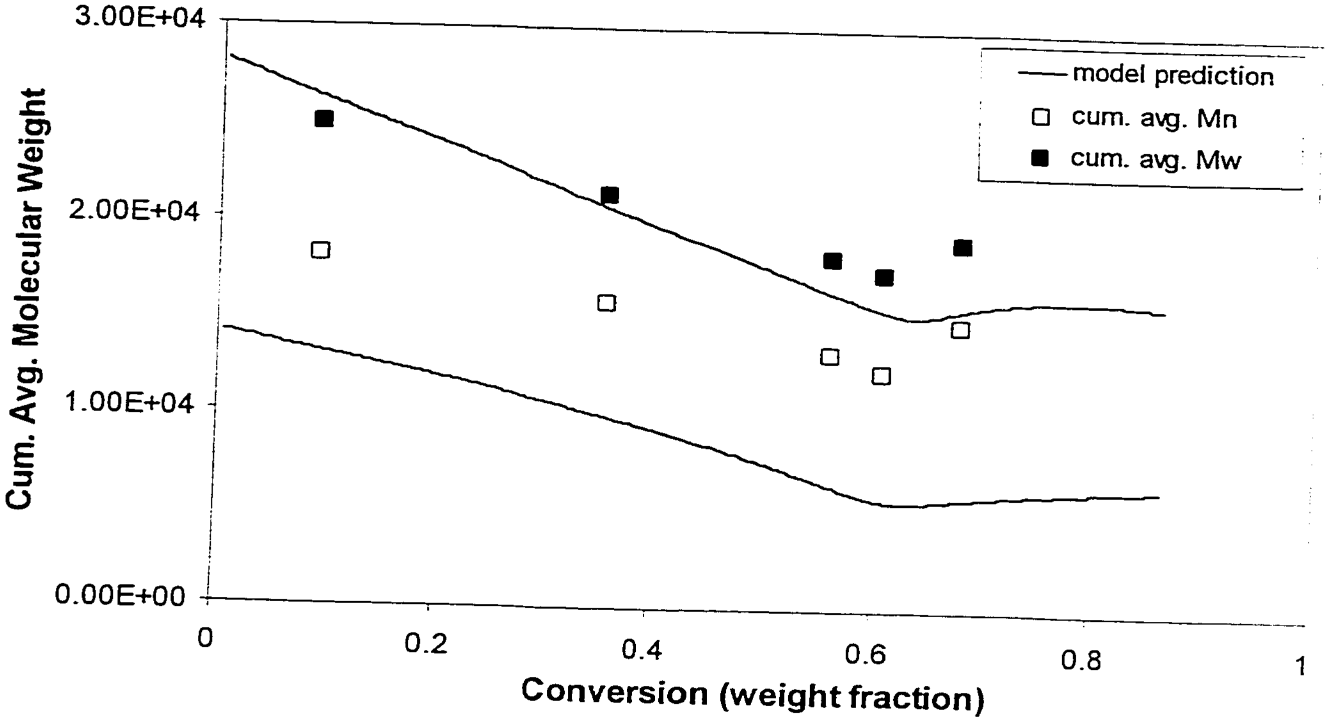


Figure 2.20: MMA/VAc solution copolymerization run MV3: cumulative number- and weight-average molecular weight vs. conversion

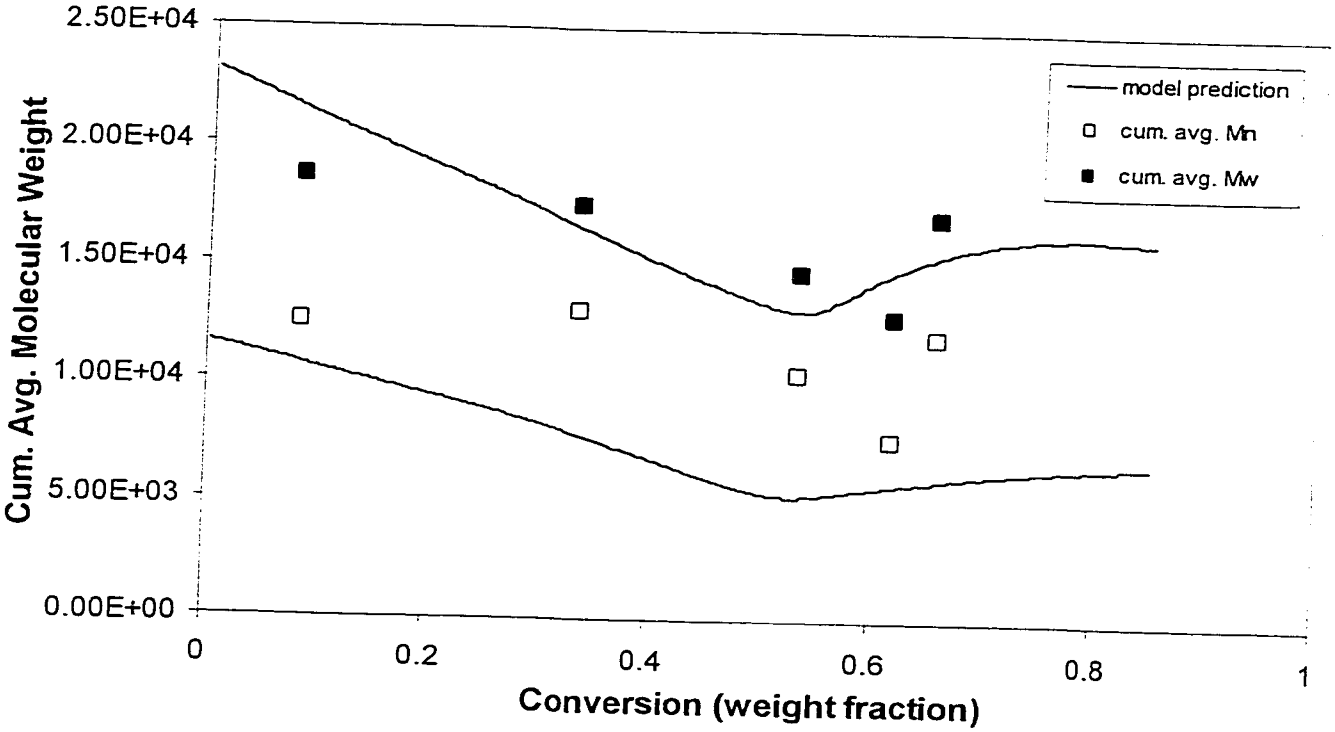


Figure 2.21: MMA/VAc solution copolymerization run MV4: cumulative number- and weight-average molecular weight vs. conversion

parameters for each system directly. Efforts are currently underway to improve the model predictions by investigating alternative models and improving parameters estimates in light of the effects of solvent.

Conclusions

The results obtained from off-line monitoring of BA, MMA, and VAc solution homo- and copolymerizations showed that ATR-FTIR spectroscopy is well suited for polymerization reaction monitoring and kinetic investigations. The data acquired through ATR-FTIR spectroscopy showed good agreement with data from conventional gravimetric and ^{1}H-NMR analysis.

A great deal of information on the characteristic absorbances of the monomers in this study was collected. This information can be used for further application of the ReactIR™ 1000 ATR-FTIR probe to study in-line solution and emulsion polymerization monitoring.

The incorporation of solvent effects on model parameters for BA and VAc resulted in improved predictions on conversion, copolymer composition and molecular weight averages. Predictions of MMA and BA/MMA solution polymerizations were in good agreement with the experimental results. Improvements to the model predictions for the MMA/VAc system at high conversion are the subject of future work.

These findings should have an impact on our ability to implement improved process control strategies on polymer systems that exhibit large composition drift.

Acknowledgements

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CHAPTER 3

(PAPER 2)

In-Line Monitoring of Emulsion Homo- and Copolymerizations Using ATR-FTIR Spectroscopy

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Abstract

An ATR-FTIR spectroscopy technique with light conduit and diamond-composite sensor was used to perform in-line monitoring of butyl acrylate, methyl methacrylate, and vinyl acetate batch emulsion homo- and copolymerizations. This technique was found to be ideal for determining individual monomer conversions and copolymer composition changes as a function of time when those polymerizations were carried out in aqueous media. The results obtained from the ReactIR™ 1000 reaction analysis system agreed well with those determined by traditional gravimetric and ^{1}H-NMR spectroscopy methods.

Keywords: butyl acrylate, methyl methacrylate, vinyl acetate, IR spectroscopy, emulsion polymerization, copolymerization kinetics, in-line monitoring

Introduction

The increasing demand for the efficient production of high quality polymers with prespecified properties and the improvement of plant operability and economics requires the development of robust sensors to carry out on-line measurements of the polymerization reaction evolution.[1,2] The task is often difficult due to the physical-chemical nature of the polymerization processes.

Due to their relatively low viscosity, emulsion polymerizations may be simpler to monitor than bulk and solution polymerizations. On-line gas chromatography (GC), on-line densimetry, and on-line calorimetric methods have all been used to monitor emulsion polymerizations.[3-6] Either the residual monomer content or the polymer content was measured on-line to estimate individual monomer conversions or copolymer composition. Careful calibration for each method was needed and occasional delays were observed between the sampling and the analysis responses. Sampling difficulties also arose from coagulation of the latex particles due to the thermodynamically unstable nature of latexes. Both on-line densimetry and calorimetry techniques had to be used coupled with conversion-composition prediction models to follow the reaction evolution in cases of copolymerizations, which might increase the errors in conversion estimates.

Compared to the techniques mentioned above, mid-infrared (MIR) spectroscopy has intriguing potential. The MIR range from 4000 to 400 cm^{-1} includes the frequencies corresponding to fundamental vibrations of almost all of the functional groups of organic molecules.[7] The spectral peaks in this region are typically narrow and distinctive, unlike peaks due to third overtone or combinations of the fundamental infrared bands in the near-infrared (NIR) region of 14,000 to 4,000 cm^{-1}, making it possible to identify and monitor the peak changes during a reaction. In-situ Fourier transform infrared (FTIR) spectroscopy can be used as a monitoring technique to obtain real-time structural and kinetic information on a polymerization process. In addition, it can be used to analyze polymerizations without expensive and complicated hardware and sampling techniques, and difficult experimental operations.

Recently, a number of authors have reported the use of on-line IR techniques to monitor polymerizations. He et al.[8] reported their use of a ReactIR™2000 reaction analysis system (ASI Applied Systems, Metter-Toledo Corp.) to monitor the consumption of isocyanate groups during an emulsion polymerization and latex film-formation process on attenuated total reflectance (ATR) FTIR germanium (Ge) discs. A well-fitted linear calibration relationship was obtained when the isocyanate concentration data from ATR-FTIR absorbances were compared to those from the titration method. Chatzi et al.[9] developed a technique using chalcogenide optical fibres to direct IR radiation from an MIR-FTIR spectrometer through an ATR immersion probe for the on-line monitoring of a 2-ethylhexyl acrylate/styrene emulsion copolymerization at the azeotropic composition. The probe was found capable of determining individual monomer conversions as well as copolymer composition from MIR spectra in aqueous media. Storey et al.[10] have reported the successful use of a ReactIR™1000 reaction analysis system to determine kinetics of the fast living cationic polymerization of isobutylene through in-situ, real-time reaction monitoring by utilizing MIR-FTIR spectroscopy.

More recently, we have reported the use of the ReactIR™1000 to monitor solution (in toluene) homo- and copolymerizations of monomers from the butyl acrylate/methyl methacrylate/vinyl acetate (BA/MMA/VAc) system.[11,12] The ReactIR™1000, using ATR-FTIR spectroscopy with a light conduit and DiComp (diamond composite) insertion probe was used off-line to monitor these polymerizations. Estimates of monomer conversion and copolymer composition were measured from the peak height changes of monomer IR characteristic absorbances during the reaction and showed good agreement with traditional gravimetric and ^{1}H-NMR spectrometry techniques.

BA/MMA/VAc terpolymers and their corresponding homo- and copolymers are commercially important components in many paints, adhesives and binders. Due to the widely differing monomer reactivity ratios in batch copolymerizations containing VAc, significant polymer composition drift is observed during the reaction[11-15]. One way to produce polymers with homogeneous properties in such systems involves the use of semi-batch policies to control the monomer feed coupled with on-line monitoring based on an analysis of the overall monomer concentrations.[16,17] Without the time lags and sampling difficulties present in many on-line techniques, ATR-FTIR spectroscopy has the potential to be suitable for implementing feedback control policies in polymerization processes.

In this work, the ReactIR™1000 reaction analysis system was used in-line to investigate its ability to estimate monomer conversions and polymer compositions from characteristic spectral changes. The term "in-line" in this context refers to a device that obtains the measurement directly in the process stream whereas the term "on-line" refers to a device for analysis that is connected to the process stream via a side-loop or sample thief.[18] It was applied to monitor the reaction kinetics of emulsion homopolymerizations of BA, MMA, and VAc and emulsion copolymerizations of BA/MMA and MMA/VAc conducted at 60°C in a pilot scale, stainless steel batch reactor. In order to evaluate the ability of the ATR-FTIR spectroscopic method, the kinetic data obtained through the IR in-line analysis were compared to results from traditional gravimetric and ^{1}H-NMR spectroscopy methods.

Experimental methods

Materials

Purification of reagents was performed by classical methods[13]. The monomers butyl acrylate and methyl methacrylate (Aldrich Chemical Co. Inc.) were washed three times with a 10% sodium hydroxide solution to remove the inhibitor and subsequently washed three times with distilled water. Calcium chloride ($CaCl_2$) was added to remove any residual water. The monomers were then freshly distilled under vacuum at most 24hrs before use. The monomer vinyl acetate (Aldrich Chemical Co. Inc.) was distilled under vacuum at most 24hrs before use. The first 20-50 ml of distillate were discarded (distillate bottoms). All purified monomers were stored at −10 °C when not in use.

Ammonium persulfate (APS) initiator and sodium dodecyl sulfate (SDS) anionic emulsifier were used in this study. Sodium bicarbonate ($NaHCO_3$) 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. All of the solvents used in these experiments and for characterization of the copolymers (ethanol, deuterated chloroform) were also used as packaged. Distilled-deionized (DDI) water was used in all polymerizations.

Instrumentation

Emulsion polymerizations were conducted in a jacketed 5L stainless steel pilot plant batch reactor. The reactor was equipped with a nitrogen purging/pressurizing line, sampling dip tube, initiator/inhibitor loading cells, monomer feed charging line, sampling line, and a port for the IR insertion probe. A reflux condenser equipped with a vent line was also used. A propeller turbine agitator with a variable speed motor was used to ensure good mixing.

The reactor setup also included a hot water bath connected to the reactor jacket, a refrigerated circulation bath connected to a stainless steel cooling coil within the reactor, and three type PR-13 platinum resistance thermometer (RTD) probes to detect the temperatures of polymerization, hot water inlet and coolant outlet, respectively. The reaction temperature was controlled using a cascade PID controller developed under the LabVIEW® environment.

A ReactIR™ 1000 reaction analysis system was used in-line to collect mid-FTIR spectra of the emulsion polymerization reactions. It was equipped with a light conduit and DiComp probe inserted into the reactor. These spectra were used to calculate monomer conversion and, for the case of copolymerization, polymer composition. Polymer compositions were also obtained through ^{1}H-NMR spectra taken by a Bruker AMX500 Fourier-transform ^{1}H-NMR spectrometer.

In conventional transmission IR spectroscopy, the intense absorption of water covers the major part of the normal analytical region, which makes it extremely difficult to record the MIR spectra of emulsion latexes. Figure 3.1a shows the spectrum of pure water with the IR absorption ranging from 4000 to 750 cm^{-1}. Even at relatively short path lengths, almost total absorption around 3400 and 1640 cm^{-1} can be observed and any absorption peaks due to the remaining emulsion latex contents will be very weak.[9] It is therefore challenging to monitor emulsion polymerizations in such cases.

Applying the principle of internal reflection spectroscopy, the ATR technique offers an advantage for analyzing strongly absorbing, i.e. low transmission materials including aqueous solutions. It is a contacting sampling method involving a crystal, used as an internal reflection element, with high refractive index and low IR absorption in the region of interest. When the IR beam enters the internal reflection element below an angle that exceeds the critical angle for total internal reflection, an evanescent wave is set up which penetrates a small distance beyond the crystal surface into space. A sample brought into intimate contact with the crystal can interact with the evanescent wave, absorb infrared radiation, and have its infrared spectrum detected. The evanescent wave is attenuated by the sample's absorbance. The depth of penetration in ATR, analogous to the idea of path length in transmission sampling techniques, can be designed as sample independent to be well suited to quantitative analysis.

Diamond and silicon can be used as ATR crystal elements. Because ATR crystals are impervious to water and due to the very short effective pathlength (penetration depth) in ATR, the water will not be totally absorbing and its absorbances can be effectively subtracted from sample spectra to obtain the spectra of monomer components in emulsion latexes. Figure 3.1b shows the spectrum of BA/MMA monomer mixture in emulsion. The spectrum is composed of the monomer peaks superimposed on the absorbance bands of water. After the water spectrum without monomer was recorded as a background, the spectrum of the BA/MMA monomer mixture in emulsion was automatically ratioed against the water background by the spectra manipulation software without any manual subtraction so that the spectrum of monomer was obtained as shown in Figure 3.1c. Compared to the spectrum of a pure BA/MMA monomer mixture shown in Figure 3.1d, this spectrum differed only in intensity.

Procedures

High conversion emulsion polymerizations of BA, MMA and VAc homopolymers and two copolymer pairs, BA/MMA and MMA/VAc, were run at 60°C. The polymerization recipes are shown in Table 3.1. The ingredients are listed in parts per hundred parts monomer (phm) with the total charge being up to 3L.

Table 3.1: Reaction conditions (all values in phm)

Ingredient	BA1	MMA1	VAc1	BM1	MV1
BA	100.00	-	-	56.14	-
MMA	-	100.0	-	43.86	53.76
VAc	-	-	100.0	-	46.24
DDI Water	200.00	200.0	200.0	200.00	200.00
APS	0.15	0.2	0.3	0.25	0.36
SDS	3.75	4.0	5.0	5.00	6.00
$NaHCO_3$	0.15	0.2	0.3	0.125	0.36

Predetermined amounts of SDS, $NaHCO_3$ and DDI water were first charged into the reactor. Then, the reactor was sealed and heated while under agitation and nitrogen purge. The IR probe was set up and immersed in the reaction mixture to record the spectra of the monomer-free emulsion as background. Next, monomers were pumped from a bottle to the reactor through a monomer loading line. N_2 purging was continued for about 15 minutes. When the temperature reached the prespecified level, the initiator solution in DDI water was deoxygenated, charged to the loading cell, and charged to the reactor. This corresponded to polymerization time t=0.

The standard reaction acquisition mode of the ReactIR™ 1000 was used to collect the IR spectra of the reaction mixture during the polymerization process at certain time intervals starting from the time of addition of the initiator (t=0). The data comprised spectra collected

Figure 3.1a: ATR-FTIR spectrum of pure water.

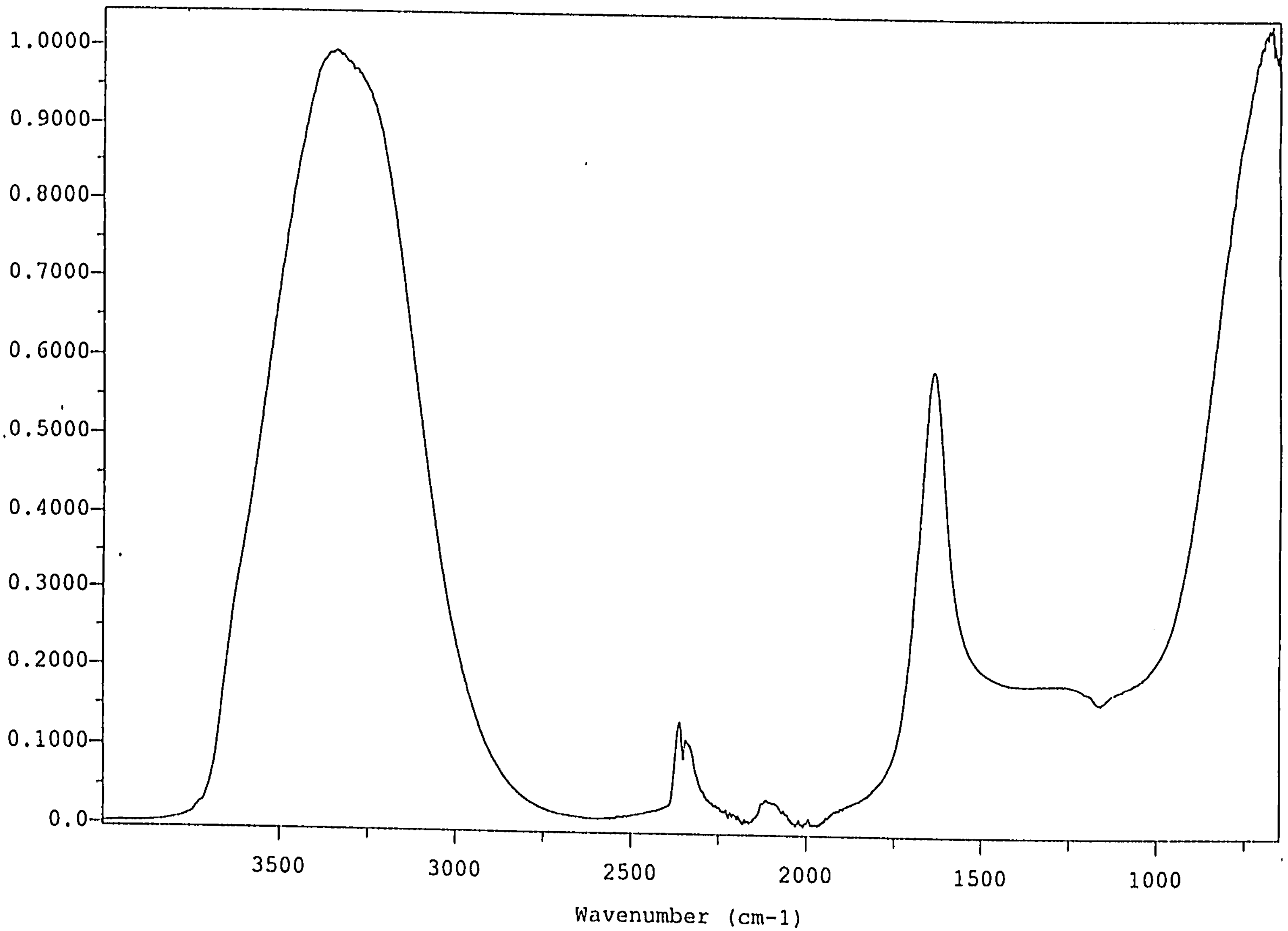


Figure 3.1b: ATR-FTIR spectrum of BA/MMA monomer mixture emulsion latex.

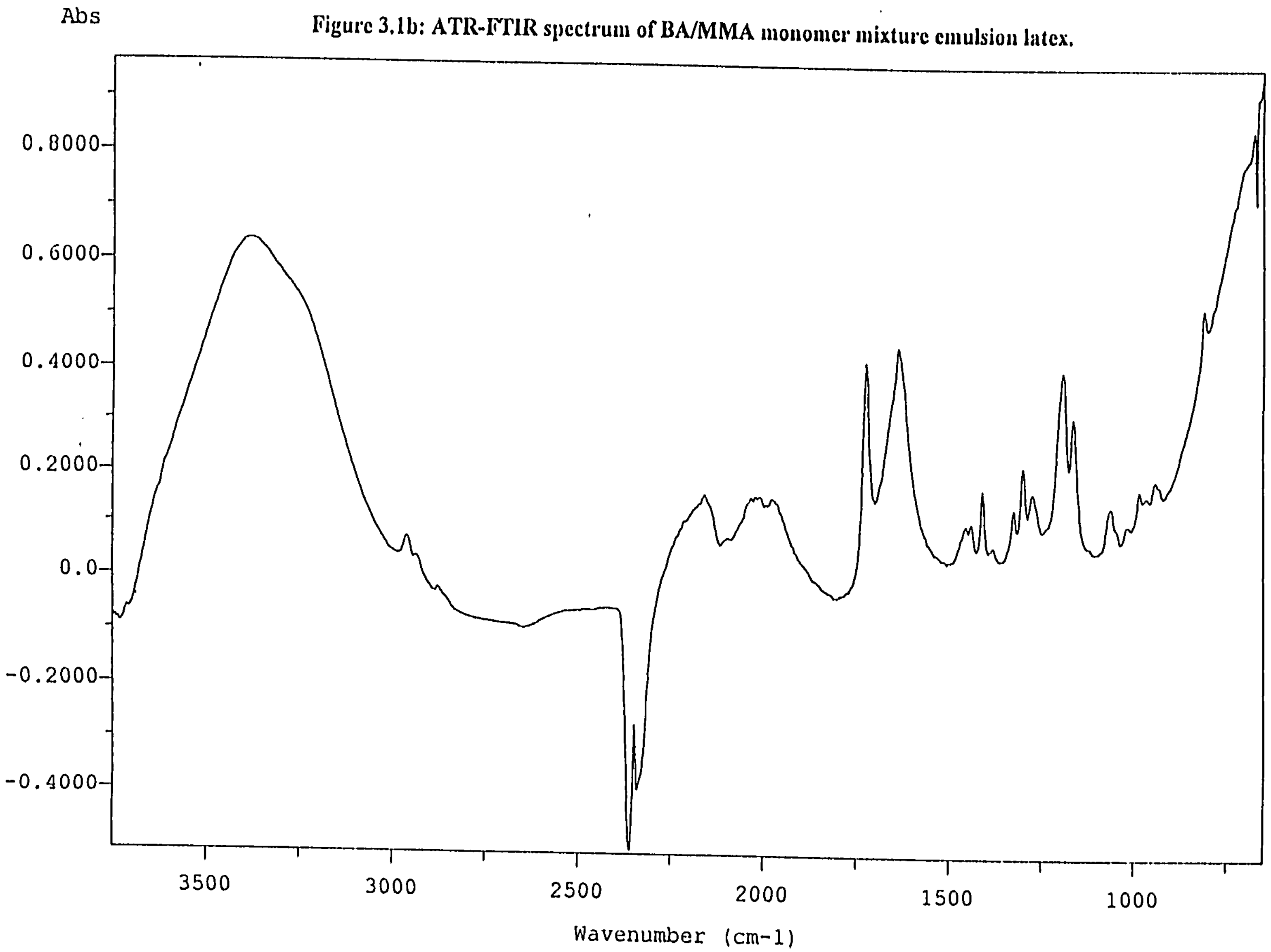


Figure 3.1c: ATR-FTIR spectrum of BA/MMA monomer mixture emulsion latex after ratioed against the water background spectrum.

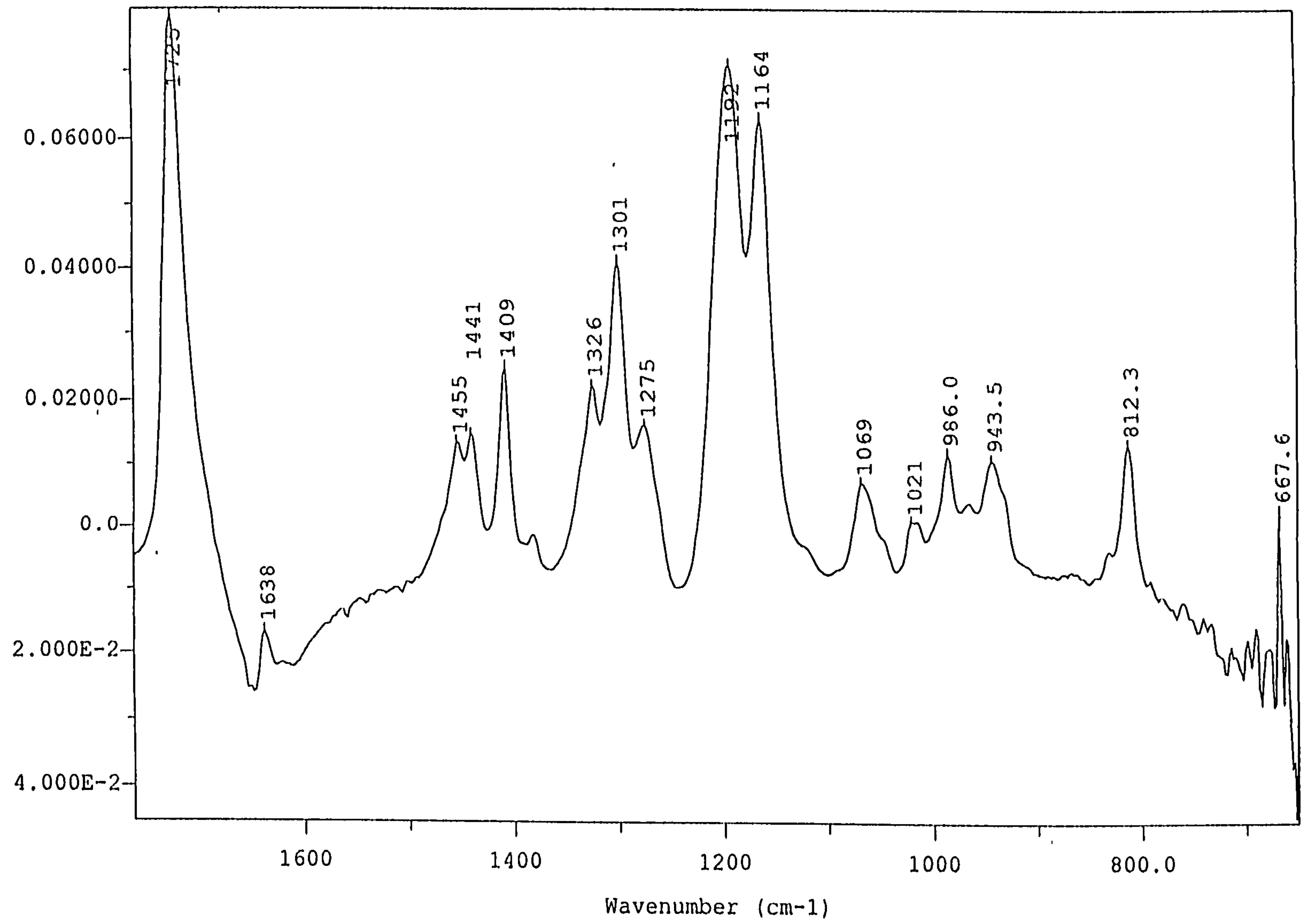
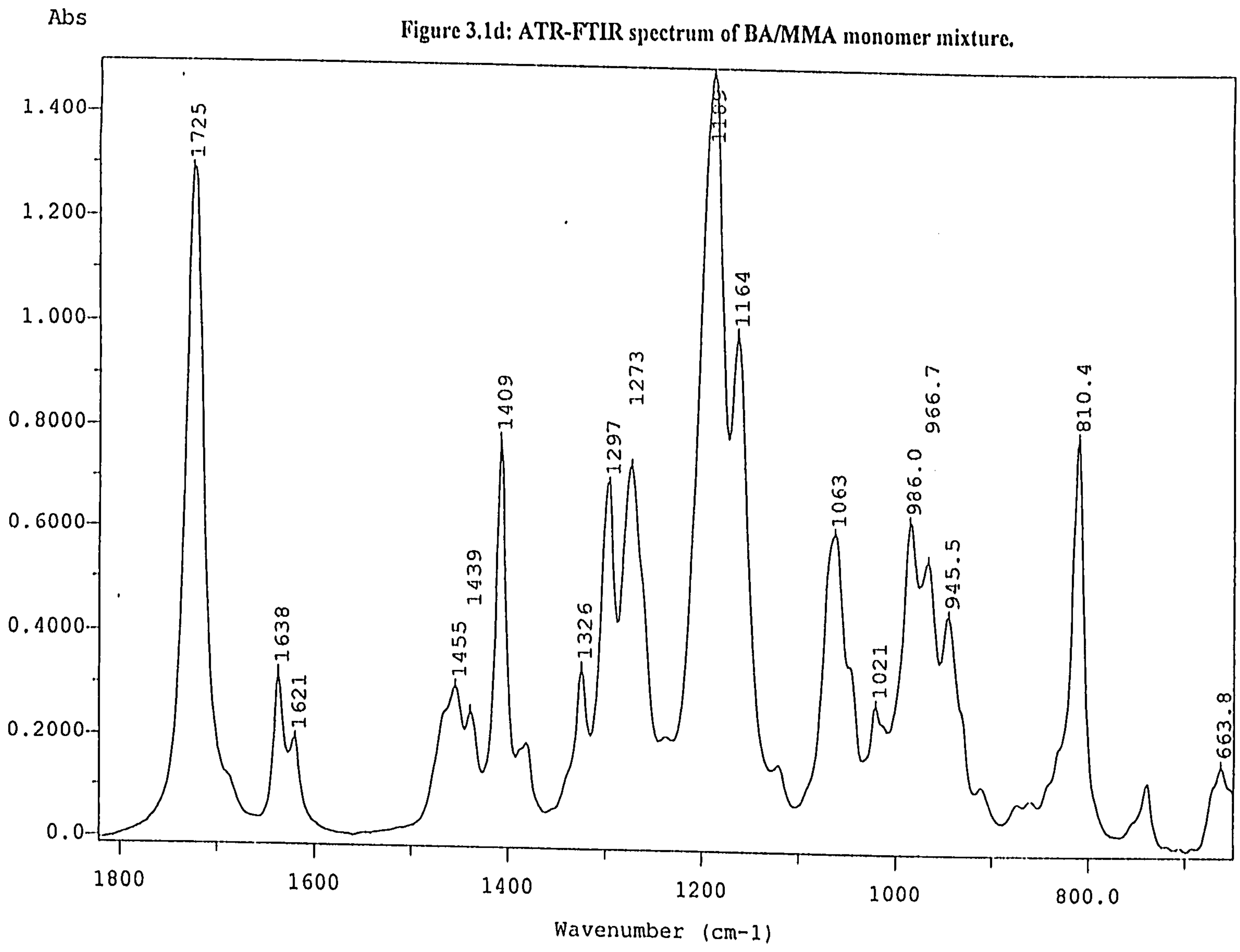


Figure 3.1d: ATR-FTIR spectrum of BA/MMA monomer mixture.



from 254 and 1022 scans, over the spectral ranges of 4000 – 700 cm^{-1}, with 4 cm^{-1} resolution. At 4 cm^{-1} resolution, the spectral acquisition times associated with those numbers of scans were approximately 84.7 and 340.7s, respectively. The spectra were recorded and further analyzed using the ReactIR™ (version 2.2) software.

Monomer conversion monitoring was accomplished by following the change of certain characteristic peaks in the MIR spectra during the polymerization process. It was assumed that the component concentrations were proportional to absorbances that could be measured as the corresponding peak heights. Equations 1 and 2, reported by Chatzi et al.,[9] were used to calculate the conversion, x, of individual monomers:

$$x(mol\%) = 1 - \frac{peak\ height\ at\ time\ t}{peak\ height\ at\ time\ t=0} \tag{1}$$

and the overall conversion, X, of the copolymerization:

$$X(wt\%) = \frac{w_i}{w_i + w_j} x_i(mol\%) + \frac{w_j}{w_i + w_j} x_j(mol\%) \tag{2}$$

where $w_i / (w_i + w_j)$ was the weight fraction of monomers i fed into the reactor at time t=0.

Typically, a resolution of 4 cm^{-1} is adequate for good peak resolution and high signal to noise ratio for most condensed phase samples such as polymer solutions. Using a higher resolution would give noisier spectra and extend the data acquisition time, while there would be no improvement in peak assignment and measurement accuracy compared to the lower resolution spectra.[19] If reaction kinetics are fast, the number of scans should be kept low in order to capture the reaction process. However, more scans would give spectra with a higher signal-to-noise ratio.

Samples were taken at various time intervals from the reactor for conventional analysis. The polymerization samples were quenched and mass conversion based on the total polymer in the sample was measured using gravimetry. In the case of copolymers, the resulting isolated polymers were analyzed for cumulative polymer composition by ^{1}H-NMR spectroscopy. Acquisition time was 4.6 seconds, and 16 scans were performed per readout (for averaging). Analysis was carried out at room temperature in deuterated chloroform (~2% (w/v) solutions), which was used as both the solvent and the reference. The relative amounts of monomer bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. All spectra exhibited good peak separations for a straightforward interpretation of the results. For BA/MMA copolymers, the spectral peaks for the $-OCH_2$ group in BA were located at ~4.0 ppm and those for the $-OCH_3$ group in MMA were at ~3.6 ppm. The MMA/VAc copolymers exhibited peaks for the α-hydrogen in VAc at ~4.9 ppm and the $-OCH_3$ group in MMA at ~3.6 ppm. The individual conversion profile for each monomer was obtained by combining results from the overall conversions through gravimetry and their corresponding mole fractions in the copolymer chain through ^{1}H-NMR spectroscopy.

Results and discussion

Data acquisition

ATR-FTIR spectroscopy was utilized to monitor several emulsion polymerization runs in real time. The assignment of the characteristic peaks of the monomers and corresponding polymers in BA/MMA/VAc solution homo- and copolymerizations were completed previously.[11,12] That information was helpful in identifying the components in the emulsion polymerizations performed in this study. Similar heuristics were used to choose characteristic absorbances for quantitative analysis. Absorbances such as those at 1409 cm^{-1} representing the CH deformation for BA, at 1326 cm^{-1} for the C-O-C stretching of MMA, and at 876 cm^{-1} for the $=CH_2$ wagging of VAc were found to be suitable to follow the polymerizations.

The ReactIR™ 1000 reaction analysis system is able to record spectra at a rate of approximately 3 scans/s at a resolution of 4 cm^{-1}. For reaction spectra acquired in standard mode, 1022 scans require 340.7s and 254 scans require 84.7s to complete. More scans would yield spectra with a higher signal-to-noise ratio. When using a higher number of scans, better signal-to-noise ratios were observed but the ability to monitor the polymerizations was compromised due to the relatively fast reaction kinetics.

One feature of the ReactIR™ software allows the user to display reaction profiles based on spectral changes at any time during a polymerization. These reaction profiles are updated with each acquired spectra. Data processing methods and sequences can be set prior to the reaction. By observing the reaction profiles, the experimenter may then terminate the polymerization if it is observed to have reached sufficient conversion, or to extend the reaction sequence to acquire additional spectra if it is observed to be incomplete.

During a batch emulsion polymerization process, volume shrinkage of the reactor contents may occur. These volume changes can lead to errors in the monomer conversion calculations based on the monomer concentrations in the reaction mixture monitored by ATR-FTIR. The ReactIR™ software provides a normalization macro to compensate for such volume changes during a reaction collection. This macro is based on the sum of squares of the absorbance values in the spectrum. The normalization macro was applied to all spectra of the emulsion polymerization runs and gave reasonable profiles of monomer conversion vs. time.

Homopolymerizations

Three batch emulsion homopolymerizations were conducted at 60°C. The recipes used are shown in Table 3.1 as runs BA1, MMA1, and VAc1. The normalized emulsion spectra in the wave number range of interest for those three runs are shown in Figures 3.2 through 3.4, respectively. The spectra were recorded at a resolution of 4 cm^{-1} with 254 scans for each spectrum.

For the BA1 run, the reaction mixture spectra were collected every 2 minutes for a total of 120 minutes. Distinct reaction mixture spectral changes as the consequence of the polymerization are shown in Figure 3.2. The characteristic peak at 1409 cm^{-1} for the BA hyperconjugated –CH deformation was observed to diminish as the reaction progressed. Figure 3.5 presents the time evolution of BA conversion determined by means of the in-line IR measurements and off-line gravimetric analysis during the run. According to Equation 1, BA monomer conversion was determined by calculating the absorbance of the 1409 cm^{-1} peak. The absorbance of the characteristic peak was measured as the peak height referred to a two-point baseline after baseline correction. The in-line estimates of the BA conversion agreed well with those from off-line gravimetric analysis as shown in Figure 3.5. The ATR-FTIR probe also correctly monitored a 40 minute induction period. The choice of 254 scans per spectrum appeared to be appropriate for the observed reaction rate.

For the MMA1 run, the spectra of the reaction contents were recorded every 2 minutes for a total of 90 minutes. Characteristic absorbance bands for MMA monomer were easily identified in the emulsion spectra such as the O-CH_3 stretching at 1015 cm^{-1}. As shown

Figure 3.2: ATR-FTIR spectra of BA emulsion polymerization run BA1.

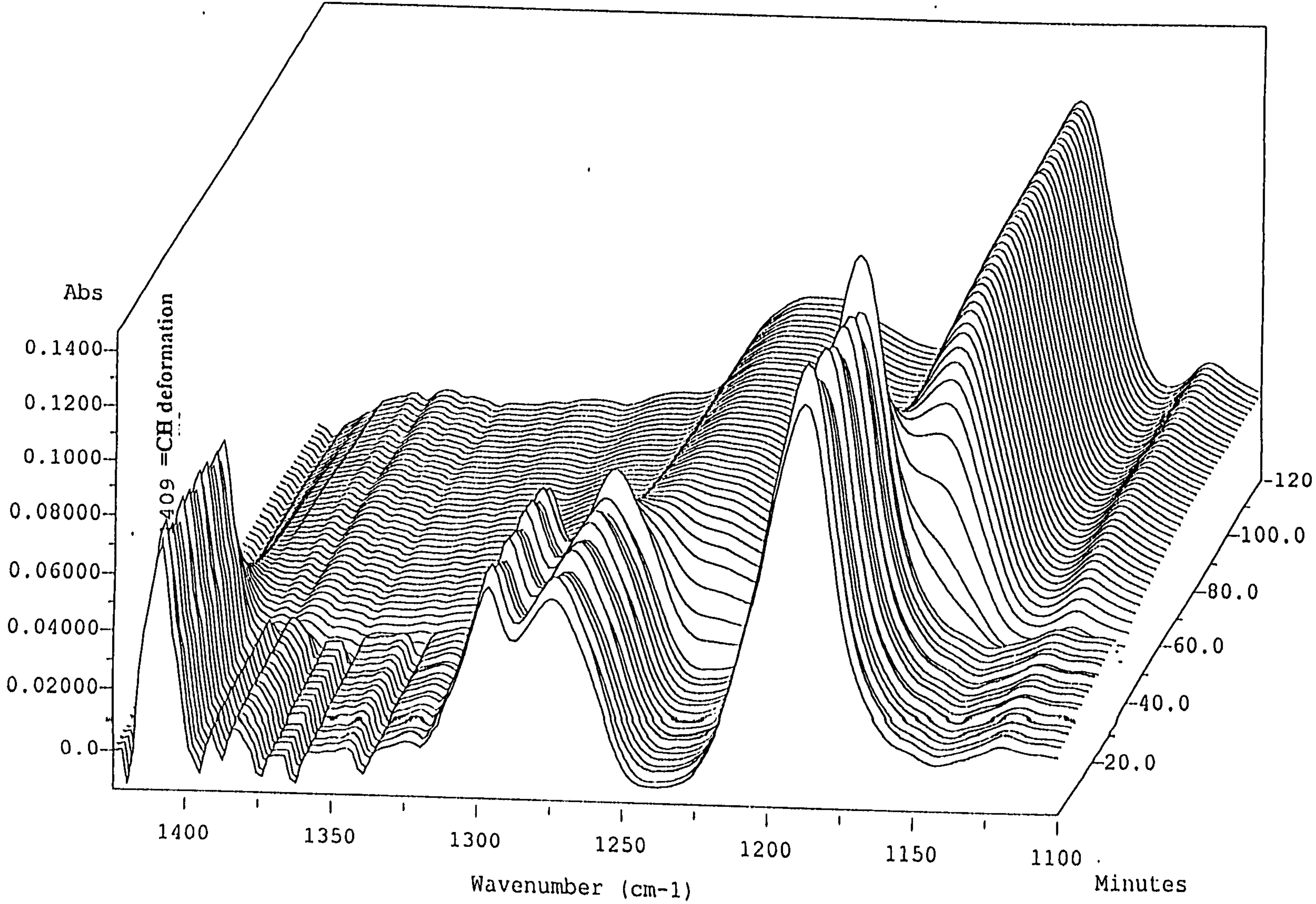


Figure 3.3: ATR-FTIR spectra of MMA emulsion polymerization run MMA1.

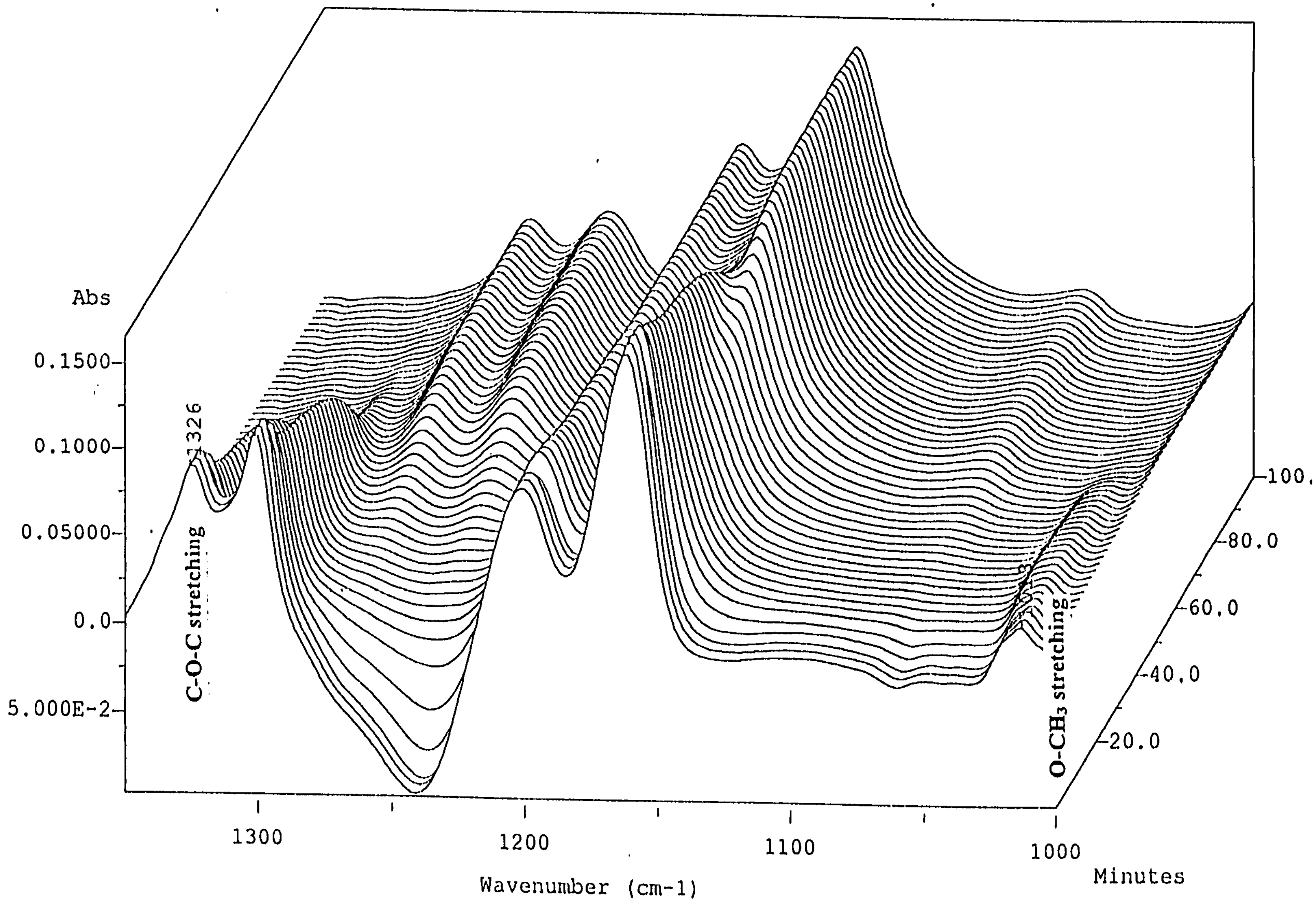
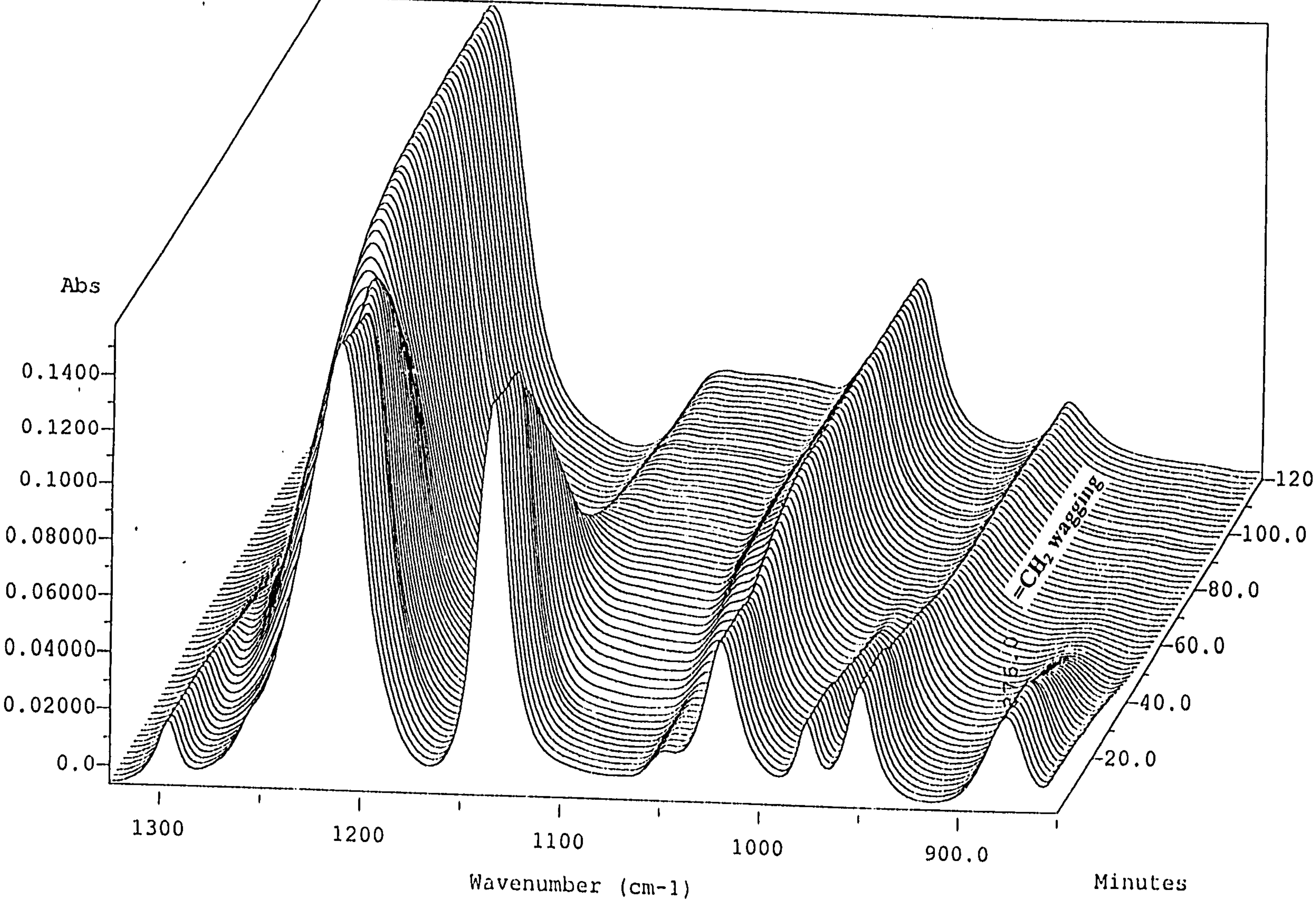


Figure 3.4: ATR-FTIR spectra of VAc emulsion polymerization run VAc1.



in Figure 3.3, these peaks diminished with increasing reaction time and did not overlap with the peaks from other reaction ingredients nor from the produced polymer. Characteristic peaks of C=C stretching at 1640 cm^{-1} and C=O wag at 652 cm^{-1}, which were used previously in a solution polymerization,[11] were not clearly observed in the emulsion spectra and could not be used for quantitative analysis. A quantitative estimate of the monomer conversion during the reaction was made by calculating the ratio of the absorbances of the 1015 cm^{-1} characteristic absorption bands at reaction time t to their corresponding peaks at the start of the polymerization reaction (t=0), according to equation 1. The absorbance of each peak was measured as the peak height referred to a two-point baseline after baseline correction. The monomer conversion estimated from the in-line IR spectra was compared with the conversion values obtained from conventional gravimetry measurements in Figure 3.6. Good agreement was observed between the obtained conversion-time curve based on the 1015 cm^{-1} peak and the values measured by gravimetry.

The reaction mixture spectra of the VAc1 run were collected every 2 minutes for a total of 150 minutes. The characteristic peak at the 876 cm^{-1} for VAc $=CH_2$ wagging was easily identified in the emulsion spectra. It diminished with increasing reaction time as shown in Figure 3.4. Figure 3.7 shows good agreement between the in-line IR spectral estimates and the values measured by conventional gravimetric measurements. The monomer conversion during the reaction was estimated by calculating the ratio of the absorbance of the 876 cm^{-1} characteristic absorption band at reaction time t to its corresponding peak at the start of the polymerization reaction (t=0), according to Equation 1. Previous analysis of error in the characteristic absorbance peak heights indicated that a precision of ±3 wt% conversion was

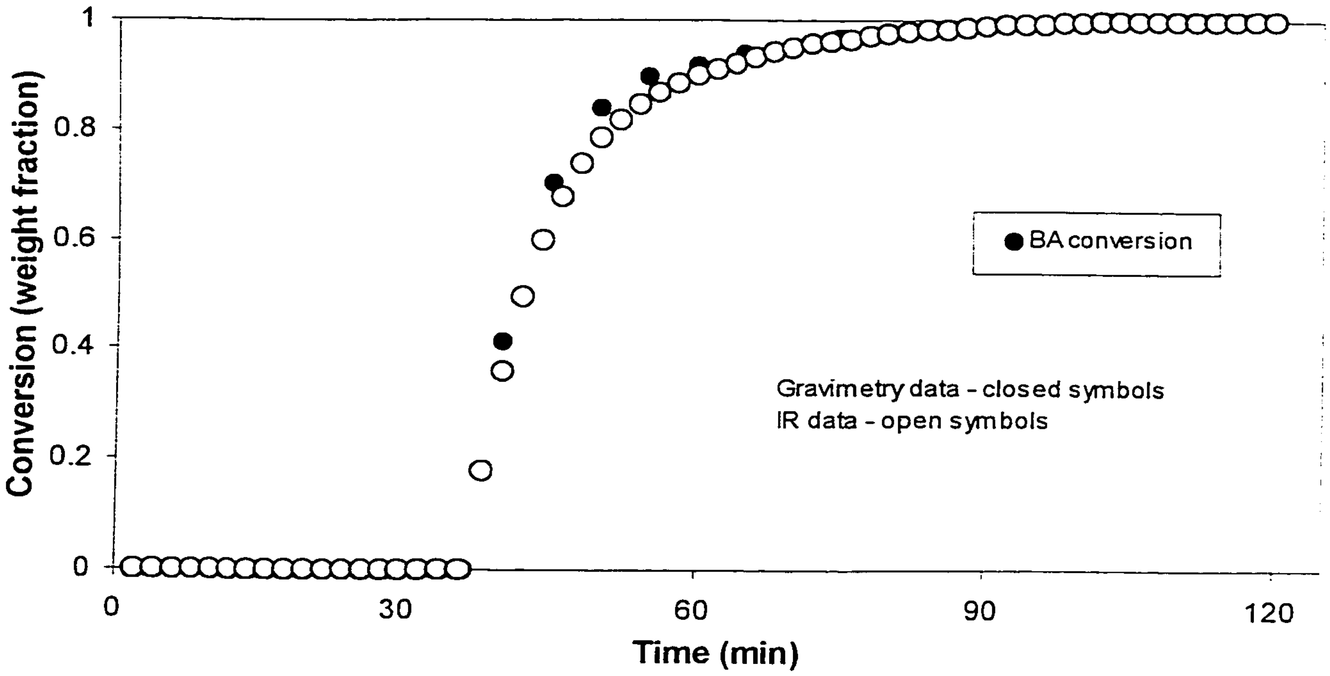


Figure 3.5: BA emulsion homopolymerization run BA1: conversion vs. time

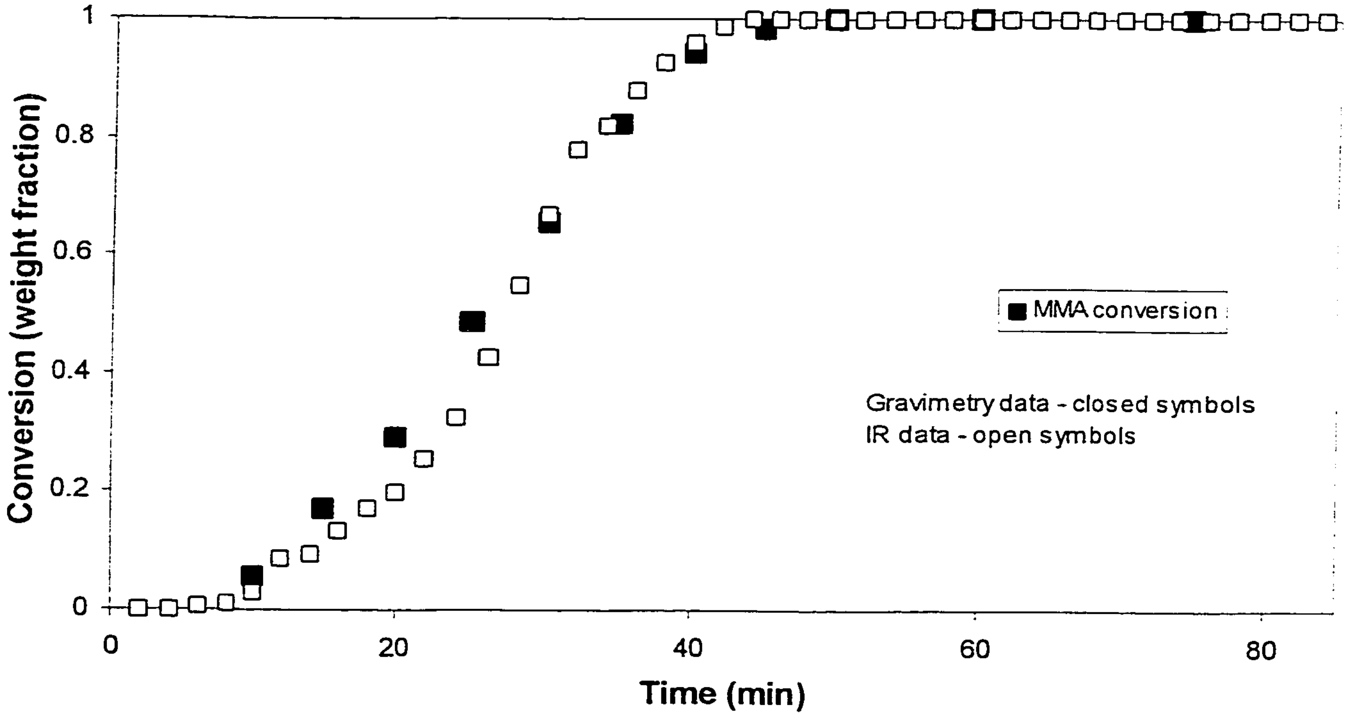


Figure 3.6: MMA emulsion homopolymerization run MMA1: conversion vs. time

expected with 95% confidence in solution runs. This analysis was also applied to emulsion runs and is indicated by the confidence intervals in Figure 3.7. These confidence intervals show that there is no significant difference between the IR and gravimetric data..

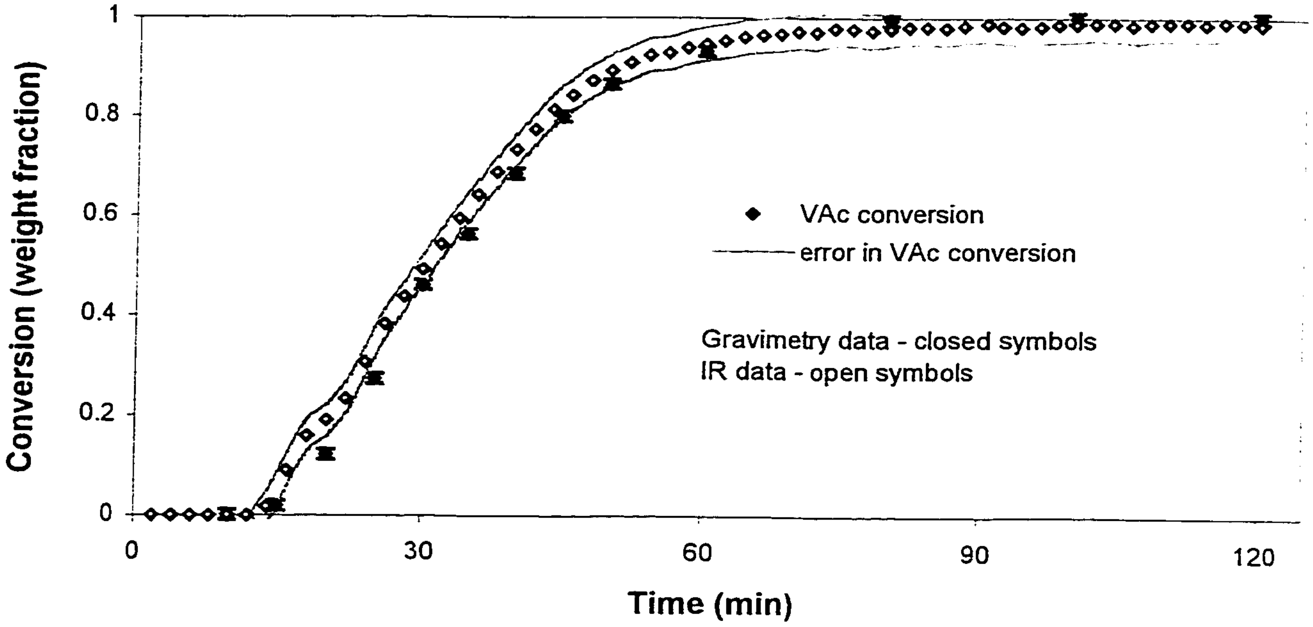


Figure 3.7: VAc emulsion homopolymerization run VAc1: conversion vs. time

Copolymerizations

BA/MMA and MMA/VAc emulsion copolymerization experiments were run at 60°C. The reaction ingredients are shown in Table 3.1 as runs BM1 and MV1, respectively. The spectra of these two polymerization reactions are shown in Figures 3.8 and 3.9, respectively. 254 scans were acquired for each spectrum at a resolution of 4 cm^{-1}.

For run BM1, reaction mixture spectra were collected every 2 minutes for a total of

Figure 3.8: ATR-FTIR spectra of BA/MMA emulsion copolymerization run BM1.

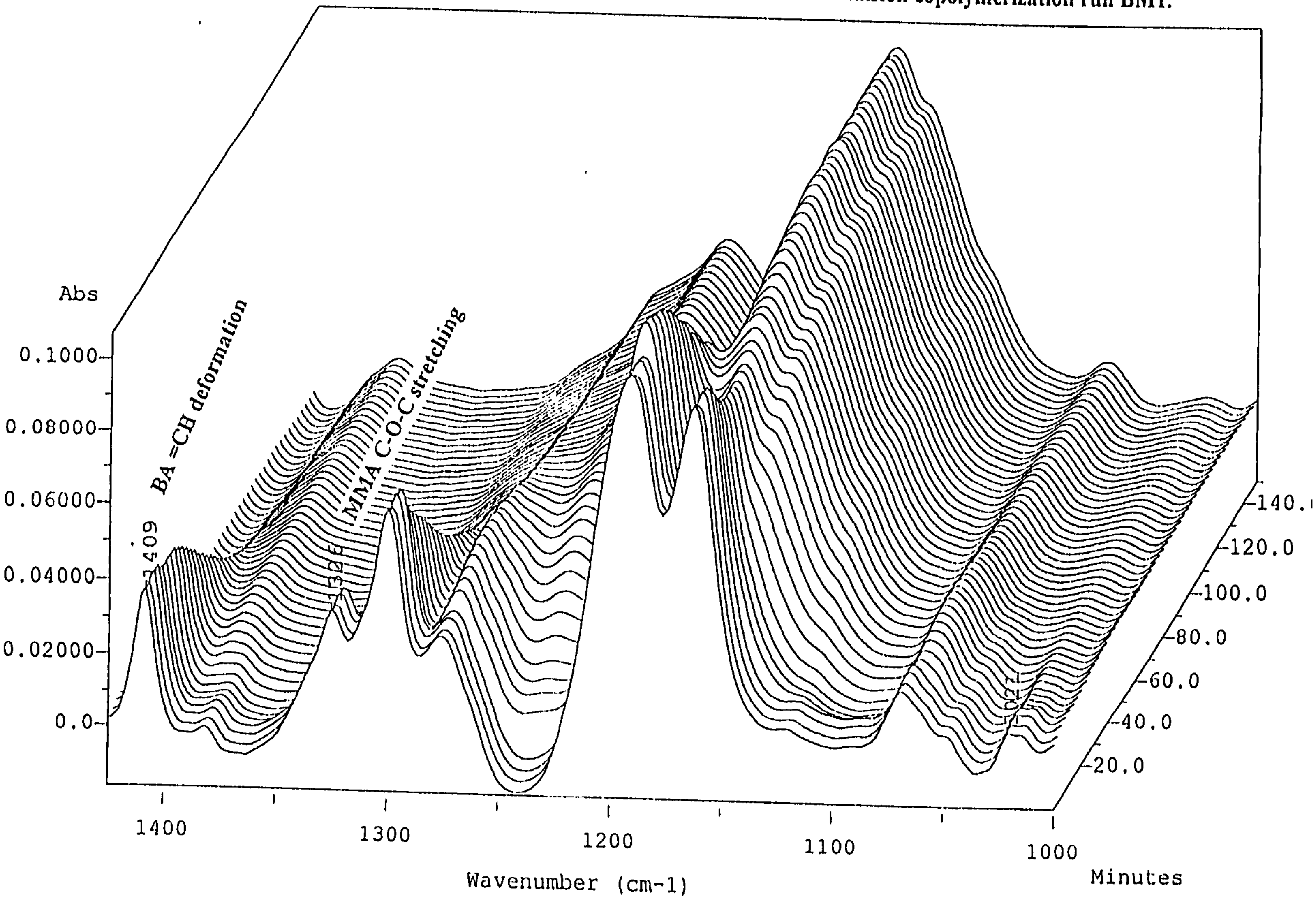
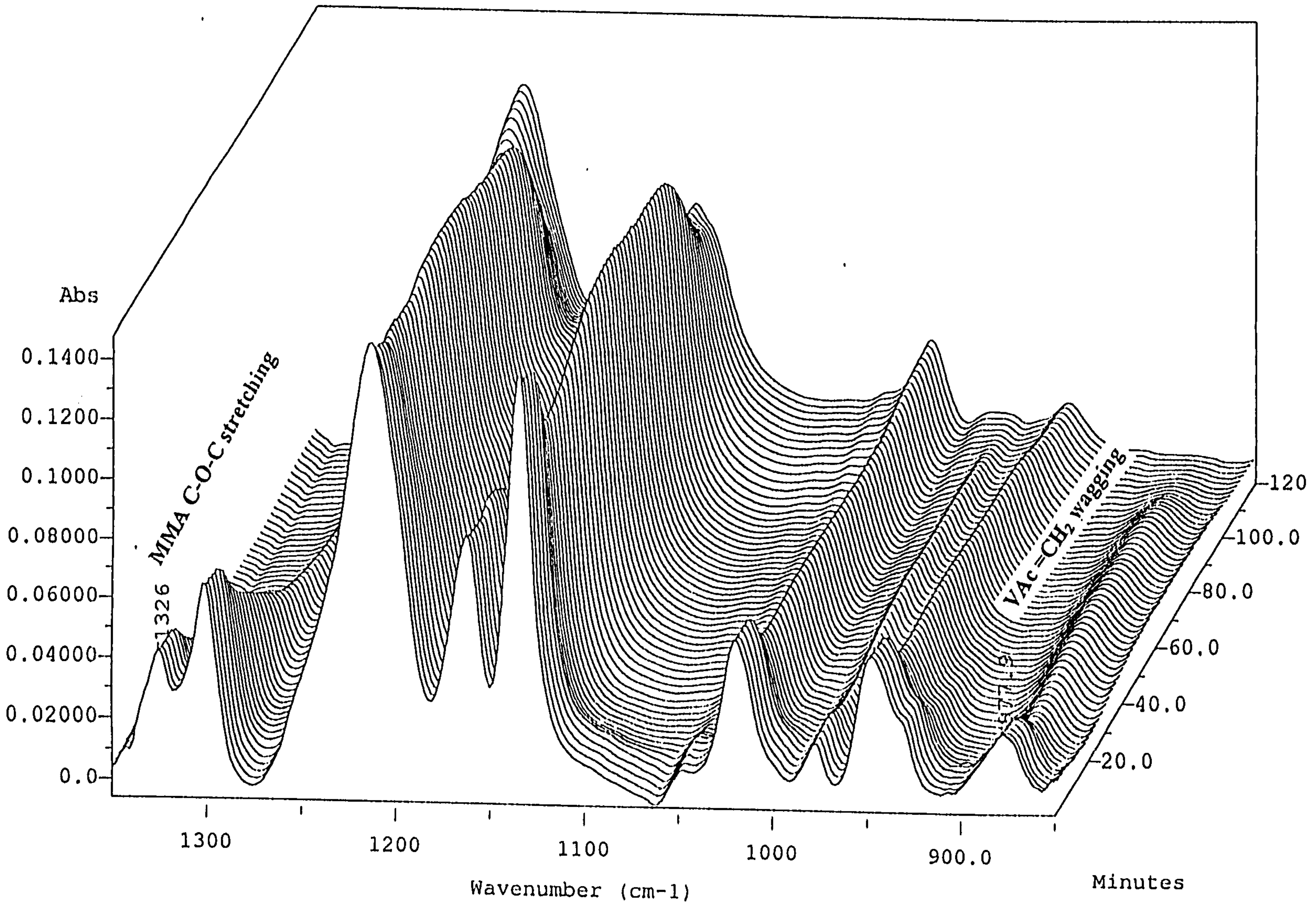


Figure 3.9: ATR-FTIR spectra of MMA/VAc emulsion copolymerization run MV1.



120 minutes. Distinct changes as the consequence of the polymerization reaction were observed in Figure 3.8 on characteristic absorbance bands of the two monomers at 1409 cm^{-1} for the BA hyperconjugated –CH deformation and at 1326 cm^{-1} for the MMA C-O-C stretching vibration of the aliphatic ester group, both of which diminished with increasing reaction time. These two peaks were used for tracking the reaction without any interference from the produced copolymer absorbances nor from the other reaction ingredients. For the MMA1 homopolymerization run, the MMA monomer conversion calculation based on the absorbance at 1015 cm^{-1} gave better results than the absorbance at 1326 cm^{-1}. However, in the case of the BA/MMA copolymerization, the peak at 1015 cm^{-1} for the MMA O-CH_3 stretching interfered with the absorbance at 1063 cm^{-1} from BA =CH_2 rock. The resulting peak shifted to 1021 cm^{-1} as can be seen in Figure 3.8.

The individual conversions of both monomers during the reaction were estimated similar to the previous homopolymerization runs by calculating the ratio of the absorbances (peak heights referred to a two-point baseline after baseline correction) of the 1409 and 1326 cm^{-1} characteristic absorption bands for BA and MMA, respectively, at reaction time t to their corresponding peaks at the start of the polymerization reaction (t=0), according to equation 1. The overall weight percentage conversion was subsequently calculated according to equation 2. Figure 3.10 shows good agreement of the overall and individual monomer conversion data obtained between traditional gravimetry and ^{1}H-NMR spectroscopy techniques and ATR-FTIR spectroscopy.

The composition data of the produced copolymers were calculated based on individual monomer conversions from IR measurements and are also shown in Figure 3.12. The data

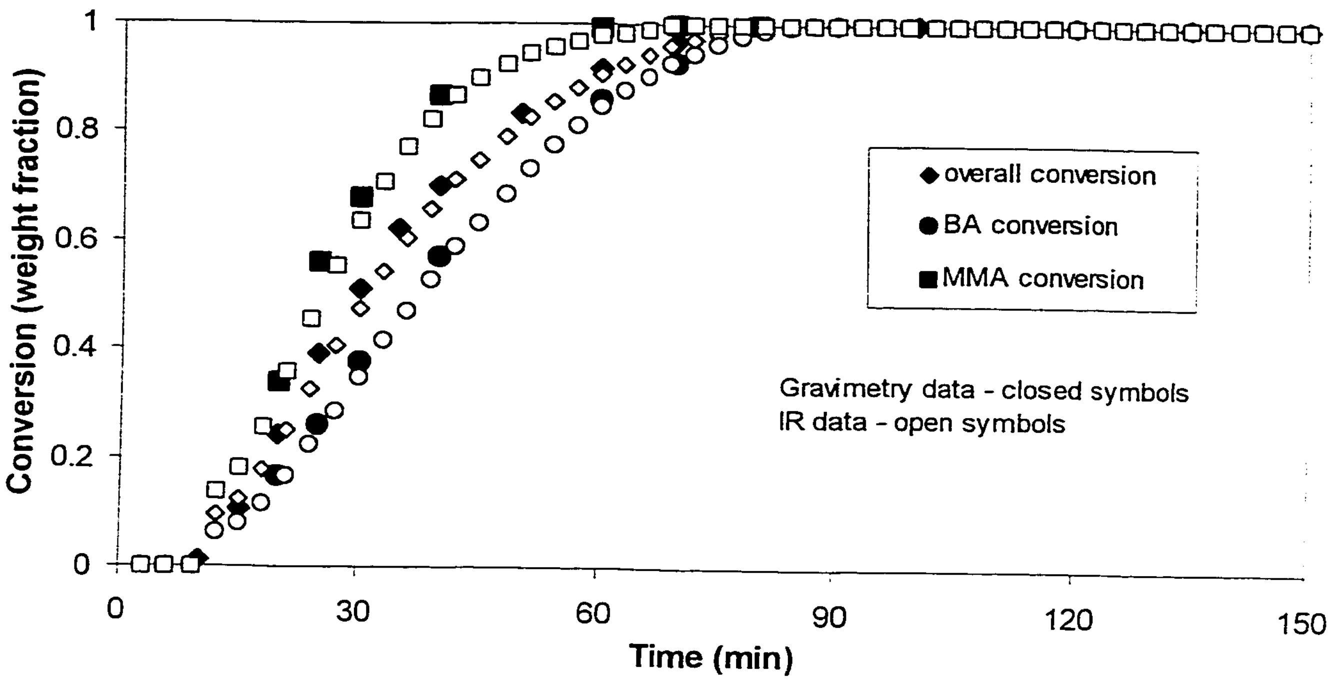


Figure 3.10: BA/MMA emulsion copolymerization run BM1: conversion vs. time

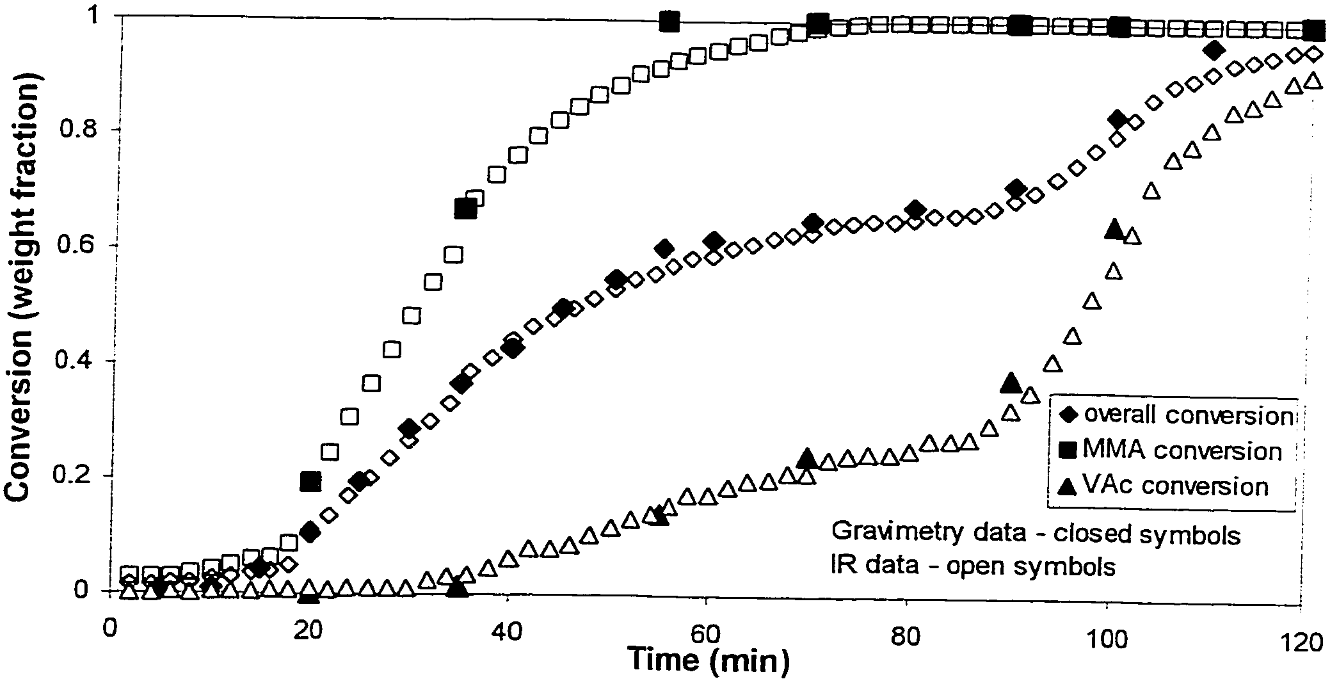


Figure 3.11: MMA/VAc emulsion copolymerization run MV1: conversion vs. time

agreed well with measurements from ^{1}H-NMR. The reactivity ratios for the BA/MMA monomer pair are $r_{BA} = 0.291$ and $r_{MMA} = 1.871$.[20] The difference of the reactivity ratios between those two monomers causes the slight composition drift that can be seen in Figure 3.12.

Reaction mixture spectra for the MMA/VAc emulsion copolymerization were collected every 3 minutes for a total of 150 minutes. 1022 scans were acquired for each spectrum at a resolution of 4 cm^{-1}. Figure 3.9 demonstrates the spectral changes as a consequence of the polymerization reaction. Characteristic absorbance bands for both monomers at 1326 cm^{-1} for the MMA C-O-C stretching vibration of the aliphatic ester group and at 877.9 cm^{-1} for the VAc $=CH_2$ wagging diminished with increasing reaction time.

The individual conversions of both the MMA and VAc monomers during the reaction were estimated in a way similar to that for the BA/MMA copolymerization. The overall weight percentage conversion was subsequently calculated according to Equation 2. Monomer conversion versus time data obtained from the different techniques is plotted in Figure 3.11. Good agreement was observed between the ATR-FTIR data and that from gravimetry and ^{1}H-NMR techniques. The evolution of the conversion exhibited a two-stage rate effect as noted by Dubé and Penlidis.[15] Because the reactivity ratios for this system are widely different ($r_{MMA} = 24.025$, $r_{VAc} = 0.0261$)[22], MMA was much more reactive than VAc and dominated the reaction up to about 50 wt% overall conversion. This corresponded to the MMA feed content of about 50 wt%. The resulting polymer was mostly composed of MMA while VAc reacted in small quantities relative to the dominant MMA monomer during this period and was mostly incorporated into the copolymer chains only after all of the MMA was depleted.

Cumulative copolymer composition data are plotted against conversion in Figure 3.13. It confirms the two-stage rate effect phenomenon revealed in the reaction evolution of the conversion vs. time plot. Significant copolymer composition drift was observed.

Conclusions

The results obtained from in-line monitoring of BA, MMA, and VAc batch emulsion homo- and copolymerizations demonstrate that ATR-FTIR spectroscopy with a light conduit and diamond-composite probe is well suited for polymerization reaction monitoring and kinetic investigations in aqueous media. The data acquired through ATR-FTIR spectroscopy showed good agreement with data from conventional gravimetric and ^{1}H-NMR analysis. The ReactIR™ 1000 ATR-FTIR probe can be used to record spectra for systems with relatively fast kinetics. Compared to many other on-line monitoring techniques, it overcomes the problem of time lags in taking samples and clogging of the sampling devices.

Previous work on the determination of characteristic absorbance assignments for both monomers and polymers was found to be helpful in the development of methods to apply this ATR-FTIR probe to in-line emulsion polymerization monitoring. This procedure will be applied further to studies of the terpolymerization of BA/MMA/VAc. That is, solution terpolymerization runs will be conducted first, characteristic IR absorbances will be identified and ATR-FTIR spectroscopy will be used to monitor the reaction off-line. Then, emulsion terpolymerizations will be conducted and the ATR-FTIR probe will be used to monitor the reaction kinetics in-line.

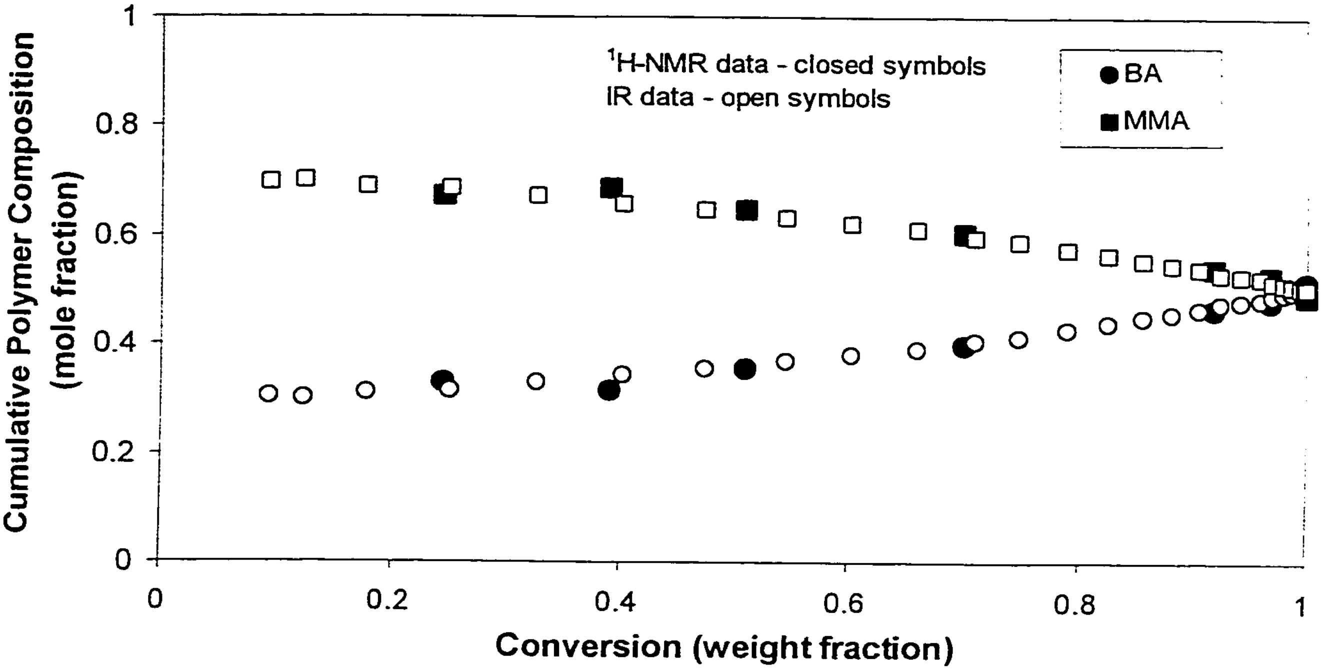


Figure 3.12: BA/MMA emulsion copolymerization run BM1: cumulative copolymer composition vs. conversion

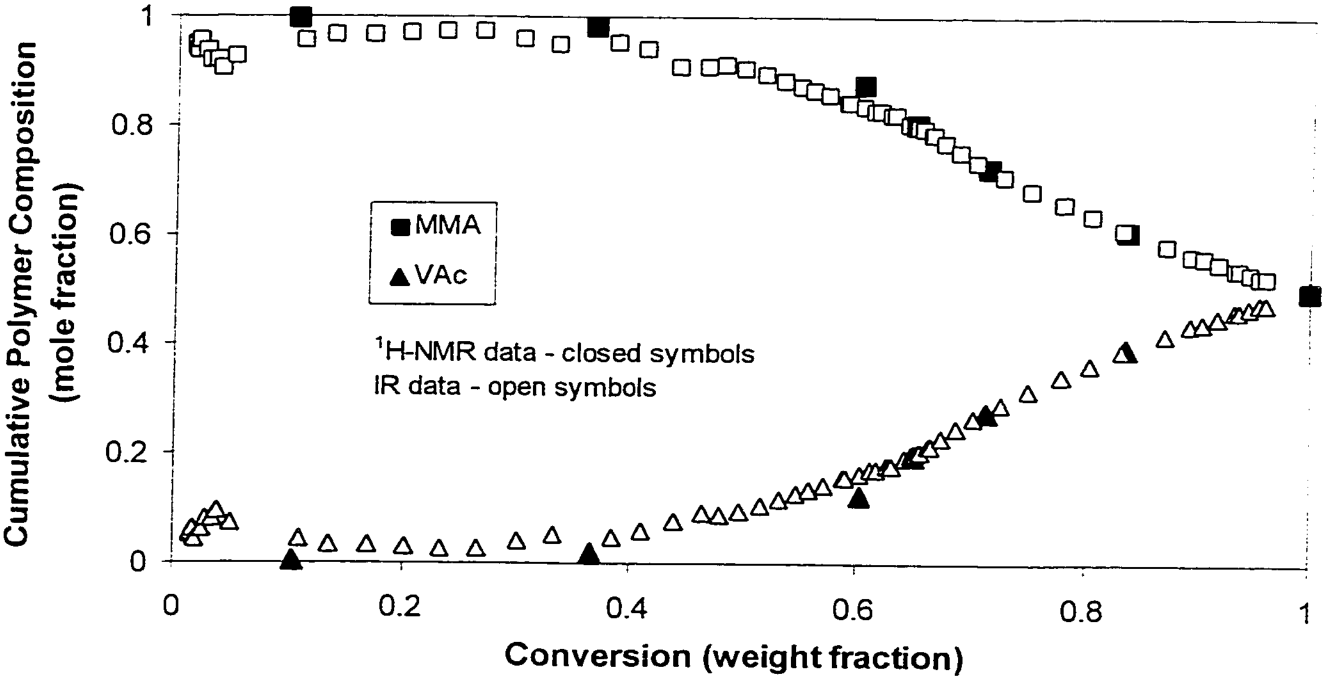


Figure 3.13: MMA/VAc emulsion copolymerization run MV1: cumulative copolymer composition vs. conversion

Significant composition drift was evident in the MMA/VAc copolymerization and heterogeneous copolymer was produced in the batch reactor. It is widely known that semi-batch reactions are needed to produce homogeneous MMA/VAc copolymers. This ATR-FTIR probe could be used as a polymerization monitoring tool in a semi-continuous process to implement improved process control strategies. This is especially important for systems prone to composition drift.

Acknowledgements

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CHAPTER 4

(PAPER 3)

Terpolymerization Monitoring Using ATR-FTIR Spectroscopy

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Abstract

Butyl acrylate, methyl methacrylate, and vinyl acetate solution and emulsion terpolymerizations were conducted. ATR-FTIR spectroscopy with conduit and diamond-composite sensor technology was used to monitor the solution terpolymerizations off-line and monitor the emulsion runs in-line. Monomer conversion and terpolymer composition changes as a function of time were calculated by monitoring the peak height of characteristic absorbances of monomers. Results obtained from the ReactIR™ 1000 reaction analysis system agreed well with those determined by traditional gravimetry and ^{1}H-NMR spectroscopy. For cases of solution terpolymerizations, improved models developed previously to incorporate solvent effects on solution polymerizations of butyl acrylate and vinyl acetate monomers were applied to predict monomer conversion, copolymer composition and molecular weight averages. Comparisons between experimental data and model predictions are also presented.

Keywords: butyl acrylate, methyl methacrylate, vinyl acetate, IR spectroscopy, solution polymerization, terpolymerization kinetics, toluene, emulsion polymerization, in-line monitoring

Introduction

Multicomponent polymerizations are important for the production of paints, adhesives, and coatings and have attracted interest from both industry and academia. Many of these products involve the polymerization of several monomers of widely different reactivity ratios that can lead to significant composition drift in the produced polymer. In order to produce tailored, high quality polymers and improve plant operability and economics, comprehensive methods to control polymer quality (in terms of polymer reactor operation and polymer property trajectory monitoring) during a polymerization are required to be developed.

Recent kinetic studies have been conducted on the batch bulk, solution and emulsion terpolymerizations of butyl acrylate/methyl methacrylate/vinyl acetate (BA/MMA/VAc) systems.[1-3] Significant polymer composition drift was observed during the process due to the widely differing reactivity ratios of the BA, MMA, and VAc monomers and hence, heterogeneous terpolymers were obtained. In such cases, semicontinuous processes may be used to overcome the composition drift problem. These semi-batch processes are usually coupled with some form of process monitoring in order to manipulate the monomer feed rates.

Leiza et al.[4] developed an automatic computer-controlled apparatus for on-line monitoring of conversion and polymer composition in emulsion polymerizations systems. The system is based on gas chromatograph (GC) measurements of the liquid reaction medium. This installation was able to monitor the semicontinuous emulsion terpolymerization of BA/MMA/VAc with high solids content latexes successfully with five minute time lags between samples. This apparatus was also used by Urretabizkaia et al.[5,6] to implement an open loop control scheme in the high solids content semicontinuous emulsion terpolymerizations of BA/MMA/VAc. They developed a method for the calculation of optimal monomer addition policies in semicontinuous emulsion terpolymerization processes for composition control purposes.

Recently, we have reported the use of the ReactIR™1000 to monitor solution (in toluene) homo- and copolymerizations of monomers from the BA/MMA/VAc system.[7,8] The ReactIR™1000 reaction analysis system, using ATR-FTIR spectroscopy with a light conduit and DiComp (diamond composite) insertion probe was used off-line to monitor these polymerizations. The characteristic absorbances of each monomer in toluene solution were assigned. Estimates of monomer conversion and copolymer composition were measured from the peak height changes of monomer IR characteristic absorbances during the reaction and showed good agreement with traditional gravimetric and ^{1}H-NMR spectrometry techniques.

The ReactIR™1000 reaction analysis system was also used in-line (the term "in-line" in this context refers to a device that obtains the measurement directly in the process stream whereas the term "on-line" refers to a device for analysis that is connected to the process stream via a side-loop or sample thief[9]) to monitor the reaction kinetics of emulsion homopolymerizations of BA, MMA, and VAc and emulsion copolymerizations of BA/MMA and MMA/VAc conducted in a pilot scale, stainless steel batch reactor.[10] Spectral measurements were obtained directly in the process stream without the need of sampling devices connected to the process stream for "on-line" analysis. The ATR-FTIR spectra of the reaction emulsion latexes were used to estimate monomer conversions and polymer compositions. The kinetic data obtained through the IR in-line analysis on characteristic spectral changes agreed well with results from traditional gravimetric and ^{1}H-NMR spectroscopy methods. Without the time lags and sampling difficulties present in many on-line techniques, ATR-FTIR spectroscopy has the potential to be quite suitable for the implementation of feedback control policies in polymerization processes.

In this work, the ReactIR™1000 reaction analysis system was applied to evaluate its ability to estimate monomer conversions and polymer compositions from characteristic spectral changes during terpolymerizations of BA/MMA/VAc. Similar to previous studies, BA/MMA/VAc terpolymerizations were first conducted in toluene solution initiated with 2,2'-azobisisobutyronitrile (AIBN) at 60°C. The ReactIR™1000 was used for off-line analysis of reaction mixture samples to identify characteristic peaks from the monomers to follow the terpolymerization reaction kinetics. Kinetic data obtained through IR analysis were compared to results from the traditional gravimetric and ^{1}H-NMR methods. Results were also compared to predictions from a mechanistic model. Next, several batch emulsion terpolymerizations of BA/MMA/VAc were run at 60°C in a pilot scale, stainless steel batch reactor. The probe was used in-line to record the spectra of the reaction contents. In order to evaluate the applicability of the ATR-FTIR spectroscopic method, the kinetic data obtained through the IR in-line analysis are presented and compared to results from traditional gravimetric and ^{1}H-NMR spectroscopy methods.

Experimental section

Materials

Purification of reagents was performed by classical methods.[1] The monomers butyl acrylate and methyl methacrylate (Aldrich Chemical Co. Inc.) were washed three times with a 10% sodium hydroxide solution to remove the inhibitor and subsequently washed three times with distilled water. Calcium chloride ($CaCl_2$) was added to remove any residual water. These monomers were freshly distilled under vacuum at most 24hrs before use. The monomer vinyl acetate (Aldrich Chemical Co. Inc.) was also distilled under vacuum at most 24hrs before use. The first 20-50 ml of distillate were discarded (distillate bottoms). All purified monomers were stored at -10 °C when not in use. The chain transfer agent 1-dodecanethiol (Acros Organics) was used as received. All of the solvents used in these experiments and for characterization of the terpolymers (toluene, ethanol, deuterated chloroform, tetrahydrofuran (THF)) were also used as packaged.

For the solution polymerization runs, 2,2'-azobisisobutyronitrile (Polysciences Inc.) (AIBN) was used as initiator. It was recrystallized three times from absolute methanol.

For the emulsion polymerization runs, ammonium persulfate (APS) was used as initiator and sodium dodecyl sulfate (SDS) was used as emulsifier. Sodium bicarbonate ($NaHCO_3$) 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 the emulsion polymerization runs.

Instrumentation

A ReactIR™ 1000 reaction analysis system equipped with a light conduit and DiComp (diamond composite) insertion probe was used to collect mid-FTIR spectra of the polymerization components. These spectra were used to calculate monomer conversions and terpolymer compositions. Resulting terpolymer compositions were also obtained through ^{1}H-NMR spectra taken by a Bruker AMX500 Fourier-transform ^{1}H-NMR spectrometer. 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, thermostated to 30°C, and a Waters 410 differential refractometer thermostated to 38°C. THF was used as the mobile phase and was delivered at 0.3 mL/min.

Emulsion polymerizations were conducted in a jacketed 5L stainless steel pilot plant batch reactor. The reactor was equipped with a nitrogen purging/pressurizing line, sampling dip tube, initiator/inhibitor loading cells, monomer feed charging line, sampling line, and a port for the IR insertion probe. A reflux condenser equipped with a vent line was also used. A propeller turbine agitator with a variable speed motor was used to ensure good mixing.

The reactor setup also included a hot water bath connected to the reactor jacket, a refrigerated circulation bath connected to a stainless steel cooling coil within the reactor, and three type PR-13 platinum resistance thermometer (RTD) probes to detect the temperatures of polymerization, hot water inlet and coolant outlet, respectively. The reaction temperature was controlled using a cascade PID controller developed under the LabVIEW® environment.

The ReactIR™ 1000 probe was inserted into the reactor and was used in-line to collect mid-FTIR spectra of the emulsion polymerization reactions for monomer conversion and terpolymer composition monitoring. As demonstrated in previous work,[10] applying the principle of internal reflection spectroscopy, the ATR-FTIR technique offers an advantage for analyzing strongly absorbing (i.e. low transmission) materials including samples in aqueous media. After the water spectrum without monomer was recorded as a background, the spectra of the emulsion latexes were automatically ratioed against the water background by the spectra manipulation software without any manual subtraction so that the spectra of the reaction mixture were obtained.

Solution polymerization experiments

High conversion solution terpolymerizations of BA/MMA/VAc were run at 60°C in a 50 wt% toluene solution. Further details of the reaction conditions are shown in Table 4.1.

Polymerizations were carried out in glass ampoules of length 20 cm and outer diameter 0.8 cm. The monomers and initiators, together with solvent and chain transfer agent (CTA), were weighed into a flask and an amount of about 2.7 mL was then pipetted into several numbered ampoules. Next, the ampoules were degassed through several vacuum freeze-thaw cycles and subsequently submerged in a water bath for a recorded time interval with the temperature controlled at 60°C. Two ampoules were taken out at the same time, one for traditional polymer analysis and the other for IR spectroscopy analysis, and submerged in liquid nitrogen to quench the reaction.

Table 4.1: BA/MMA/VAc solution terpolymerizations in 50 wt% toluene (all monomer values in weight fraction)

Ingredient	BMV1	BMV2	BMV3
BA	0.3	0.25	0.2
MMA	0.4	0.35	0.3
VAc	0.3	0.4	0.5
AIBN (mol/L)	0.1	0.1	0.1
CTA (mol/L)	0.025	0.025	0.025

For the traditional analysis, the contents of one ampoule were poured into a 10-fold excess of ethanol. Mass conversion based on the total polymer in the reaction mixture was measured using gravimetry. ^{1}H-NMR spectroscopy was used to determine the cumulative composition of the resulting isolated polymers. Analysis was carried out at room temperature in deuterated chloroform (~2% (w/v) solutions), which was used as both the solvent and the reference. Acquisition time was 4.6 seconds, and 16 scans were performed per readout (for averaging). The relative amounts of monomer bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. All spectra exhibited good peak separation for a straightforward interpretation of the results. BA/MMA/VAc terpolymers exhibited spectral peaks for the $-OCH_2$ group in BA at ~4.0 ppm, for the $-OCH_3$ group in MMA at ~3.6 ppm, and for the α-hydrogen in VAc at ~4.9 ppm. The individual conversion profiles for each monomer were obtained by combining results from the overall conversions through gravimetry and their corresponding mole fractions in the terpolymer chains through ^{1}H–NMR spectroscopy.

The resulting polymer molecular-weight averages and molecular-weight distributions were determined by GPC. THF (HPLC grade) was used as the carrier fluid and 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 μm filters to remove any high molecular weight gel. 200μL 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 shown in Table 4.2. K and α values for the terpolymers were obtained using weighted averages based on the cumulative terpolymer composition data.

Table 4.2: Mark-Houwink parameters

Polymer	K (× 10^3 mL/g)	α
Polystyrene[11]	16	0.700
Polybutyl acrylate[12]	11	0.708
Polymethyl methacrylate[11]	12.8	0.690
Polyvinyl acetate[13]	15.6	0.708

The contents in each duplicate ampoule were poured into 5-dram vials and were analyzed using the ATR-FTIR insertion probe. The standard acquisition mode of the ReactIR™ 1000 was used to collect the IR spectra. The ATR-FTIR data comprised spectra collected from 128 scans, over the spectral ranges of 4000 – 700 cm^{-1}, at 4 cm^{-1} resolution. The spectral acquisition time associated with this number of scans was approximately 42.7s. The insertion probe was put into the vial to record the spectra of the polymerization contents. The spectra were recorded and further analyzed using the ReactIR™ (version 2.2) software.

Monomer conversion monitoring was accomplished by following the change of certain characteristic peaks in the MIR spectra during the polymerization process. It was assumed that the component concentrations were proportional to absorbances that could be measured as the corresponding peak heights. Equations 1 and 2, reported by Chatzi et al.,[14] were used to calculate the conversion, x, of individual monomers:

$$x(mol\%) = 1 - \frac{peak\ height\ at\ time\ t}{peak\ height\ at\ time\ t = 0} \tag{1}$$

and the overall conversion, X, of the copolymerization:

$$X(wt\%) = \frac{w_i}{w_i + w_j} x_i(mol\%) + \frac{w_j}{w_i + w_j} x_j(mol\%) \tag{2}$$

where $w_i/(w_i + w_j)$ was the weight fraction of monomers i fed into the reactor at time t=0.

Typically, a resolution of 4 to 8 cm^{-1} is adequate for good peak resolution and high signal to noise ratio for most condensed phase samples such as polymer solutions. Using a higher resolution would give noisier spectra and extend the data acquisition time, while there would be no improvement in peak assignment and measurement accuracy compared to the lower resolution spectra.[15] If reaction kinetics are fast, the number of scans should be kept low in order to capture the reaction process. However, more scans would give a spectrum with a higher signal-to-noise ratio.

Emulsion polymerization experiments

High conversion emulsion terpolymerizations of BA/MMA/VAc were run at 60°C. The polymerization recipes are shown in Table 4.3. The ingredients are listed in parts per hundred parts monomer (phm) with the total charge being up to 3L.

Table 4.3: BA/MMA/VAc emulsion terpolymerizations (all values in phm)

Ingredient	BMV4	BMV5	BMV6
BA	30.00	25.00	20.00
MMA	40.00	35.00	30.00
VAc	30.00	40.00	50.00
DDI Water	180.00	180.00	180.00
APS	0.40	0.40	0.40
SDS	6.0	6.0	6.0
$NaHCO_3$	0.40	0.40	0.40
CTA	1.0994	1.0982	1.10

Predetermined amounts of SDS, $NaHCO_3$ and DDI water were first charged into the reactor. Then, the reactor was sealed and heated while under agitation and nitrogen purge. The IR probe was set up and immersed in the reaction mixture to record the spectra of the monomer-free emulsion as background. Next, monomers were pumped from a bottle to the reactor through a monomer loading line. N_2 purging was continued for about 15 minutes. When the temperature reached the prespecified level, the initiator solution in DDI water was deoxygenated, charged to the loading cell, and charged to the reactor. This corresponded to the polymerization time t=0.

The standard reaction acquisition mode of the ReactIR™ 1000 was used to collect the IR spectra of the reaction mixture in-line during the polymerization process at certain time intervals starting from the time of addition of the initiator (t=0). The data comprised spectra collected from 254 scans, over the spectral ranges of 4000 – 700 cm^{-1}, with 4 cm^{-1} resolution. At 4 cm^{-1} resolution, the spectral acquisition time associated with 254 scans was approximately 84.7s. The spectra were recorded and further analyzed using the ReactIR™ (version 2.2) software. As verified previously,[10] the resolution and the number of scans chosen here were adequate for good peak resolution and to monitor the reaction process.

Monomer conversion monitoring was accomplished by following the change of certain characteristic peaks in the MIR spectra during the polymerization process. It was assumed that the component concentrations were proportional to absorbances that could be measured as the corresponding peak heights. The calculations based on Equations 1 and 2 were used in the same way as for the solution runs.

Samples were taken at various time intervals from the reactor for conventional analysis. The polymerization samples were quenched first and mass conversion based on the total polymer in the sample was measured using gravimetry. ^{1}H-NMR spectroscopy was used to determine the mole fractions of each monomer in the terpolymer chains. Thus, the individual conversion profile for each monomer was obtained by combining results from the overall conversion through gravimetry with results from ^{1}H-NMR spectroscopy.

Results and discussion

Solution polymerizations

The ReactIR™ 1000 reaction analysis system was utilized to perform off-line monitoring of three solution terpolymerization runs. In previous studies, characteristic peaks were assigned for the monomers and their corresponding polymers in BA/MMA/VAc solution homo- and copolymerizations.[7,8] That information was helpful in identifying the components in the solution terpolymerizations performed in this study. An FTIR spectrum of a solution terpolymerization will include absorbances of three kinds of monomers, the produced polymer, and solvent. This can be more complicated than a spectrum for the case of solution homo- or copolymerization. Careful assignment should be made on absorbances from different components in the reaction mixture such that absorbance bands from different monomers chosen for quantitative analysis should not overlap with each other.

The solvent absorbance may interfere with the quantitative analysis of monomer and polymer absorbances if it overlaps with them. One way to solve this problem is to subtract the solvent spectrum to show the pure component spectrum of the reaction mixture. This manipulation may introduce error to the quantitative analysis. Therefore, a spectral region without solvent absorbance interference should be chosen for quantitative analysis to render the spectral subtraction unnecessary.

Figures 4.1a through 4.1d shows the spectra of pure BA, MMA, VAc and toluene. Based on similar heuristics for choosing characteristic absorbances for quantitative analysis in cases of solution copolymerizations, absorbances such as those at 1409 cm^{-1} representing the CH deformation for BA, at 1326 cm^{-1} for the C-O-C stretching of MMA, and at 876 cm^{-1} for the $=CH_2$ wagging of VAc were found suitable to follow the solution terpolymerizations.

Three BA/MMA/VAc solution terpolymerization runs were conducted in 50 wt% toluene and are described in Table 4.1 as runs BMV1 through BMV3. Figure 4.2 shows

Figure 4.1a: ATR-FTIR spectrum of butyl acrylate monomer.

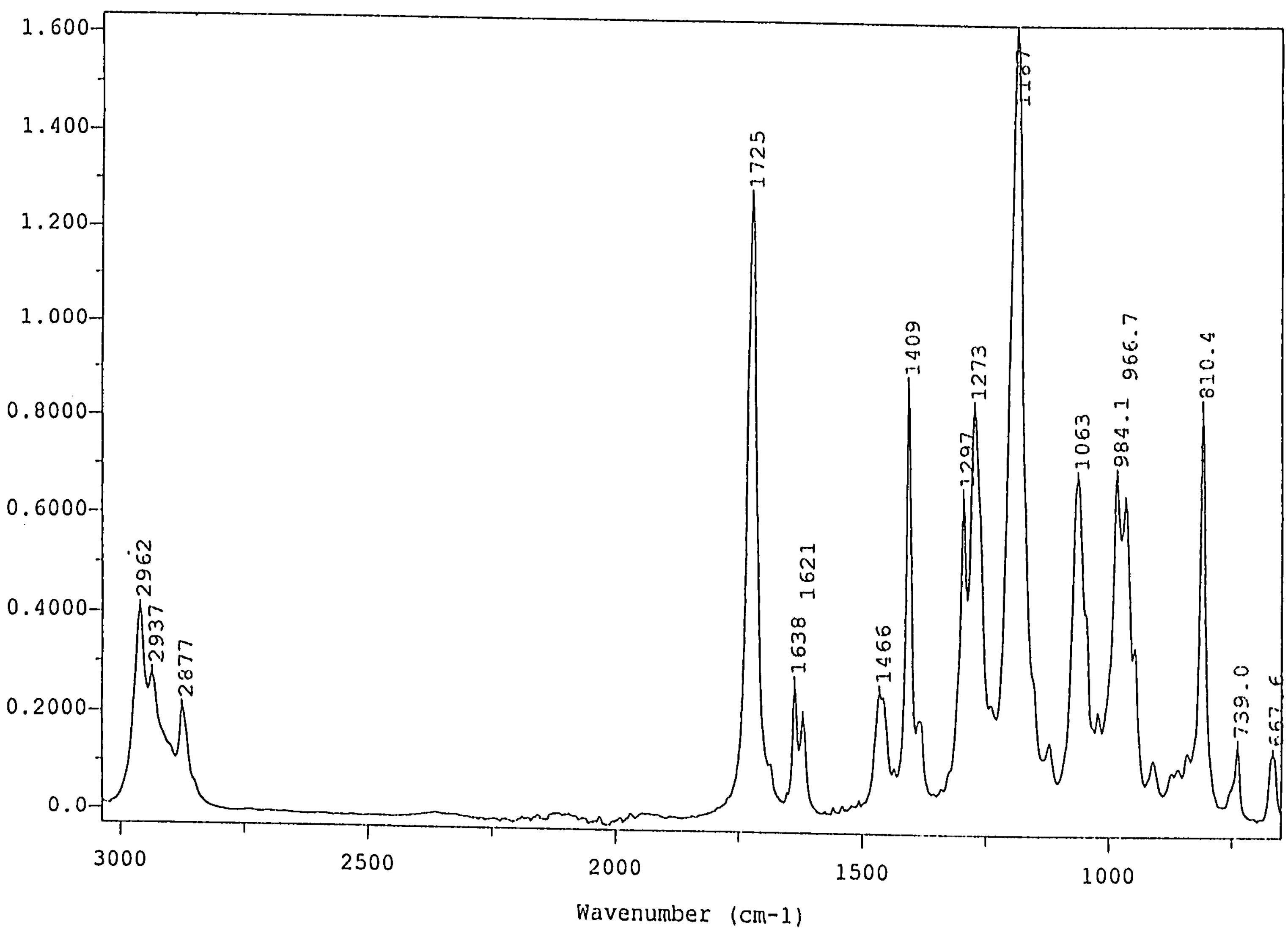


Figure 4.1b: ATR-FTIR spectrum of methyl methacrylate monomer.

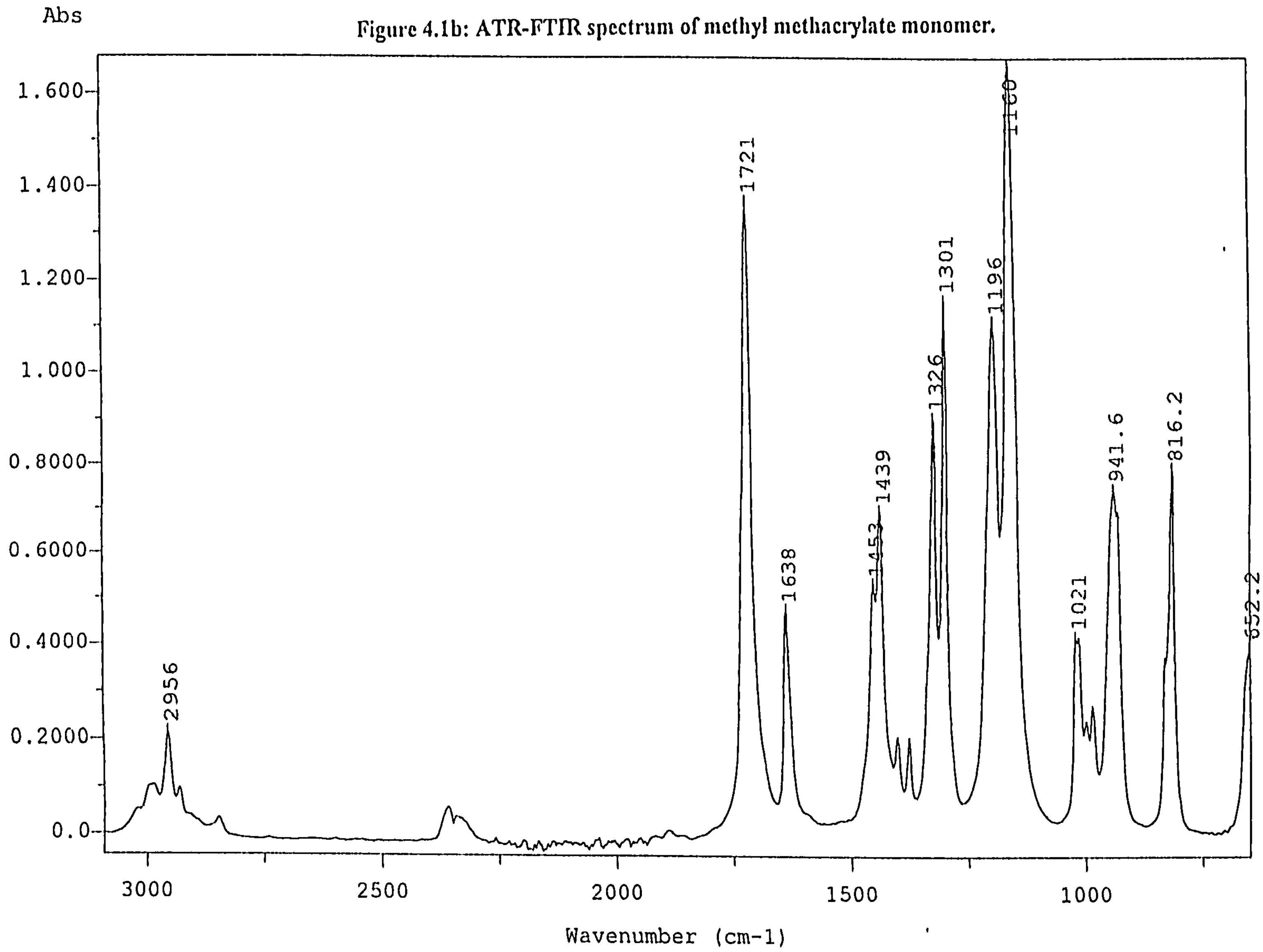
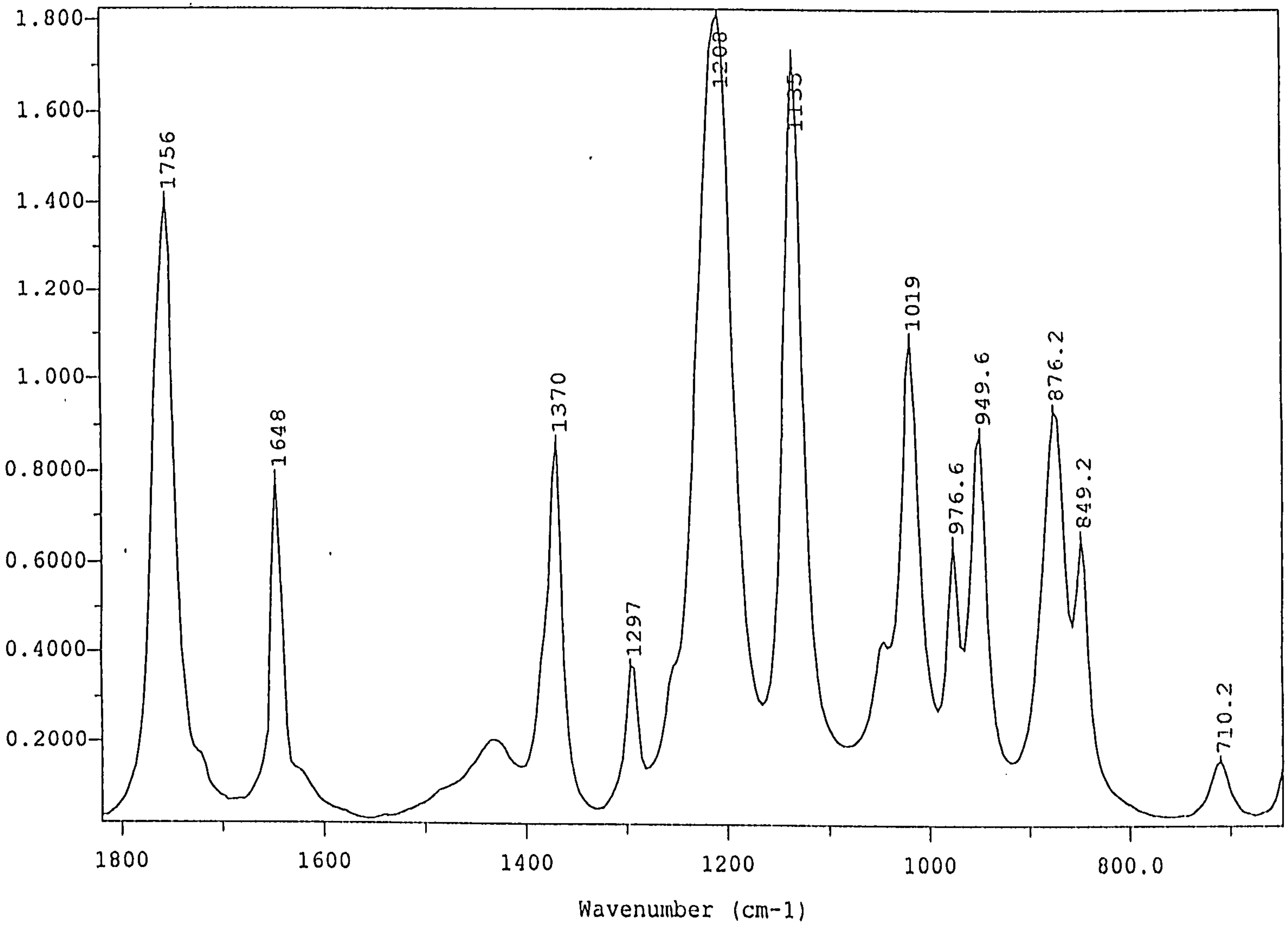


Figure 4.1c: ATR-FTIR spectrum of vinyl acetate monomer.



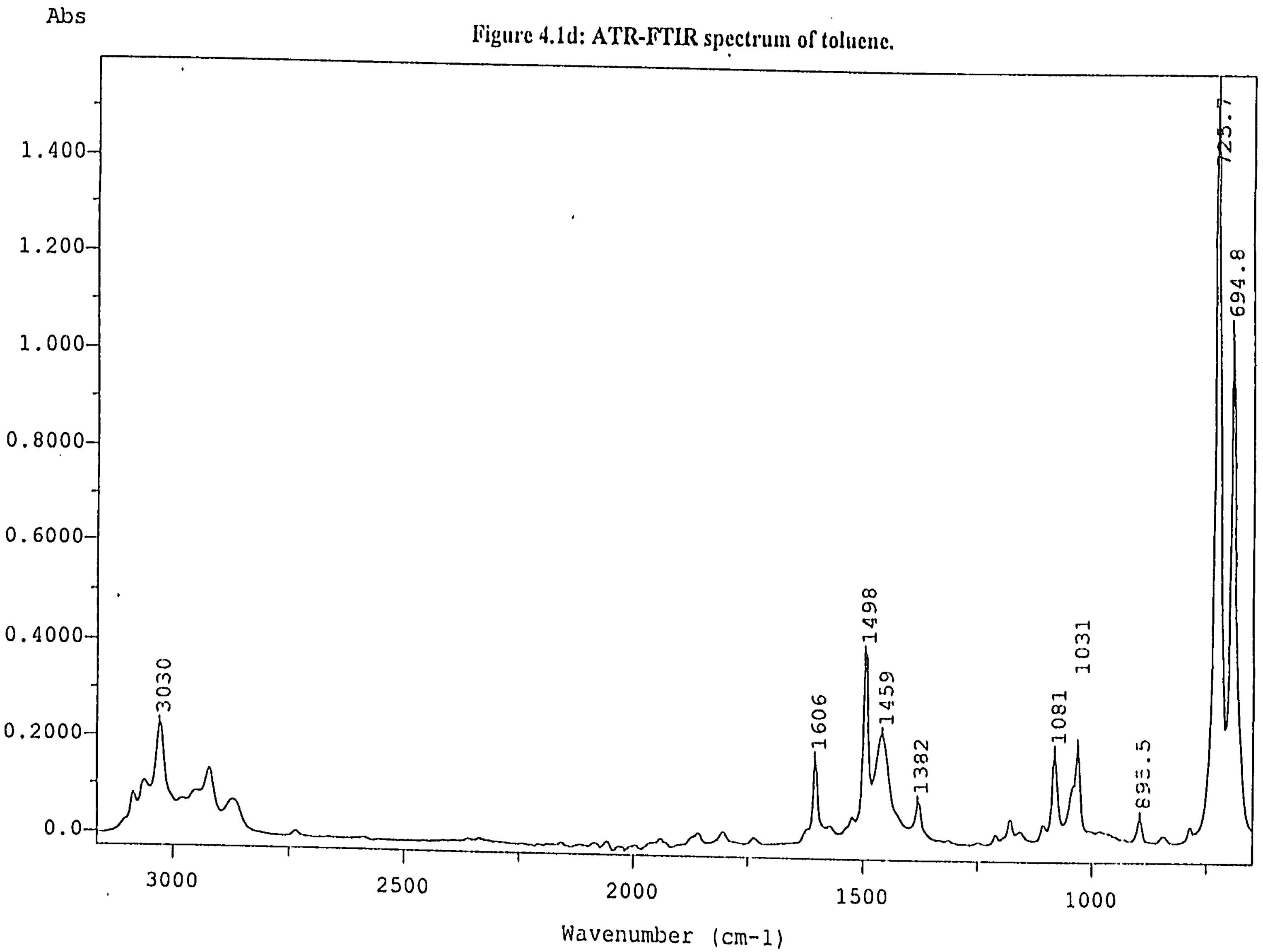
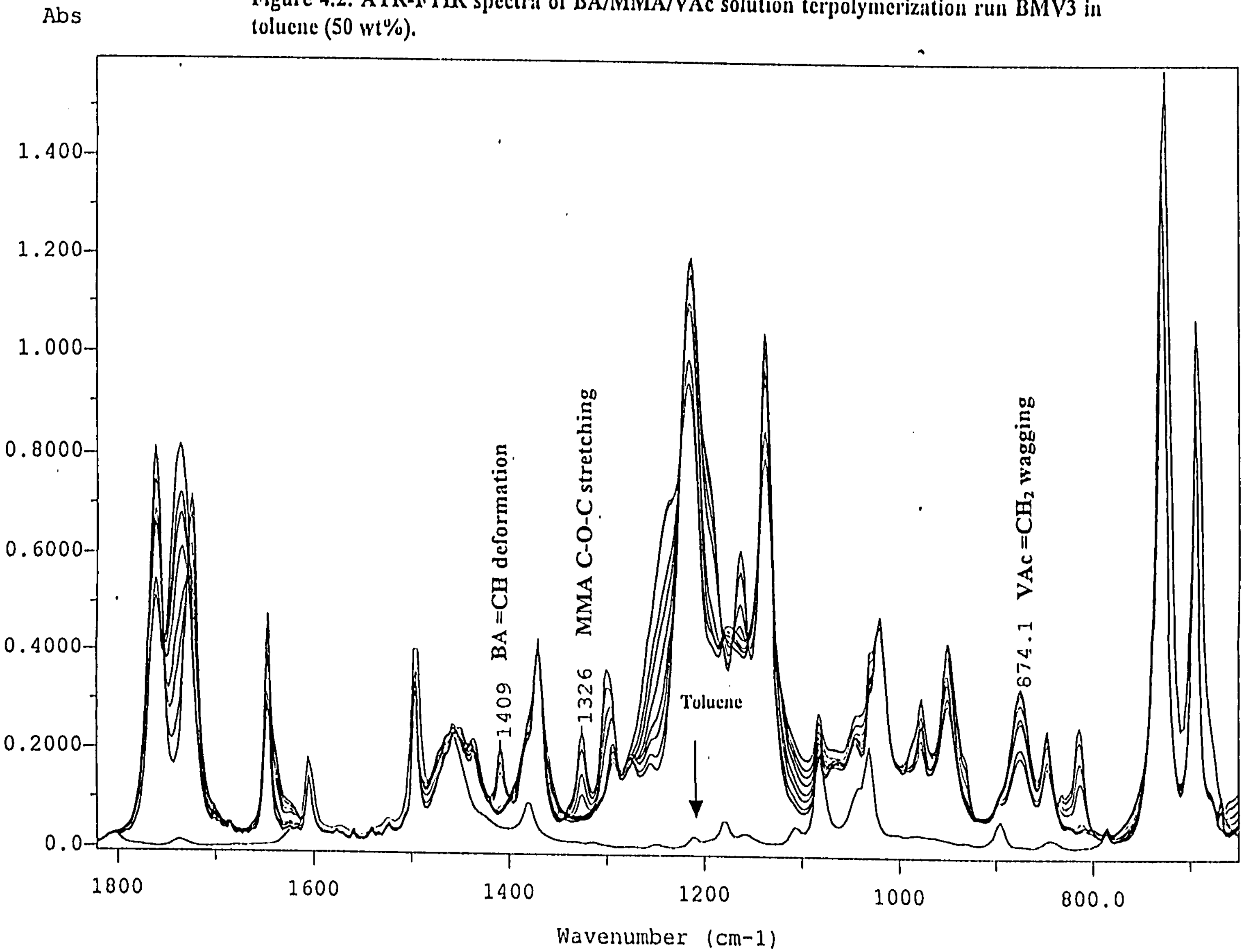


Figure 4.1d: ATR-FTIR spectrum of toluene.

Figure 4.2: ATR-FTIR spectra of BA/MMA/VAc solution terpolymerization run BMV3 in toluene (50 wt%).



typical spectra for the reaction contents of run BMV2 where distinct changes as the consequence of the polymerization reaction are observed. Characteristic absorbance bands for the three monomers were identified at 1409 cm^{-1} for the BA hyperconjugated –CH deformation, at 1326 cm^{-1} for the MMA C-O-C stretching vibration of the aliphatic ester group, and at 874 cm^{-1} for the VAc $=CH_2$ wagging, each of which diminished with increasing reaction time. There was no interference from the polymer nor from the solvent absorbances around these regions. Thus, these peaks were used for tracking the reaction.

The individual conversion of each monomer during the reaction was estimated by calculating the ratio of the absorbances (peak height referenced to a single-point baseline after baseline correction) of the 1409, 1326, and 874 cm^{-1} characteristic absorption bands, for BA, MMA and VAc, respectively, at reaction time t to their corresponding peaks at the start of the polymerization reaction (t=0), according to equation 1. The absorbances at the start of the reaction were the absorbances of the reaction contents measured prior to polymerization. The overall weight percentage conversion was subsequently calculated according to equation 2. Figures 4.3 through 4.5 show good agreement of both the overall and individual monomer conversion data for each run obtained between traditional gravimetry and ^{1}H-NMR spectroscopy techniques and ATR-FTIR spectroscopy.

Considering the monomer feed compositions as acrylic (i.e. BA+MMA) to VAc ratios, it is straightforward to see how monomer feed compositions affect the rates of terpolymerization. All of the reaction conditions, except for monomer feed compositions, were the same for three BA/MMA/VAc runs. Comparing Figures 4.3 through 4.5, a slightly decreasing overall terpolymerization rate during the early stages of the

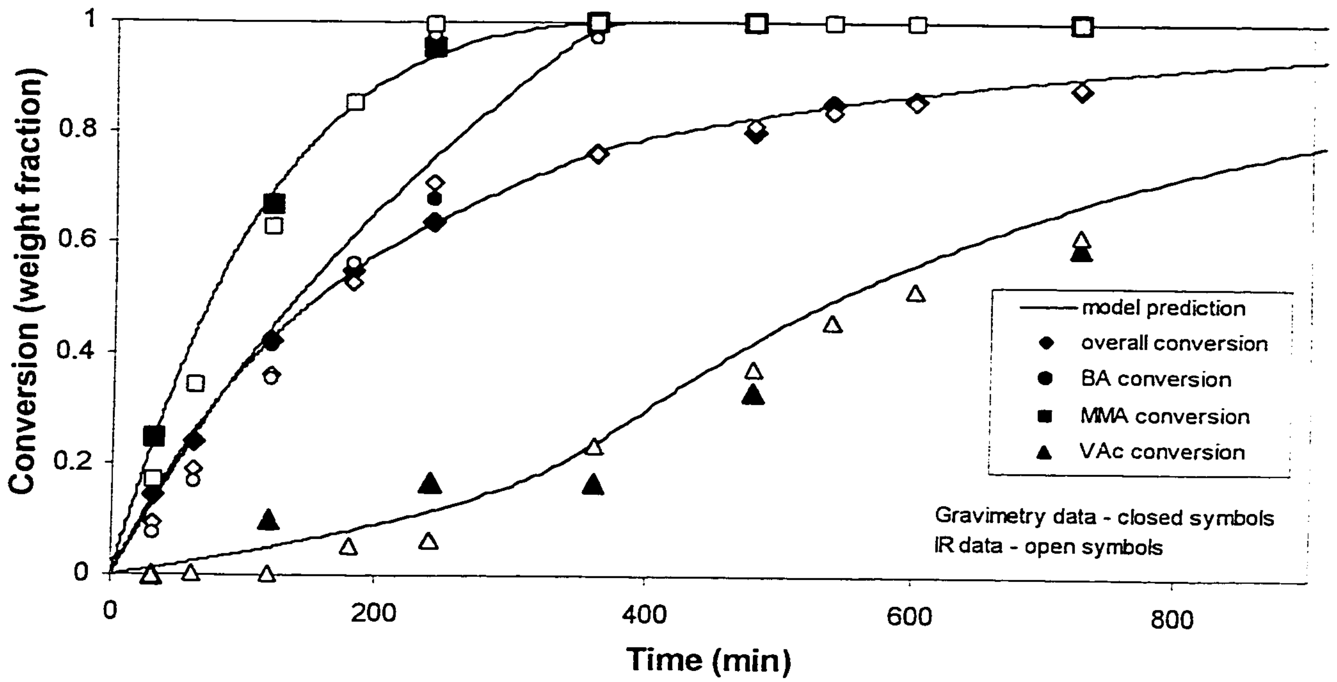


Figure 4.3: BA/MMA/VAc solution terpolymerization run BMV1: conversion vs. time.

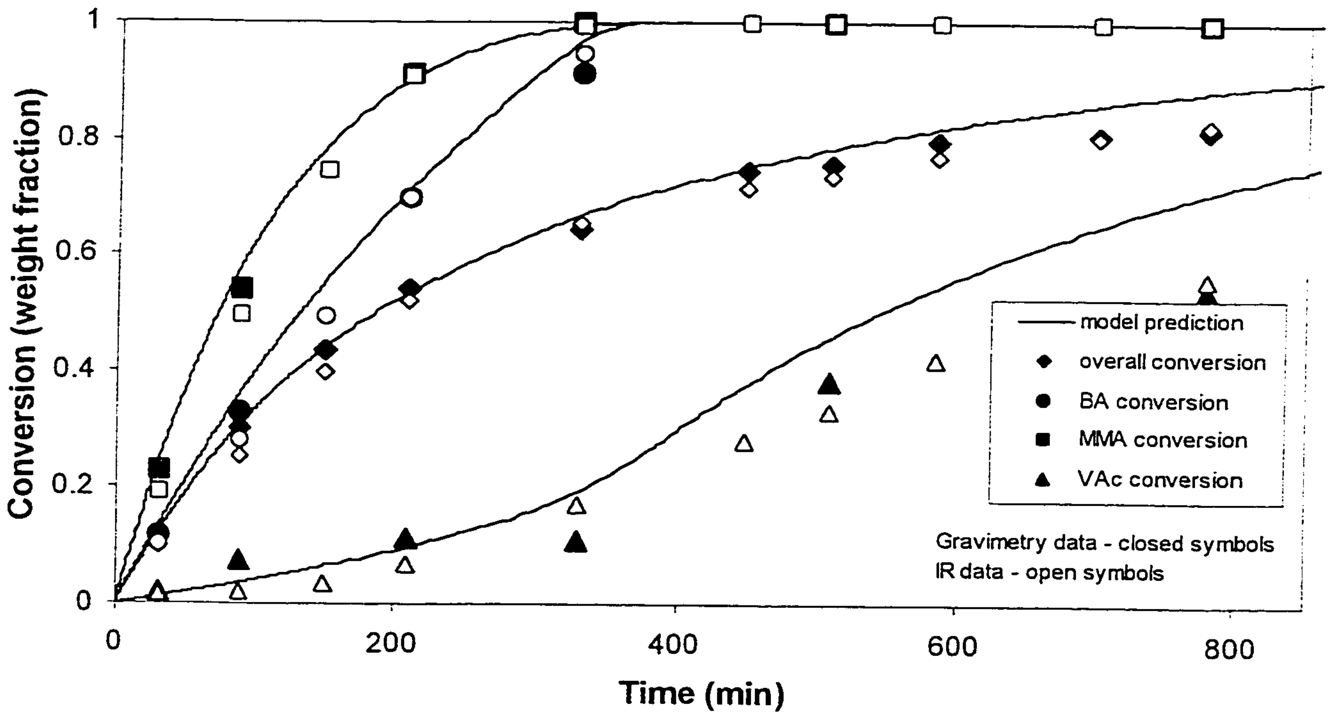


Figure 4.4: BA/MMA/VAc solution terpolymerization run BMV2: conversion vs. time.

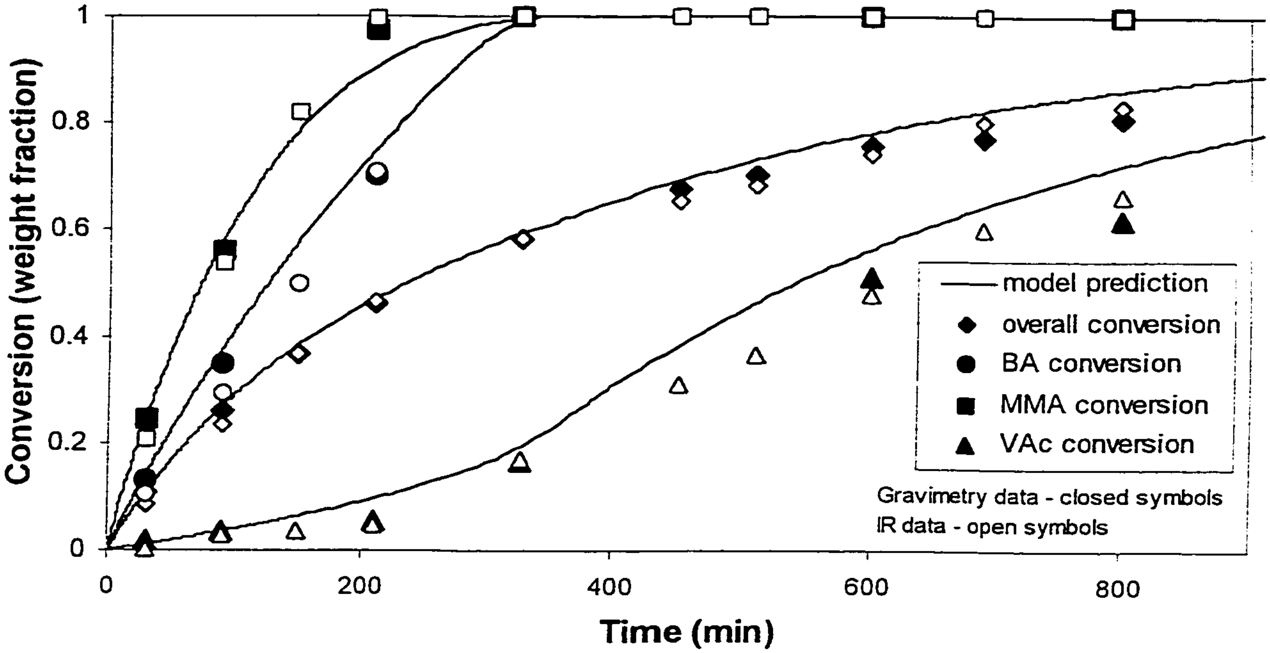


Figure 4.5: BA/MMA/VAc solution terpolymerization run BMV3: conversion vs. time.

terpolymerizations is observed as the VAc weight fraction in the feed was increased from 0.3 to 0.5. For example, one can see at a reaction time of 200 minutes, the overall conversion of run BMV1 reached about 58 wt% while for runs BMV2 and BMV3, the overall conversions were about 51 wt% and 45 wt%, respectively. At the same time, the weight fraction ratios of MMA/BA in the monomer feeds were increased gradually from runs BMV1 to BMV3. Comparison of the individual monomer conversions vs. time between Figures 4.3 and 4.5 indicates that when the weight fraction ratios of BA/MMA were decreased from 3/4 to 2/3, both BA and MMA monomers were consumed faster during the early stage of the reaction. As shown by Dubé and Penlidis,[16] the more BA there is in the BA/MMA system, the slower the copolymerization rate observed. This is due to the fact that MMA is slightly more reactive than BA according to the reactivity ratios shown in Table 4.4. The effect of increasing the VAc weight fraction in the feed competed with the effect of increasing the MMA/BA feed ratio. Evidently, the former effect was dominant for these reaction conditions.

Table 4.4: Reactivity ratios for BA/MMA/VAc evaluated at 60°C

Monomer	r_1	r_2
BA/MMA[17]	0.291	1.871
BA/VAc[16]	5.939	0.0262
MMA/VAc[18]	24.025	0.0261

These three runs all exhibited a two-stage rate effect as described in Dubé and Penlidis.[1] This behaviour is similar to VAc-containing copolymerizations. Because the acrylic monomers are much more reactive than VAc according to the reactivity ratios shown in Table 4.4, the acrylic monomers dominated the beginning of the reaction to form polymer mostly composed of BA and MMA while VAc dominated the polymerization after the BA and MMA were depleted. As shown in Figures 4.3 through 4.5, VAc was not reacting much during the first period of the terpolymerizations. During the latter stages of reaction, the VAc homopolymer was being generated.

Cumulative copolymer compositions were plotted as a function of conversion for three runs and are shown in Figures 4.6 through 4.8. Significant copolymer drift was observed at higher conversion levels (above 50 wt%). Up to 50 wt%, which coincides with the overall acrylic monomer feed of 50 wt%, very little VAc (< 10 wt%) was incorporated into the terpolymer while above 50 wt% conversion, the VAc content in the terpolymer increased dramatically. This concurs with the two-stage rate effect shown described earlier. Furthermore, when the VAc fraction in the monomer feed was decreased, the two-stage rate effect was delayed to higher conversions. Clearly, heterogeneous polymer mixtures were obtained during these batch terpolymerizations.

Changes in the cumulative number- and weight-average molecular weights with conversion are plotted in Figures 4.9 through 4.11, and are compared to model predictions. Comparing Figures 4.9 through 4.11, a higher acrylic monomer fraction in the monomer feed resulted in slightly faster polymerization rates and thus, higher molecular weight averages. The use of CTA and the high chain transfer to solvent rate helped keep the terpolymer molecular weights low.

All of the solution terpolymerization data were compared to predictions from a JAVA™-based computer simulation (see solid lines in Figures 4.3 through 4.11).[19] This computer simulation was developed using the mathematical model described by Dubé et al.[20] The model has been validated for a wide range of homopolymerization and copolymerization systems including BA, MMA, and VAc by Gao and Penlidis.[21,22] The model predictions were achieved using the homopolymerization parameters for each system using the pseudo-kinetic rate constant method.[23]

The issue of solvent effects on the propagation and/or termination rate constants of this terpolymer system is of concern. For MMA, solvent effects are considered small for its solution homopolymerization in toluene.[24,25] Thus, no modification for solvent effects was made on MMA parameters. However, significant solvent effects on the polymerizations of BA and VAc have been reported.[7,8,12] For BA solution homopolymerization, the lumped parameter, ${}^{k_p}\!/\!{}_{k_t^{0.5}}$ (where k_p is the propagation rate constant and k_t is the termination rate constant), was found to increase when the

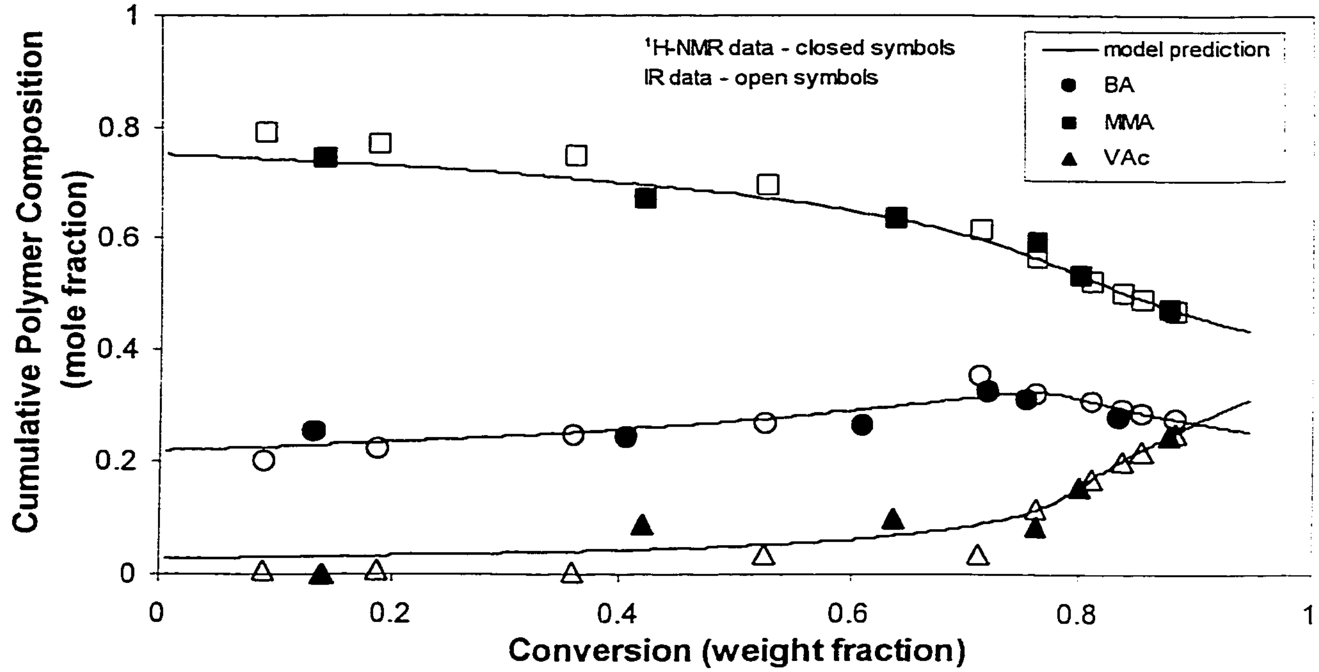


Figure 4.6: BA/MMA/VAc solution terpolymerization run BMV1: cumulative terpolymer composition vs. conversion.

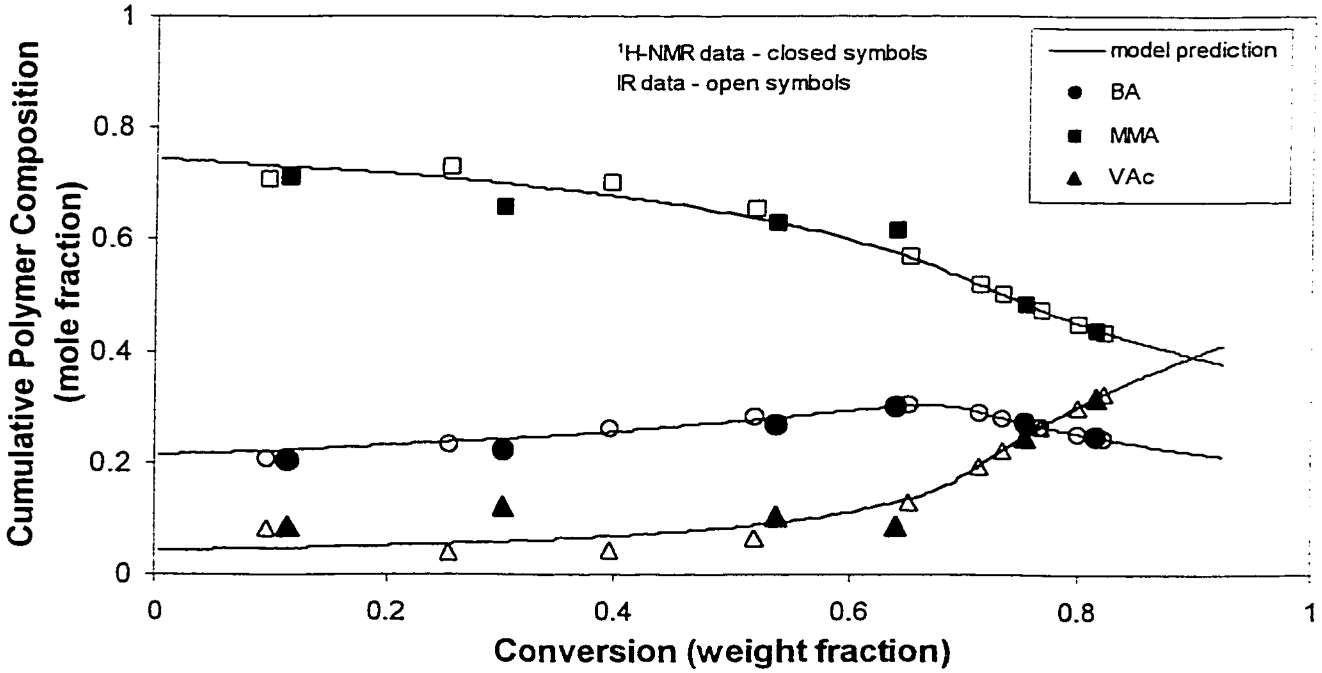


Figure 4.7: BA/MMA/VAc solution terpolymerization run BMV2: cumulative terpolymer composition vs. conversion.

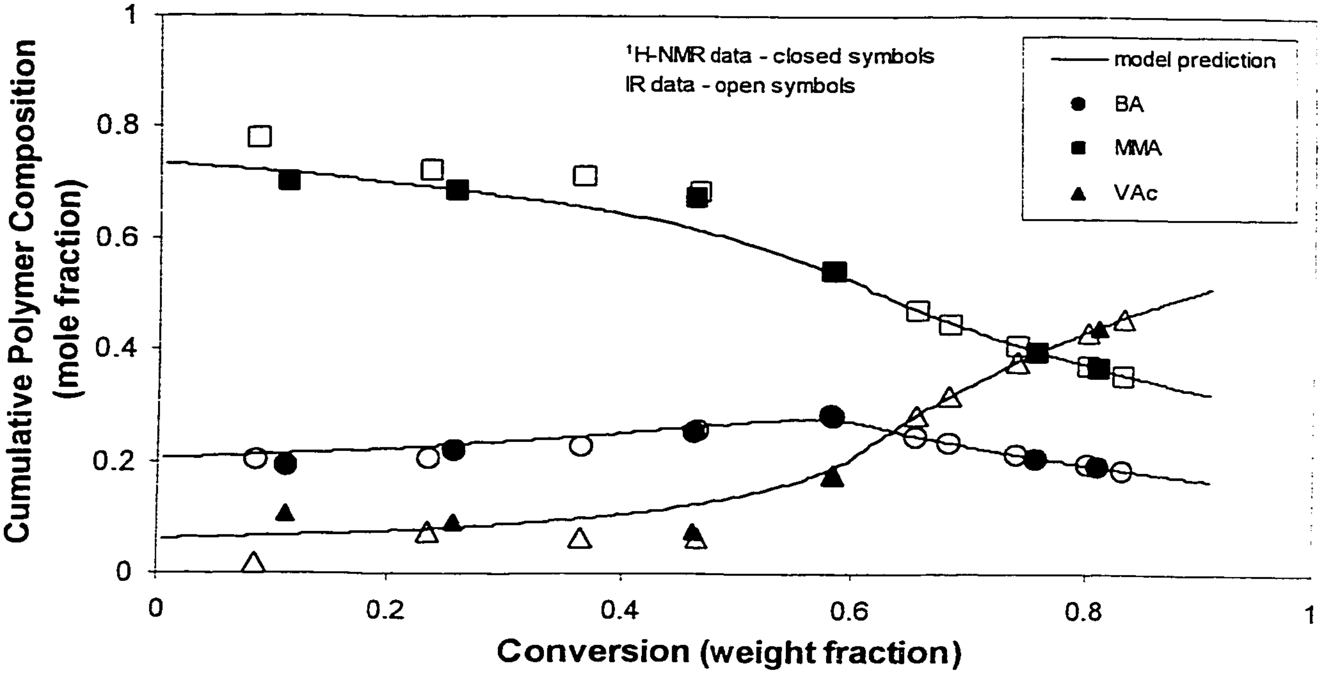


Figure 4.8: BA/MMA/VAc solution terpolymerization run BMV3: cumulative terpolymer composition vs. conversion.

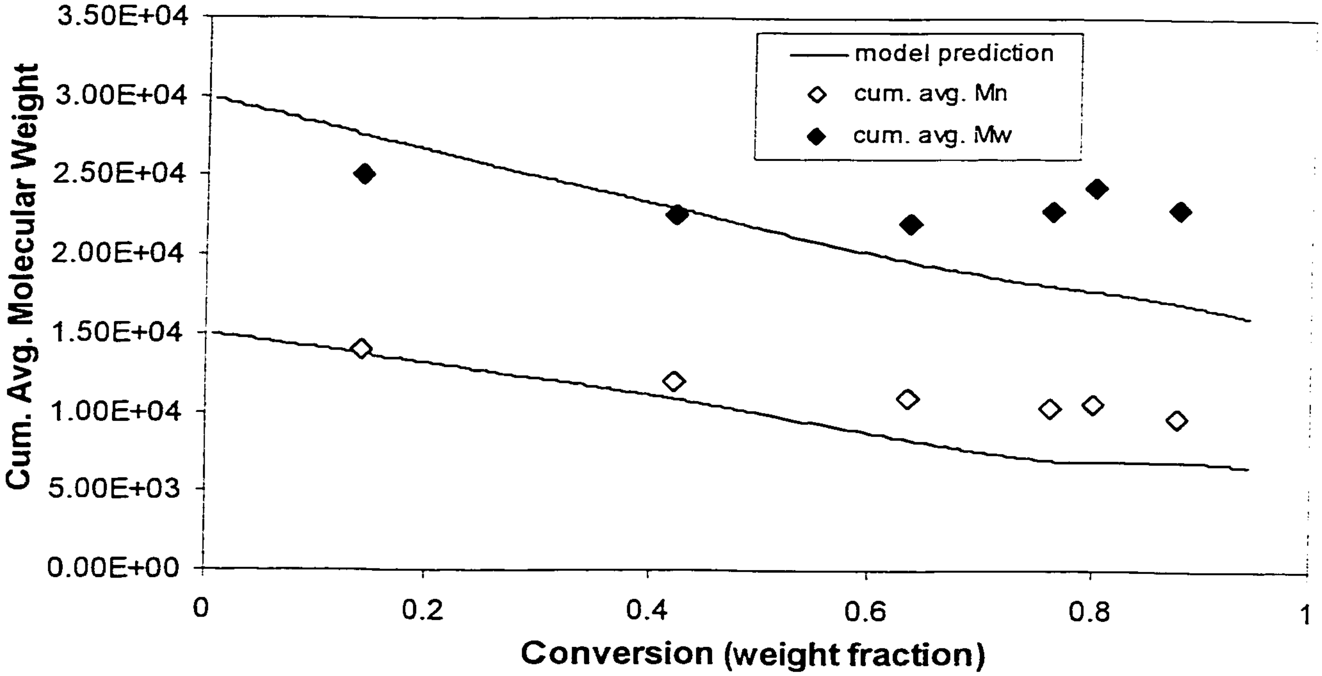


Figure 4.9: BA/MMA/VAc solution terpolymerization run BMV1: cumulative number- and weight-average molecular weight vs. conversion.

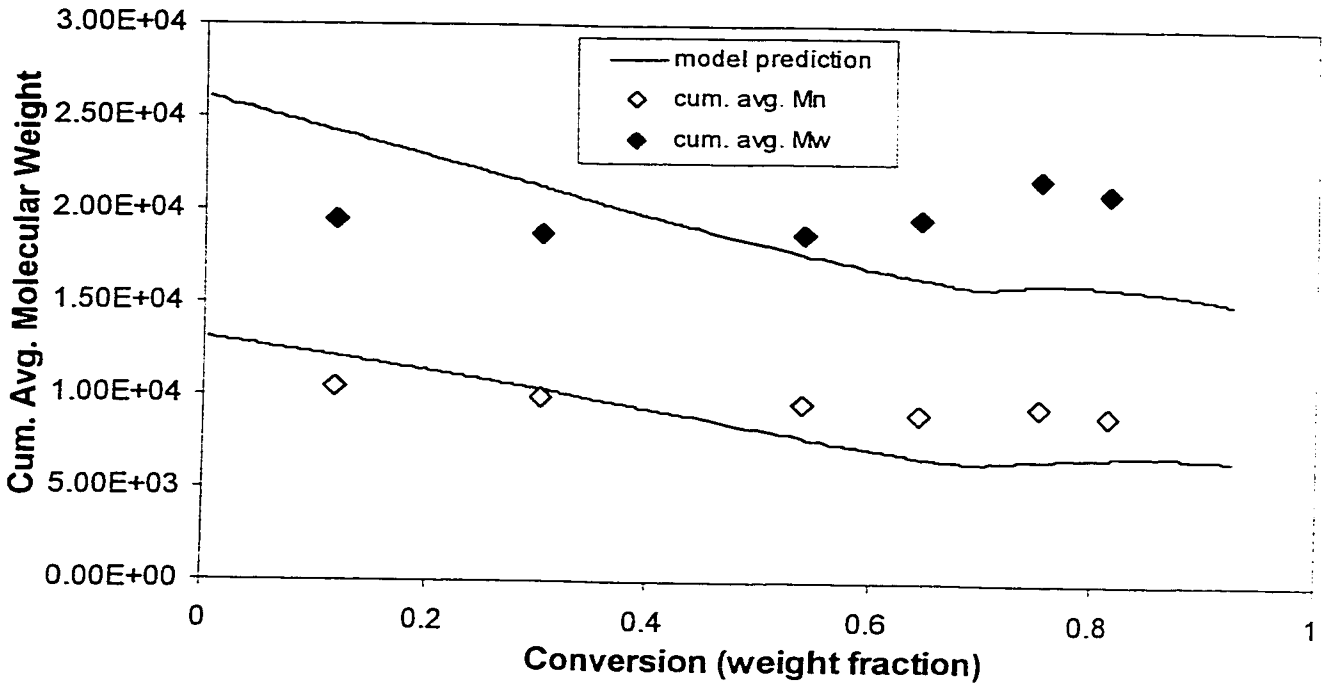


Figure 4.10: BA/MMA/VAc solution terpolymerization run BMV2: cumulative number- and weight-average molecular weight vs. conversion.

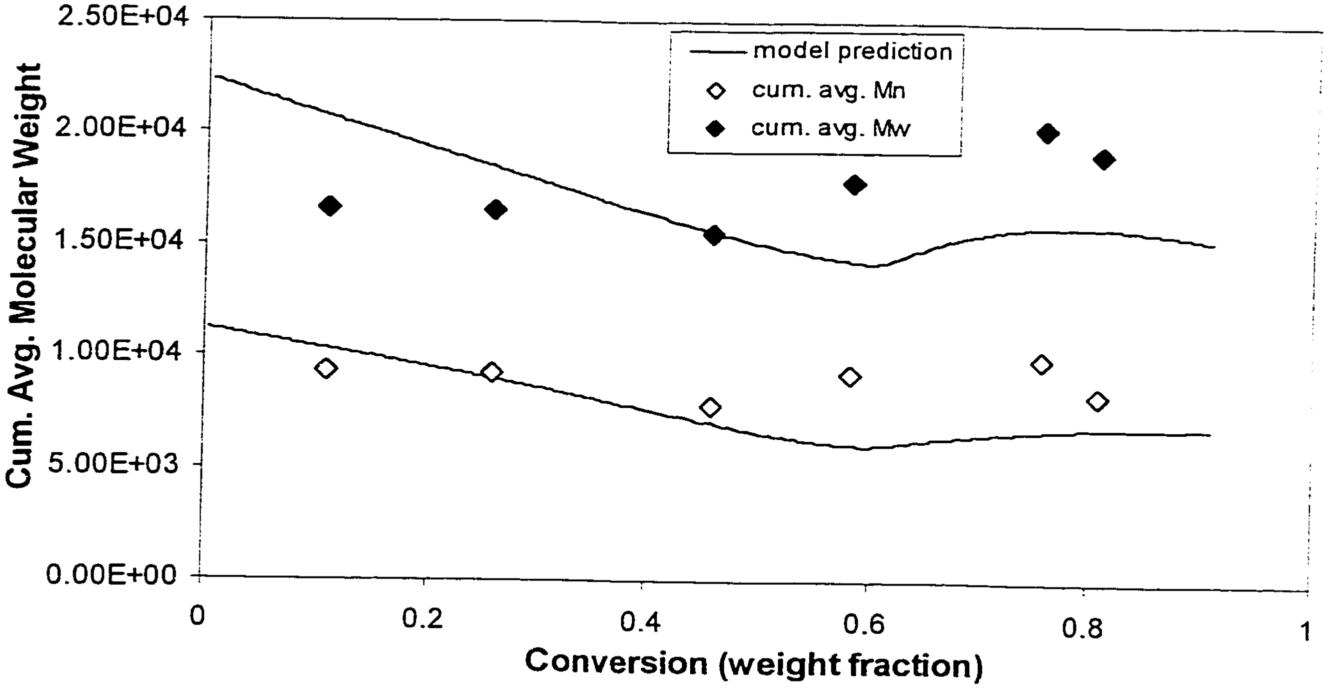


Figure 4.11: BA/MMA/VAc solution terpolymerization run BMV3: cumulative number- and weight-average molecular weight vs. conversion.

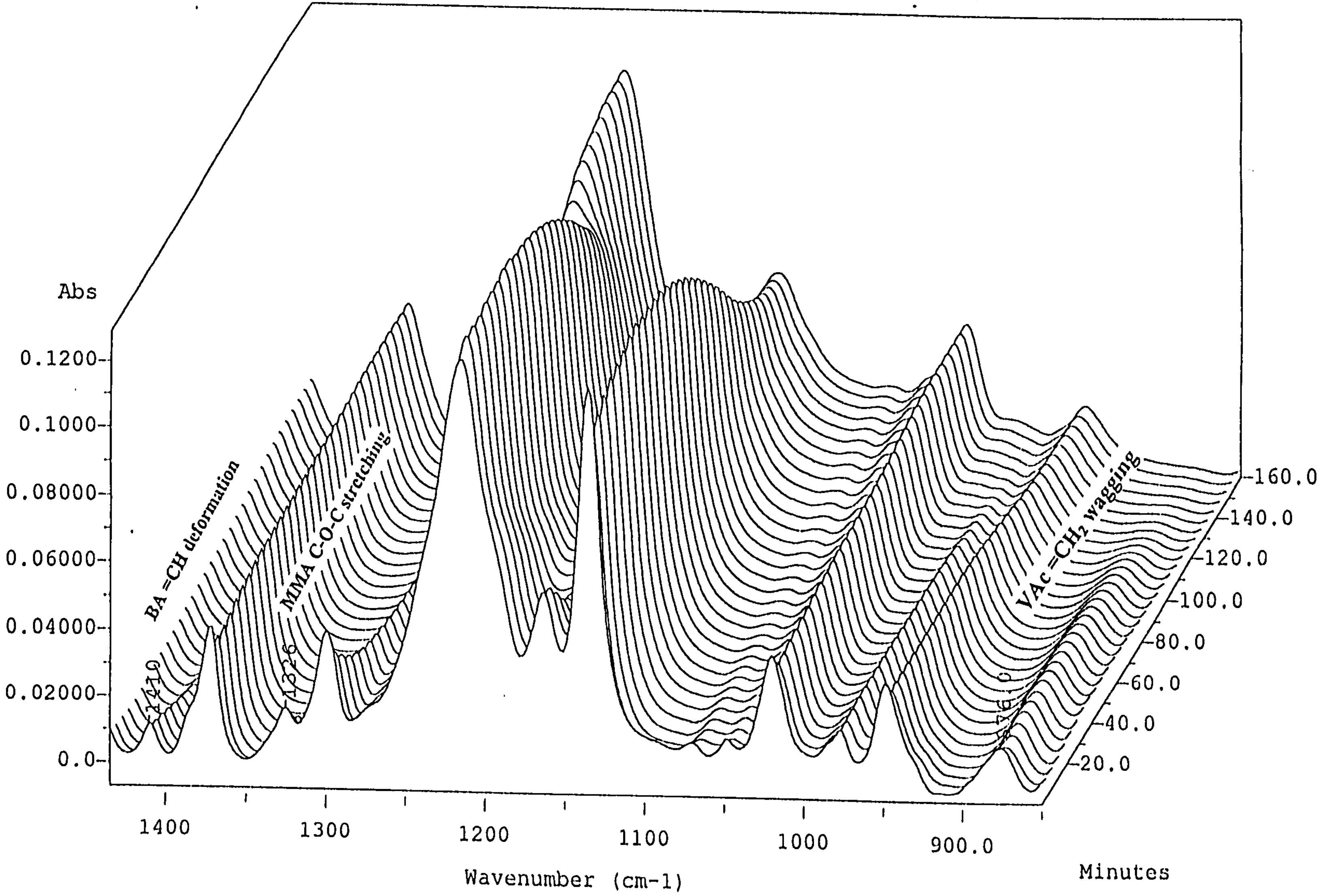
monomer concentration in the solution increased.[26] For the case of VAc, solvent effects on VAc rate coefficients can be significant because the toluene acts as a strong retardant for VAc homopolymerization.[25] Thus, modified lumped parameters used to incorporate the solvent effect for both BA and VAc polymerization modelling were introduced from similar modelling efforts for BA/VAc solution copolymerizations in toluene.[8] Model predictions for overall conversions, copolymer compositions, and molecular weight averages for the most part, appear to be reasonably good (see Figures 4.3 through 4.11). There are some discrepancies between model predictions of VAc conversion and experimental data at high overall conversions. Efforts are currently underway to improve the model predictions by investigating alternative models and improving parameter estimates in light of the significant solvent effects.

Emulsion polymerizations

BA/MMA/VAc emulsion terpolymerization experiments were run at 60°C. The reaction ingredients are shown in Table 4.3 as runs BMV4 through BMV6. Reaction mixture spectra were collected every 5 minutes during the reaction. 254 scans were acquired for each spectrum at a resolution of 4 cm^{-1}.

Distinct changes as the consequence of the polymerization reaction were observed, as shown in Figure 4.12, on characteristic absorbance bands of the three monomers. The absorbance bands at 1410 cm^{-1} for the BA hyperconjugated –CH deformation, at 1326 cm^{-1} for the MMA C-O-C stretching vibration of the aliphatic ester group, and at 876 cm^{-1} for the VAc $=CH_2$ wagging, all diminished with increasing reaction time. These three peaks were used for tracking the reaction without any

Figure 4.12: ATR-FTIR spectra of BA/MMA/VAc emulsion terpolymerization run BMV6.



interference from the produced copolymer absorbances nor form the other reaction ingredients.

The individual conversions of each monomer during the reaction were estimated in a way similar to that of the solution terpolymerizations. This was done by calculating the ratio of the absorbances (peak heights referred to a two-point baseline after baseline correction) of the 1410, 1326, and 876 cm^{-1} characteristic absorption bands for BA, MMA, and VAc, respectively, at reaction time t to their corresponding peaks at the start of the polymerization reaction (t=0), according to equation 1. The overall weight percentage conversion was subsequently calculated according to equation 2.

Figures 4.13 through 4.15 show the overall and individual monomer conversion data of each run obtained from ATR-FTIR spectroscopy compared to traditional gravimetry and ^{1}H-NMR spectroscopy techniques. Good agreement between the in-line and conventional off-line techniques is observed.

The composition data of the produced terpolymers for each run were calculated based on individual monomer conversions from IR measurements and are also shown in Figures 4.16 through 4.18. The data agreed well with measurements from ^{1}H-NMR spectroscopy.

The evolution of the conversion exhibited a two-stage rate effect similar to the solution runs and as previously noted by Dubé and Penlidis.[27] As an example, one can look at run BMV6 in Figure 4.15. The polymerization of the acrylic monomers dominated the reaction up to about 50 wt% conversion, which corresponds to the weight fraction of acrylic monomers in the feed (i.e. 20 wt% BA and 30 wt% MMA). Above 50 wt% conversion, the VAc dominated the remainder of the reaction. Comparing Figures

4.13 through 4.15, one can also see that a decrease in the weight fraction of VAc in the feed caused an increase in the polymerization rate during the initial stage of the reaction. This is consistent with our findings for the solution terpolymerizations discussed earlier.

The composition results (see Figures 4.16 through 4.18) also exhibit the two-stage rate effect phenomenon as revealed by the conversion vs. time plot. For example, from Figure 4.16 (run BMV4), it is observed that at low conversion (<60 wt%), the amount of bound VAc in the terpolymer was very low (~ 5 mol%) and the bound VAc started to accumulate at up to 70 wt% conversion. This corresponded to the acrylic monomer content of 70 wt%. Thus, significant copolymer composition drift was observed during the high conversion stage of the terpolymerizations.

In Figure 4.13, good agreement was observed between the ATR-FTIR data and that from gravimetry and ^{1}H-NMR techniques for the acrylic monomer conversion profiles. However, there were discrepancies for the estimates of VAc conversion. This discrepancy might be due to experimental error. During the polymerizations, collection of the reaction spectra was long relative to the reaction rate. The spectrum at a certain time point was the averaged absorbance spectrum over a period of time. Thus, one could expect discrepancies between conversions estimated from these averaged spectra and those determined by conventional gravimetric methods at certain time points.

Another possible explanation is the presence of an error in the initial absorbance peak height (see *peak height at time t=0* in equation 1). An error of this type would result in a consistent offset of the conversion vs. time plot. This is observed for the VAc conversion vs. time curve in Figure 4.13, which leads one to question for the reason for this initial error. One possible reason is that of a temperature effect. Sensitivity of the IR

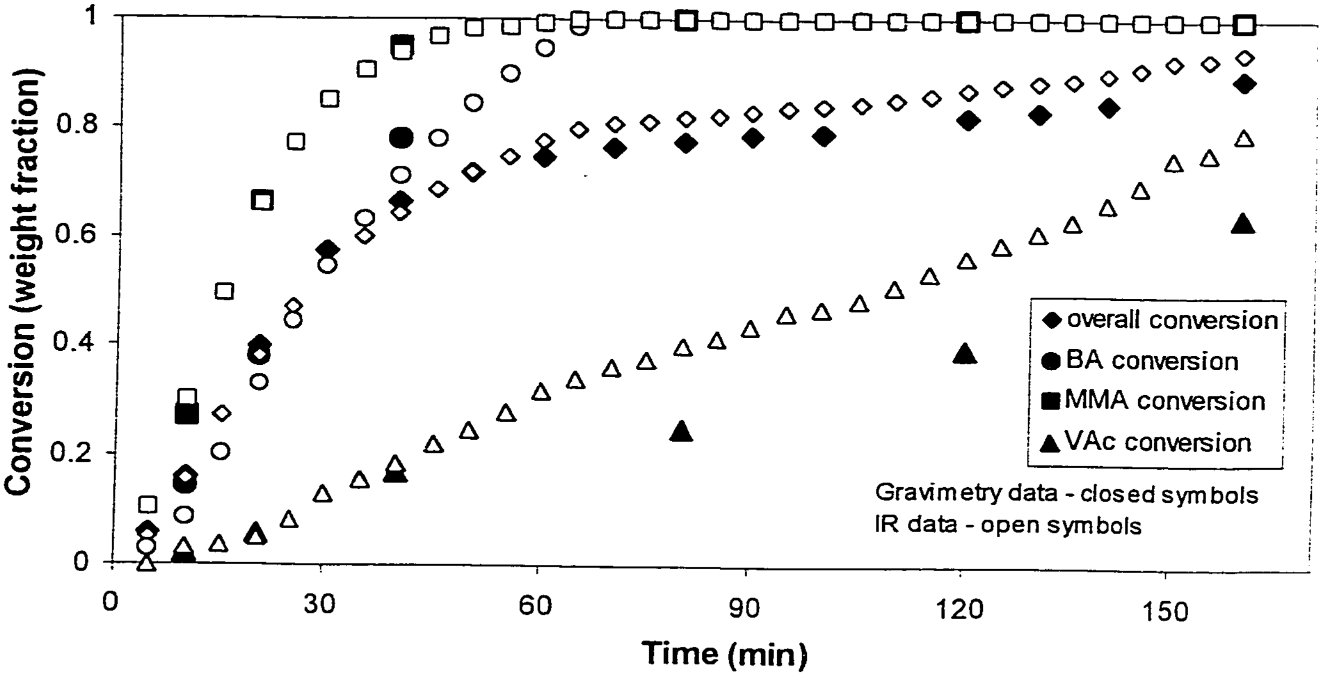


Figure 4.13: BA/MMA/VAc emulsion terpolymerization run BMV4: conversion vs. time.

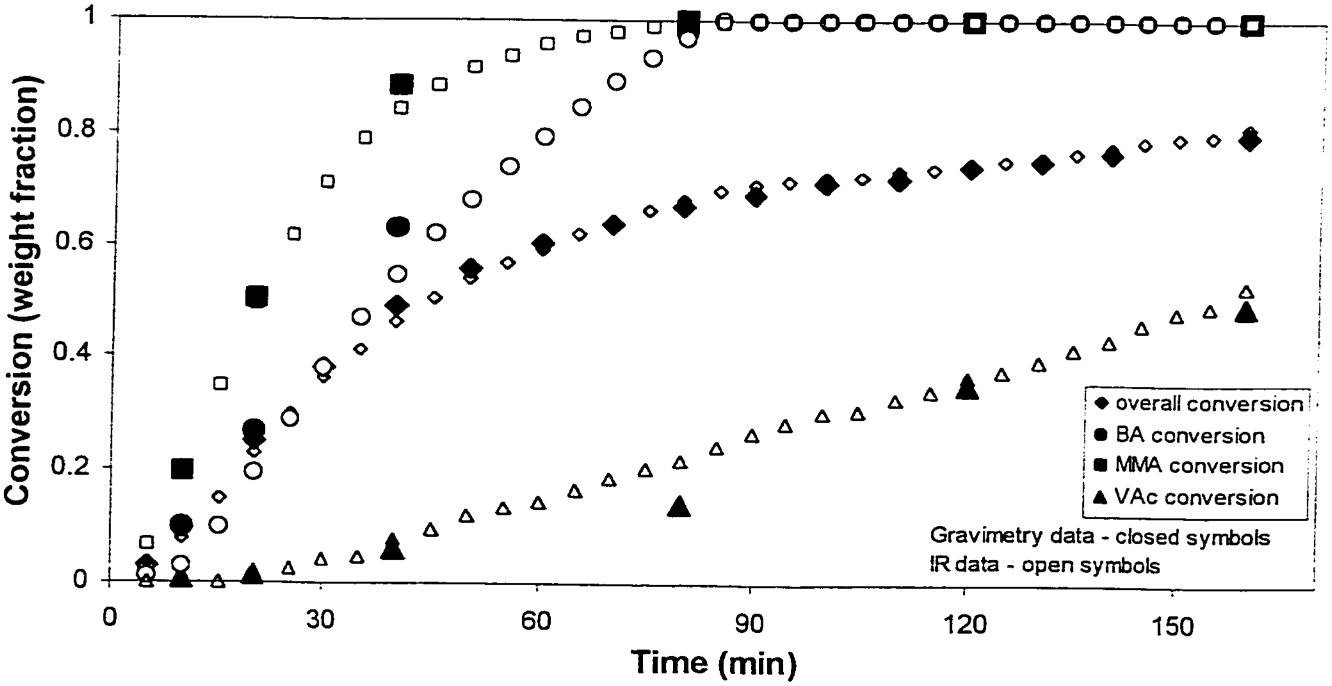


Figure 4.14: BA/MMA/VAc emulsion terpolymerization run BMV5: conversion vs. time.

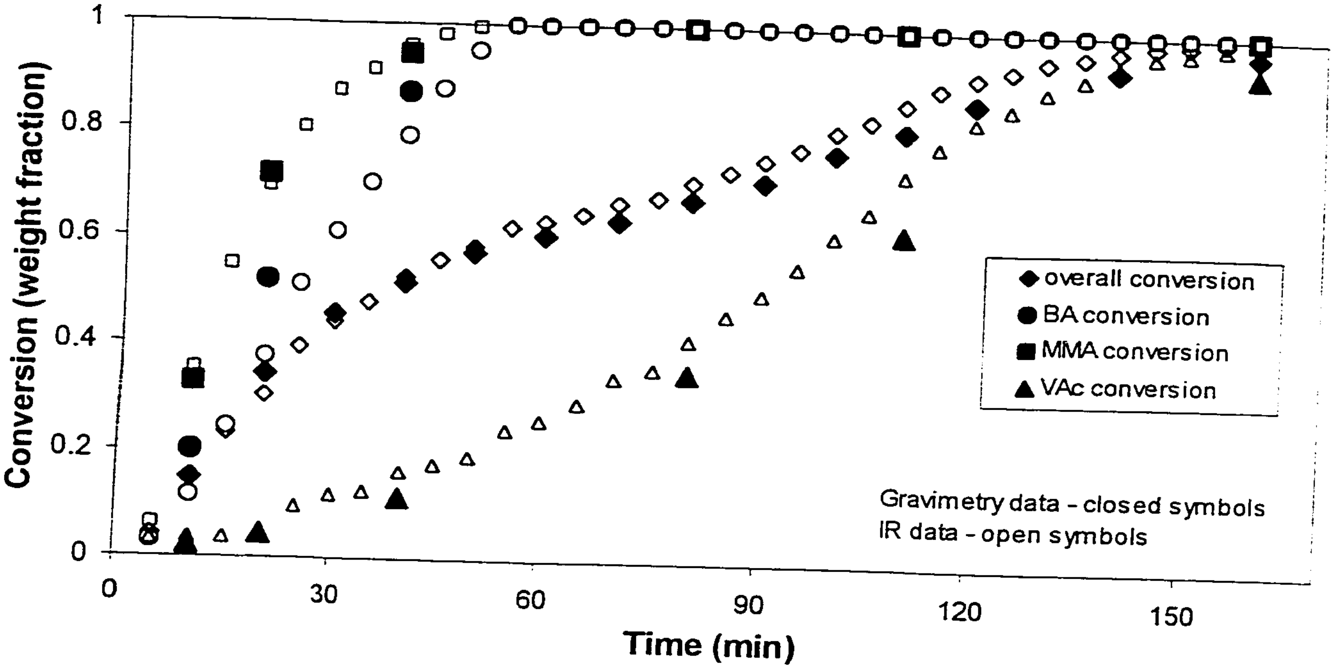


Figure 4.15: BA/MMA/VAc emulsion terpolymerization run BMV6: conversion vs. time.

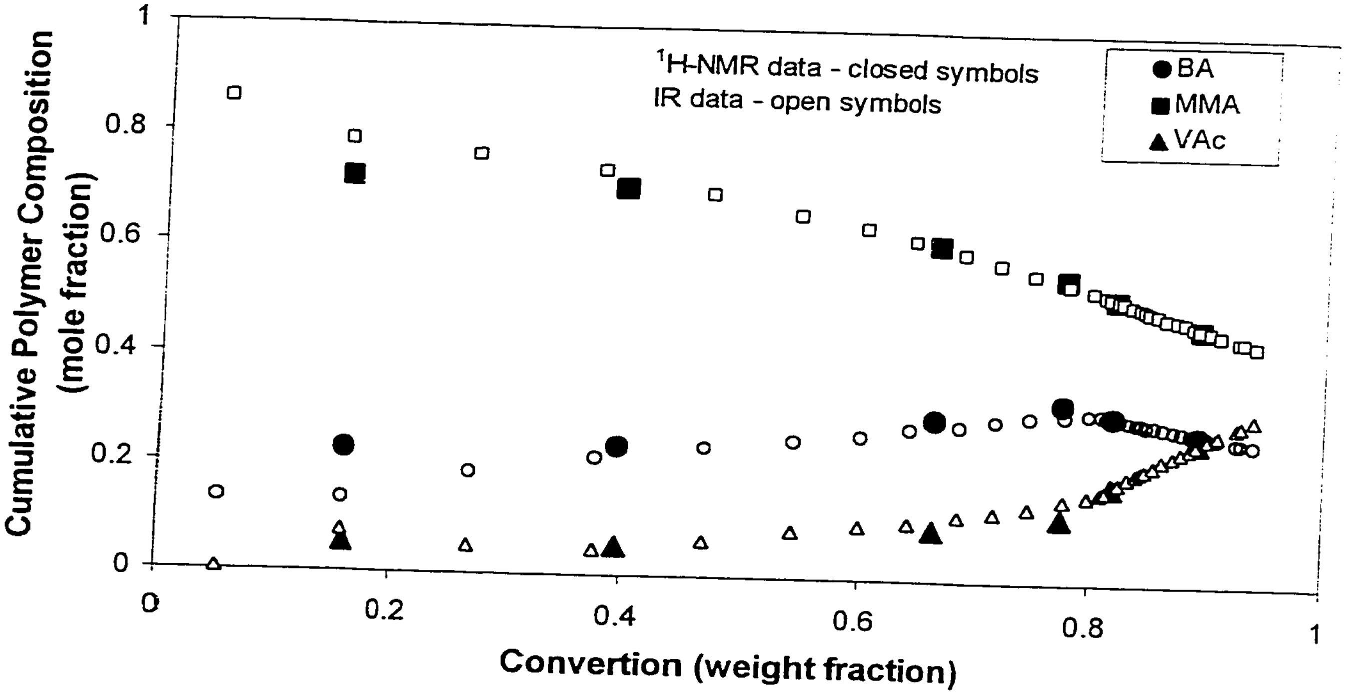


Figure 4.16: BA/MMA/VAc emulsion terpolymerization run BMV4: cumulative terpolymer composition vs. conversion.

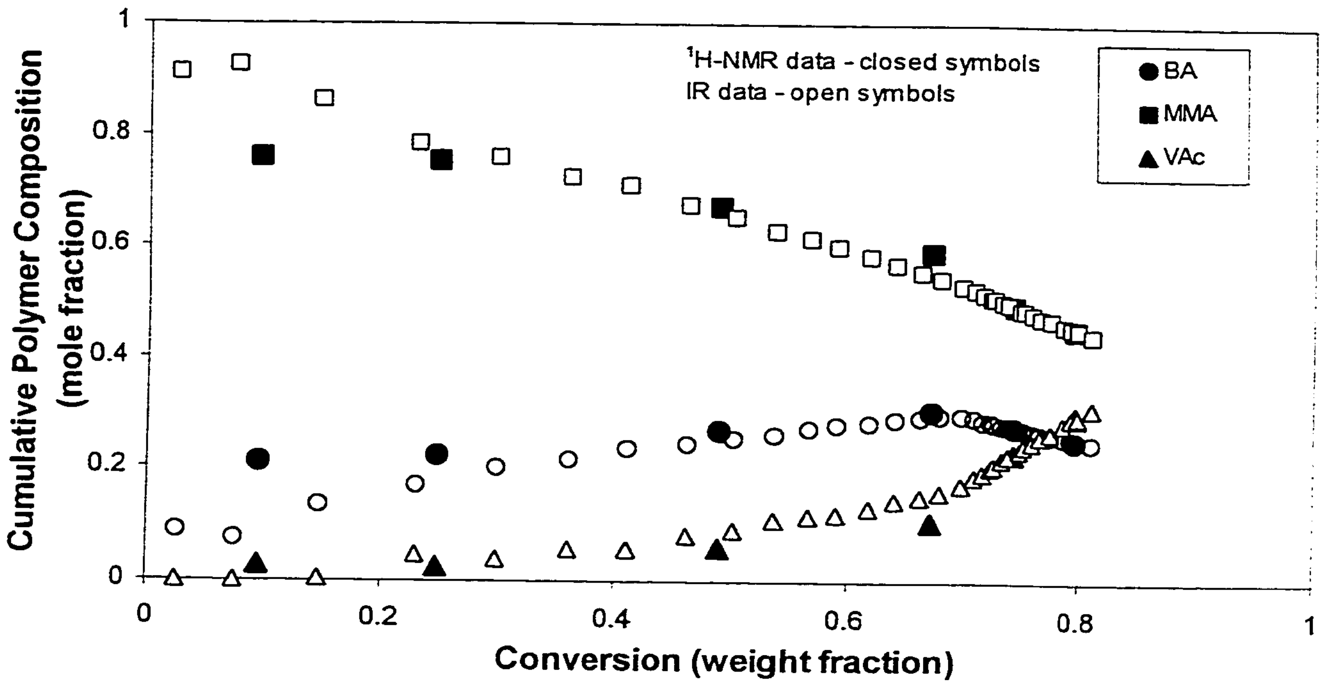


Figure 4.17: BA/MMA/VAc emulsion terpolymerization run BMV5: cumulative terpolymer composition vs. conversion.

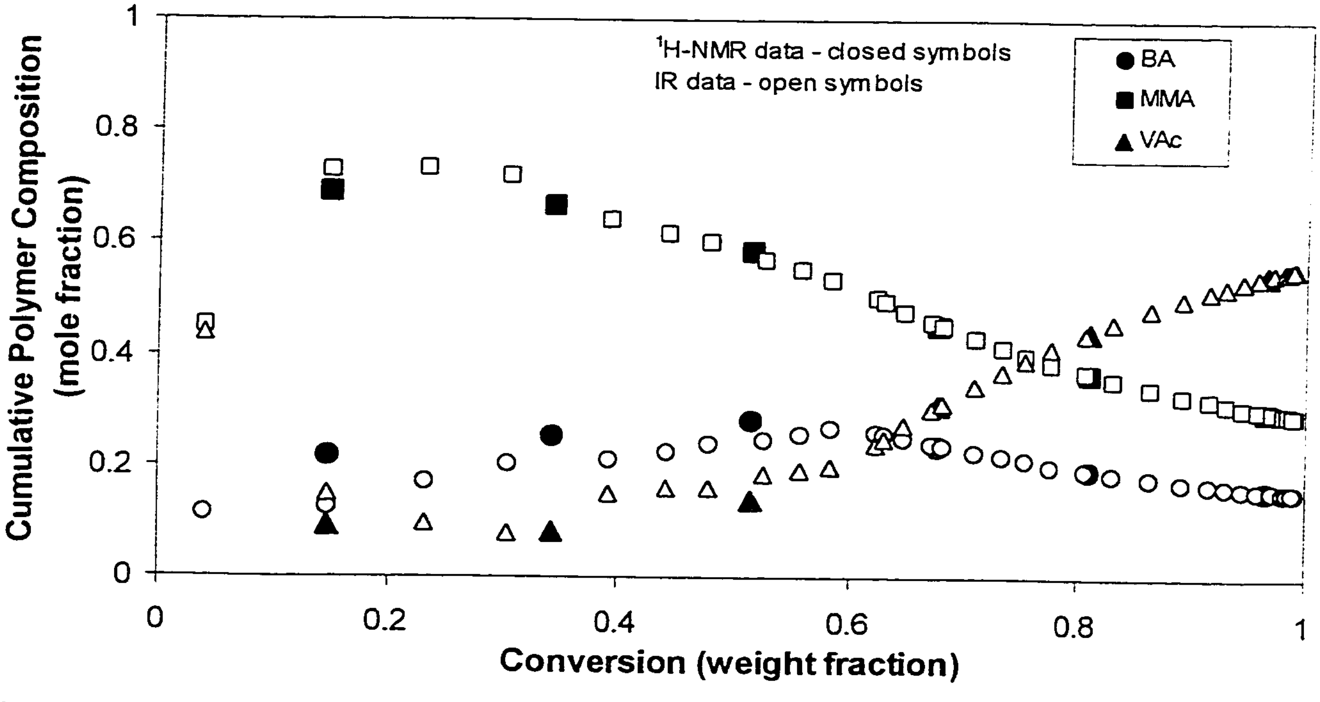


Figure 4.18: BA/MMA/VAc emulsion terpolymerization run BMV6: cumulative terpolymer composition vs. conversion.

absorbance peak height to temperature was observed for a number of runs not reported here. The beginning of the reaction, as discussed in the experimental methods section, immediately followed the injection of an initiator solution. This solution often caused a slight initial temperature excursion that was quickly converted by the reactor's temperature control system. Thus, a small temperature deviation resulting from the initiator injection could have caused a small, yet significant error in the initial peak height for VAc. This error would have caused a consistent offset of the conversion vs. time curve according to equation 1.

Conclusions

Previous studies on BA, MMA, and VAc batch solution and emulsion homo- and copolymerizations demonstrated the ability of ATR-FTIR spectroscopy for polymerization monitoring. The current study of the more complicated case of terpolymerization reveals a similar ability. ATR-FTIR spectroscopy with a light conduit and diamond-composite probe shows again that it is well suited for polymerization reaction monitoring and kinetic investigations in either solvent or aqueous media. The data acquired through ATR-FTIR spectroscopy showed good agreement with data from conventional gravimetric and ^{1}H-NMR analysis.

Used in-line for emulsion polymerization monitoring, the ReactIR™ 1000 ATR-FTIR probe is fast in recording spectra and does not required additional sampling devices. Compared to other on-line monitoring techniques, it overcomes the problem of time lags in collecting sample data and clogging in sampling devices.

This study suggests the set-up of experimental procedures that can be applied to other multicomponent polymerization systems. That is, solution polymerization runs should be conducted first for the identification of characteristic IR absorbances and off-line reaction monitoring so that its ability can be evaluated. Then polymerizations could be studied in-line using ATR-FTIR spectroscopy to follow the reaction kinetics.

Significant composition drift was evident in these VAc containing terpolymerizations and heterogeneous terpolymer was produced in the batch reactor. The typical approach to produce homogeneous terpolymers is to employ a semi-batch reaction mode. This ATR-FTIR probe could be used as a polymerization monitoring tool in a semi-continuous process to implement improved feedback process control strategies that would ensure a more homogeneous product.

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CHAPTER 5

CONCLUSIONS AND RECOMMMMENDATIONS

Conclusions and Recommendations

The ReactIR™ 1000 ATR-FTIR probe was used for the study of single and multicomponent polymerizations of BA/MMA/VAc. A series of bench scale solution and pilot scale emulsion polymerizations of terpolymers, and its associated homo- and copolymers was performed to evaluate the ability of ATR-FTIR spectroscopy to monitor monomer conversion and polymer composition.

In the first stage, the results obtained from off-line monitoring of BA, MMA, and VAc solution homopolymerizations and BA/MMA and MMA/VAc copolymerizations showed that the data acquired through ATR-FTIR spectroscopy gave good agreement with data from conventional gravimetric and ^{1}H-NMR analysis. A great deal of information on the characteristic absorbances of the monomers in this study was collected at this stage. This information was used for further application of the probe to in-line emulsion polymerization monitoring.

In the second stage, in-line monitoring of BA, MMA, and VAc batch emulsion homopolymerizations and BA/MMA and MMA/VAc copolymerizations demonstrated that this probe was well suited for polymerization reaction monitoring and kinetic investigations in aqueous media. The data acquired through ATR-FTIR spectroscopy showed good agreement with data from conventional gravimetric and ^{1}H-NMR analysis. Compared to many other on-line monitoring techniques, it overcame the problem of time lags in sample acquisition and analysis as well as the fouling of the sampling device. The work in the first part of this thesis on the determination of characteristic absorbance assignments for both monomers and polymers was found to be helpful in the application of the ATR-FTIR probe to in-line emulsion polymerization monitoring.

Finally, experimental procedures were set-up and used for the more complicated case of BA/MMA/VAc terpolymerization monitoring. The data acquired through ATR-FTIR spectroscopy again showed good agreement with data from conventional gravimetric and ^{1}H-NMR analysis in either toluene solvent or aqueous media.

These experimental procedures can be applied to other multicomponent polymerization systems. That is, solution polymerization runs should be conducted first for the identification of characteristic IR absorbances and off-line reaction monitoring. Then, polymerizations could be studied in-line using ATR-FTIR spectroscopy to follow the reaction kinetics.

Significant composition drift was evident in the VAc containing multicomponent polymerizations and thus, heterogeneous co- or terpolymers were produced in the batch reactions. These findings should have an impact on our ability to implement improved process control strategies on polymer systems that exhibit large composition drift. That is, the ATR-FTIR probe could be used as a polymerization monitoring tool in a semi-continuous process to implement improved feedback process control strategies that would ensure a more homogeneous product.

In parallel to the evaluation of the ATR-FTIR probe, the incorporation of solvent effects on kinetic model parameters for BA and VAc resulted in improved predictions of conversion, polymer composition and molecular weight averages. Model predictions were in reasonably good agreement with the experimental results.

From current studies, we can see there are still improvements that can be made on the kinetic model predictions, polymerization reaction monitoring and polymerization process control in the future. This future work forms part of the following recommendations:

1. In solution polymerization experiments, the kinetic model predictions of MMA and BA/MMA runs were in good agreement with the experiment results. For the VAc containing system at high conversion, improved parameter estimates or alternative models may be required to incorporate the solvent on VAc-containing polymerizations.
2. Kinetic models for single and multicomponent emulsions polymerization of BA/MMA/VAc have been developed by Dubé et al. (1997). Model predictions on monomer conversions, polymer composition, molecular weights, and particle size in emulsion polymerization processes should be investigated and compared to the experimental data in the future.
3. The multicomponent polymerizations of VAc-containing systems are prone to composition drift in batch reactors. They should be conducted in a semi-batch reaction mode to produce more homogeneous polymer products. In the semi-continuous process, the ATR-FTIR probe could be used for polymerization monitoring to improve process control strategies for producing homogeneous polymers.
4. The temperature variation inside the 5L pilot scale reactor might affect the reaction itself or the probe measurement and thus affect the accuracy of the monomer conversion estimates from the IR probe. Improvements to the temperature control program should be made to ensure an isothermal reaction.

Alternatively, steps should be taken to incorporate the effect of temperature on the results.

5. Impurities within the polymerization of BA/MMA/VAc systems can have a significant effect on production rates as well as product quality. Under the developed monitoring procedures using the ATR-FTIR probe, these polymerizations can be tracked in-line to acquire process knowledge that will lead to the improvement of our understanding of impurity effects.
6. The developed monitoring procedures using the ATR-FTIR probe can be evaluated on polymerizations of other systems. Further more, a host of chemical reactions other than polymerization might be monitored.

APPENDIX

Sample calculations

Emulsion polymerization

BA/MMA/VAc terpolymerization run BMV6

Let 1 denote BA, 2 denote MMA, and 3 denote VAc, respectively.

1. Reaction recipe

Monomer feed: m_1=200.0g, m_2=300.0g, m_3=500.0g

Other ingredients: m_{water}=1800.0g, m_{SDS}=60.0g, m_{APS}=4.0g, m_{NaHCO_3}=4.0g, m_{CTA}=11.0g

Total mass: 2879.0g

Monomer mole fraction f_i: $f_i = \dfrac{\dfrac{m_i}{M.W._i}}{\sum_{i=1}^{3} \dfrac{m_i}{M.W._i}}$

Given $M.W._1$=128.1706 g/mol, $M.W._2$=100.117 g/mol, $M.W._3$=86.0902 g/mol

$\therefore f_1 = 0.15, \quad f_2 = 0.29, \quad f_3 = 0.56$

Monomer moles n_i:

$$n_1 = \frac{m_1}{M.W._1} = \frac{200.0}{128.1706} = 1.561 mol, \; n_2 = 2.996\text{mol}, \; n_3 = 5.808\text{mol}$$

Monomer weight fraction w_i: $w_i = \dfrac{m_i}{Total\ mass}$

$\therefore w_1 = 0.0695, \quad w_2 = 0.104, \quad w_3 = 0.174$

Total weight fraction of monomers initially = $\dfrac{\sum_{i=1}^{3} m_i}{Total\, mass}$ = 0.347

Total weight fraction of other solids initially= $\dfrac{m_{SDS} + m_{APS} + m_{NaHCO_3} + m_{CTA}}{Total\, mass}$ = 0.027

2. Monomer conversion and polymer composition calculation by gravimetry and ^{1}H-NMR spectroscopy methods
At reaction time t = 40 min

(1) The overall conversion *X (wt%)*

$$\%\,solids=\frac{wt\ of\ dried\ sample\ and\ dish-wt\ of\ empty\ dish}{wt\ of\ dish\ and\ sample-wt\ of\ empty\ dish}=\frac{1.7563-1.263}{3.653-1.263}=0.2065$$

$$X(wt\%)=\frac{\%solids-wt\ fraction\ of\ other\ solids\ initially}{wt\ fraction\ of\ monomers\ initially}=\frac{0.2065-0.027}{0.347}=0.5155$$

(2) The terpolymer composition and individual monomer conversions

^{1}H-NMR spectroscopy data (peak integration): $S_1=0.321$, $S_2=1.000$, $S_3=0.079$

Terpolymer composition F_i:

$$F_1=\frac{S_1/2}{S_1/2+S_2/3+S_3}=0.2802$$

$$F_2=\frac{S_2/3}{S_1/2+S_2/3+S_3}=0.5819$$

$$F_3=\frac{S_3}{S_1/2+S_2/3+S_3}=0.1379$$

Individual monomer conversions x_i^*:

$$x_1=\frac{\dfrac{M.W._{\cdot1}\times f_1+M.W._{\cdot2}\times f_2+M.W._{\cdot3}\times f_3}{M.W._{\cdot1}\times F_1+M.W._{\cdot2}\times F_2+M.W.\times F_3}\times X\times F_1}{f_1}$$

$$=\frac{\dfrac{128.1706\times0.15+100.117\times0.29+86.0902\times0.56}{128.1706\times0.2802+100.117\times0.5819+86.0902\times0.1379}\times0.5155\times0.2802}{0.1506}=0.873$$

similarly,

$x_2=0.944$, $x_3=0.115$.

*For the individual monomer conversion, weight fraction or mole fraction conversion has the same value.

3. Monomer conversion and polymer composition calculation by IR spectroscopy methods

ATR-FTIR spectroscopy data

At reaction time t = 0 min

(peak height)$_1$ *= 0.007359, (peak height)*$_2$ *= 0.001694, (peak height)*$_3$ *= 0.006658*

At reaction time t = 40 min

(peak height)$_1$ *= 0.0015, (peak height)*$_2$ *= 0.000071, (peak height)*$_3$ *= 0.005586*

(1) Individual monomer conversions and terpolymer composition

Individual monomer conversions x_i:

$$x_1 = 1 - \frac{(\textit{peak height})_1 \textit{ at time } t = 40}{(\textit{peak height})_1 \textit{ at time } t = 0} = 1 - \frac{0.0015}{0.007359} = 0.796$$

similarly,
$x_2 = 0.958$, $x_3 = 0.0810$

Terpolymer compositions F_i:

$$F_i = \frac{n_i \times x_i}{\sum_{i=1}^{3} (n_i \times x_i)} \quad \therefore F_1 = 0.245,\ F_2 = 0.570,\ F_3 = 0.186$$

(2) The overall conversion X *(wt%)*

$$X(wt\%) = \sum_{i=1}^{3} \left(\frac{w_i}{\sum_{i=1}^{3} w_i} x_i \right) = 0.526$$