

Designing Safer, High-Performance Crosslinked Poly(ionic liquid)-Based Dielectrics

By

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Abstract

Next-generation organic and flexible electronics require dielectric materials that balance high electrical performance, processability, mechanical stability, and reduced environmental risk. This thesis investigates crosslinked poly(ionic liquid) (PIL)-based dielectrics for solution-processed electronic devices. A PIL system incorporating poly(ethylene glycol) methacrylate and 2-(dimethylamino)ethyl methacrylate was synthesized and crosslinked using bis(2-bromoethyl) ether to improve compatibility with multilayer fabrication. Electrochemical impedance spectroscopy was used to evaluate how polymer composition, alkylation level, crosslinking, and counterion selection affected metal–insulator–metal capacitor performance. Optimized materials achieved high capacitance density and high electrical double-layer onset frequency, enabling integration into a proof-of-concept organic thin-film transistor. Bromide and bis(trifluoromethanesulfonyl)imide counterions were further compared through electrochemical testing and zebrafish embryo toxicity assays. By linking structure, processing, dielectric response, and toxicity, this work demonstrates that PIL properties can be systematically tuned while supporting safer polymer dielectric design for emerging electronic applications and advancing a responsible materials development framework within materials research.

Résumé

Les dispositifs électroniques organiques et flexibles de la prochaine génération nécessiteront l'usage de diélectriques qui trouvent un équilibre entre haute performance, facilité de traitement, stabilité mécanique et un faible risque environnemental. Cette thèse porte sur des diélectriques à base de polymères liquides ioniques (« *poly(ionic liquid)* », PIL) réticulés et traités en solution pour la fabrication de dispositifs électroniques. Un PIL intégrant du méthacrylate de polyéthylène glycol et du méthacrylate de N,N-diméthylaminoéthyle a été synthétisé et réticulé à l'aide d'éther de bis(2-bromoéthyle) afin d'adapter le système à des procédés de fabrication multicouches. La spectroscopie d'impédance électrochimique a été utilisée pour évaluer l'effet de la composition du polymère, du niveau d'alkylation, de la réticulation et du choix du contre-ion sur la performance des condensateurs métal-isolant-métal. Les polymères optimisés atteignent une densité de capacité élevée et forment une double couche électronique à une fréquence élevée. Ces propriétés ont permis d'intégrer les polymères dans la fabrication d'un transistor organique à couches minces en guise de validation de principe. Le contre-ion a ensuite été substitué par du bromure ou du bistriflimidure afin d'évaluer l'effet de celui-ci sur la performance et la toxicité des polymères à l'aide d'essais électrochimiques et d'essais toxicologiques sur des embryons de dard-perches. En établissant des liens entre la structure, le traitement, les propriétés diélectriques et la toxicité des PIL, ces travaux démontrent que leurs propriétés peuvent être ajustées systématiquement tout en favorisant une conception plus sécuritaire des diélectriques à base de polymères pour de

nouvelles applications en électronique. Cela contribue à un cadre conceptuel plus écoresponsable en génie des matériaux.

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Abbreviations

- **¹H-NMR**: Proton nuclear magnetic resonance spectroscopy.
- **ACN**: Acetonitrile.
- **ACVS**: Animal Care and Veterinary Service.
- **AIC**: Akaike's Information Criterion.
- **BBEE**: Bis(2-bromoethyl) ether; used as the crosslinking agent.
- **BF₄⁻**: Tetrafluoroborate anion.
- **BGBC**: Bottom-Gate Bottom-Contact OTFT architecture.
- **BGTC**: Bottom-Gate Top-Contact OTFT architecture.
- **BMC**: Benchmark concentration; used in the EFSA BMC assessment tool.
- **Br⁻ / Br**: Bromide ion/counterion.
- **C**: Capacitance.
- **Cdl**: Double-layer capacitance.
- **CCAC**: Canadian Council on Animal Care.
- **CDCl₃**: Deuterated chloroform; NMR solvent.
- **CI**: Confidence interval.
- **Ci**: Capacitance density.
- **DCM**: Dichloromethane.
- **DI**: Deionized, as in DI water.
- **DMAEMA**: 2-(Dimethylamino)ethyl methacrylate.
- **DMF**: N,N-dimethylformamide.
- **DMSO**: Dimethyl sulfoxide.
- **EC₁₀**: Effect concentration associated with a 10% effect/response.
- **EC₅₀**: Effect concentration associated with a 50% developmental or sublethal effect response.
- **EDL**: Electrical double layer.
- **EFSA**: European Food Safety Authority.
- **EIS**: Electrochemical impedance spectroscopy.
- **ZFET: Zebrafish** Fish Embryo Acute Toxicity test.
- **FRA**: Frequency response analyzer.
- **GPC**: Gel permeation chromatography.
- **hpf**: Hours post-fertilization.
- **HPLC**: High-performance liquid chromatography.
- **IL**: Ionic liquid.
- **I_{on/off}**: On/off current ratio.
- **I_{SD}**: Source-drain current.
- **L:D**: Light:dark cycle.
- **LC₅₀**: Lethal concentration associated with 50% lethality.

- **MALS:** Multi-angle light scattering detector.
- **MIM:** Metal-insulator-metal.
- **M_n :** Number-average molecular weight.
- **MOSFET:** Metal-oxide-semiconductor field-effect transistor.
- **mP-D-S:** Short form for the synthesized poly(mPEGMA-DMAEMA-styrene) copolymer used in Chapter 3.
- **mPEGMA:** Poly(ethylene glycol) methyl ether methacrylate.
- **mPEGMA-DMAEMA-Sty:** Poly(poly(ethylene glycol) methyl ether methacrylate-ran-2-(dimethylamino)ethyl methacrylate-ran-styrene).
- **MMA:** Methyl methacrylate.
- **MS-222:** Tricaine methanesulfonate.
- **M_w :** Weight-average molecular weight.
- **N_2 :** Nitrogen gas.
- **NAM:** New Approach Methodology.
- **NMP:** Nitroxide-mediated polymerization.
- **NMR:** Nuclear magnetic resonance.
- **NSERC:** Natural Sciences and Engineering Research Council of Canada.
- **OECD:** Organisation for Economic Co-operation and Development.
- **OECD TG 203:** OECD Test Guideline 203.
- **OECD TG 236:** OECD Test Guideline 236.
- **OTFT:** Organic thin-film transistor.
- **PC:** Polycarbonate.
- **PCPF:** Poly(9,9'-didodecyl-fluorene-co-N-(2'-decyltetradecane)-carbazole).
- **PEG:** Poly(ethylene glycol).
- **PF_6^- :** Hexafluorophosphate anion.
- **PFAS:** Per- and polyfluoroalkyl substances.
- **PIL:** Poly(ionic liquid).
- **PROAST:** Benchmark dose/concentration modelling software used through the EFSA BMC tool.
- **PVD:** Physical vapour deposition.
- **PvDwSx-CLy-Az:** Polymer sample-code format: V, W, and X represent the percentage of mPEGMA, DMAEMA, and styrene, respectively; Y represents crosslinking percentage; Z represents alkylation percentage.
- **rpm:** Revolutions per minute.
- **sc-SWCNT / sc-SWCNTs:** Semiconducting single-walled carbon nanotube(s).
- **SEC:** Size exclusion chromatography.
- **SEC-MALS:** Size exclusion chromatography with multi-angle light scattering.
- **SG1:** Nitroxide mediator associated with BlocBuilder-MA/NMP chemistry.

- **SWCNT / SWCNTs**: Single-walled carbon nanotube(s).
- **TFSI⁻**: Bis(trifluoromethanesulfonyl)imide / bis(trifluoromethanesulfonyl)amide counterion.
- **TGBC**: Top-Gate Bottom-Contact OTFT architecture.
- **TGTC**: Top-Gate Top-Contact OTFT architecture.
- **VBBI⁺**: 1-(4-vinylbenzyl)-3-butylimidazolium cation unit used in a referenced polymer system.
- **V_{GS}**: Gate-source voltage.
- **V_{SD}**: Source-drain voltage.
- **V_T**: Threshold voltage.
- **Z**: Impedance.
- **Z' / Z'**: Real component of impedance.
- **Z'' / Z''**: Imaginary component of impedance.
- **ZFET**: Zebrafish embryo toxicity test.
- **Đ**: Dispersity.
- **κ**: Dielectric constant.
- **ε₀**: Permittivity of vacuum.
- **φ**: Phase angle.
- **ω**: Angular frequency.
- **σ**: Ionic conductivity; shown as s in some source equations/text.

1. Introduction

1.1 Overview

Rapid technological advancement has accelerated product turnover cycles, contributing to a growing consumer expectation that electronic devices are frequently replaced rather than repaired. This has driven a continuous rise in global electronics manufacturing year after year. As electronic manufacturing increases, so too does the amount of electronic waste (e-waste) generated annually. E-waste is composed of a collection of hazardous materials such as heavy metals, plastics, and other materials including other minerals, glass, and composite materials.^{1,2} Sixty-two billion kg of e-waste was generated in 2022 and only 22.3% was collected for recycling.¹ When e-waste enters the environment through improper disposal it can have several negative consequences²⁻⁴ including leaching of hazardous chemicals into the soil and groundwater, dispersal of airborne particulates, and entry into ecosystems through animal populations.^{3,4}

Approximately 27% of the 62 billion kg of global e-waste generated in 2022 consists of plastic materials.^{1,2} The plastic fraction is comprised of polycarbonate (PC), polypropylene, polyvinyl chloride, polyamide, polyethylene, and other epoxy resins.^{5,6} Despite the substantial contribution of plastics to the overall e-waste produced, a detailed compositional breakdown of plastic e-waste remains unknown.^{7,8} While the environmental impact of major plastic pollutants, such as fluorinated polymers that contribute to per and polyfluoroalkyl substances (PFAS)^{9,10} contamination, has received significant attention over the years, the effects of less common polymeric materials on the environment remain largely unexplored.⁹⁻¹² Within the broader category of plastic e-waste, polymer dielectrics deserve specific attention because of their widespread use in electronic components. In particular, current understanding and validation of the environmental impacts of polymer dielectrics designed as environmentally friendly alternatives is limited.^{8,13}

1.2 Polymer Dielectrics

Dielectric layers are key components in electronic devices, enabling capacitive energy storage and providing electrical insulation.^{14,15} They are widely used in transistors, capacitors, wire coatings, printed circuit boards, and sensors.¹⁴⁻¹⁶ Conventional dielectric materials are predominantly inorganic, with SiO₂ being among the most commonly used due to its excellent insulating properties, electrical performance, and well-established fabrication processes.^{15,16} However, inorganic dielectrics come with several limitations, including mechanical rigidity, and brittleness.^{14,16} One approach to addressing these limitations is the use of polymer dielectrics, which can achieve comparable insulating performance while also offering flexibility and improved compatibility with low-temperature, solution-based processing.¹⁴⁻¹⁶

A key feature of polymer dielectrics is that molecular design can be used to tailor a range of properties. Monomer selection and side chain chemistry can impact the material properties, the processability and recyclability, and the toxicity and end-of-life. These structural modifications of the polymer through monomer selection can offer tunability of design through both their mechanical properties and electrical performance (Figure 1.1).^{14,17} By varying the relative monomer composition, polymers can be selectively synthesized to target specific properties. The versatility of polymer design allows for precise changes of structure-property relationships, so that materials can be tailored to specific chemical and mechanical requirements. Among the properties critical to effective device operation, high capacitance is particularly important and may be optimized through monomer selection, functionalization, and related synthetic strategies. Side-chain chemistry strongly influences performance. Incorporation of polar groups can increase dipolar polarization and dielectric permittivity, whereas non-polar groups can improve solubility and solution processability.^{17,18} Side-chain length and structure play an important role in determining the thermal and mechanical properties of polymer dielectrics.^{17,18} Longer side chains generally reduce the glass-transition temperature by disrupting intermolecular packing and increasing chain mobility, thereby yielding softer materials.^{19,20} In addition, linear side chains can favour tighter packing and greater crystallinity, while branched side chains hinder efficient packing and therefore produce more flexible films.^{18,19} The chemical structure of side chains also influences the physical properties where functional groups like halogens, hydroxy, or carboxylic acid groups can also be used to tailor surface energy and hydrophobicity.^{11,12,18}

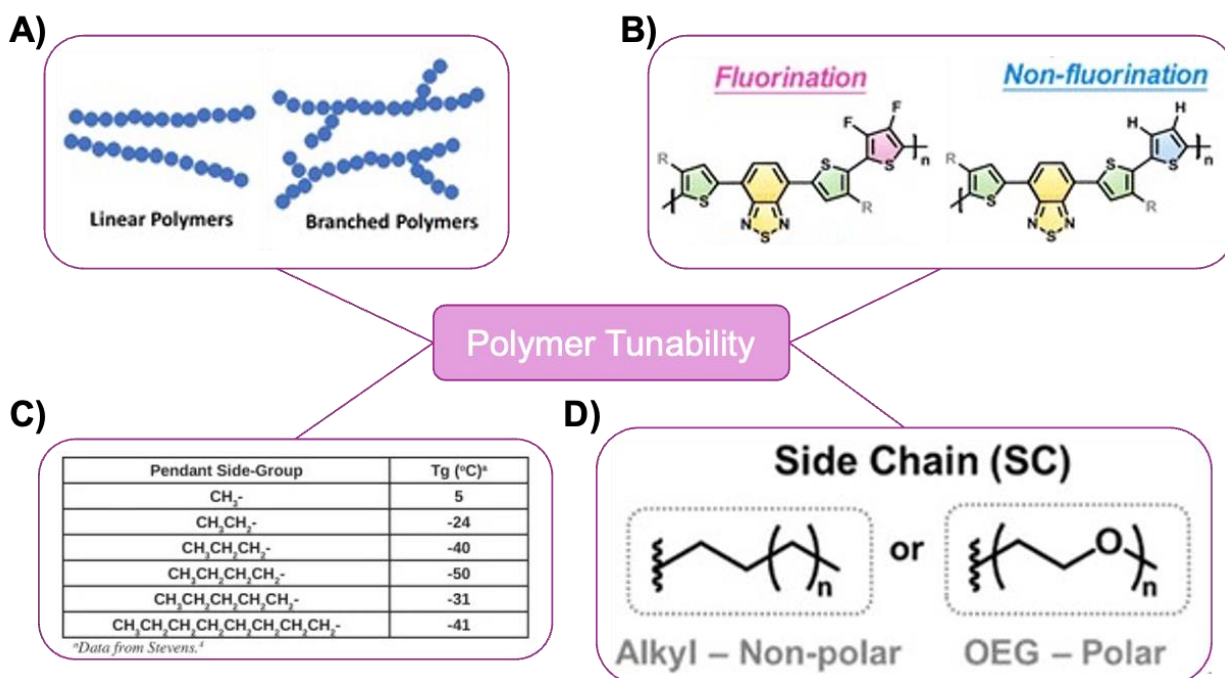


Figure 1.1 Potential tunability of polymers a) side-chain configuration²⁰, b) fluorinated species¹⁸, c) side-chain length¹⁹, d) side-chain polarity.¹⁷ Images reproduced from references 17-20 with permission.

1.3 Poly Ionic Liquids (PILs) as dielectrics

Ionic liquids (ILs) are molten salts that have been used as electrolytes in batteries, sensors, supercapacitors, transistors, and organic light-emitting diodes for their high capacitances, and highly tunable physical, chemical, and electrical properties.²¹⁻²³ Properties such as viscosity, hydrophobicity, solubility, and ionic conductivity can be adjusted through selection of the cation and anion.^{21,24} In ILs, the mobile ions migrate toward the electrode-electrolyte interface and form an electrical double layer (EDL).²³⁻²⁵ The interfacial charge accumulation is beneficial to dielectric materials as the formation is thickness independent.^{22,26,27} At the interface, ions interact with the electrode and create a layer of denser ion structuring.^{23,25} This results in the local interfacial properties contributing more to the overall material properties compared to the bulk leading to the thickness independence meaning that high capacitance can be achieved with thin layers.^{26,27} Despite these advantages, ILs are typically liquid at room temperature which can limit their use in solid-state devices due to issues such as leaks, challenges with encapsulation, and electrochemical doping.^{28,29}

PILs combine many of the advantages of ILs including high ionic conductivity, thermal stability, and non-flammability, while remaining solid materials (Figure 1.2).^{28,30,31} PILs are polymers that contain ionic groups in their structure along with free-moving counterions.^{28,30} In addition to the electrical performance benefits of the ILs, PILs offer the structural tunability and processability of polymer dielectrics.^{27,32} Their mechanical,

thermal, electrical, and physical properties can be tuned through (co)monomer selection, ionic species, and counterion.^{14,33,34} These choices influence chain interactions, flexibility, solubility, ionic conductivity, interfacial interactions, and dielectric performance.^{14,35,36} As a result, PILs are promising dielectric materials because they combine the interfacial charge-storage characteristics of ILs with the processability and tunable material properties offered through polymeric backbones.^{26,32,37}

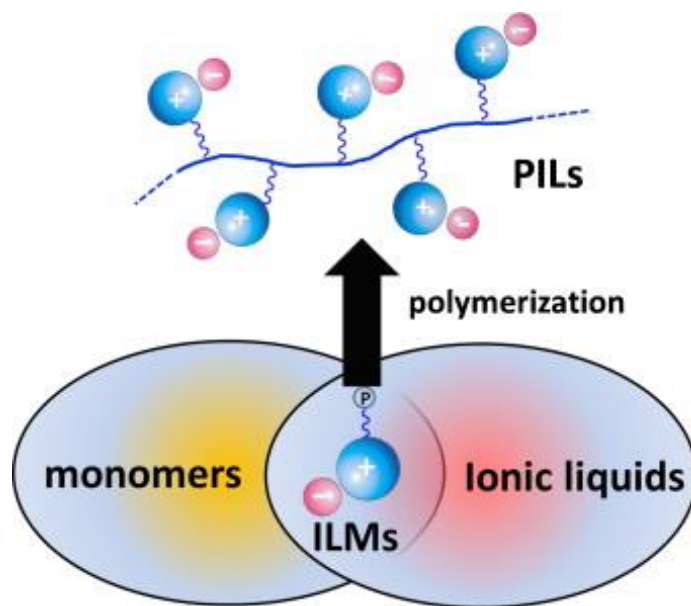


Figure 1.2 PILs from Ionic Liquids³⁰

1.3.1 Monomers incorporated into PILs

Typical monomers used in PILs commonly incorporate cationic moieties such as imidazolium, pyridinium and pyrrolidinium, and quaternary ammonium. Imidazolium is the most extensively researched cation used in PIL research, as it provides excellent thermal/chemical stability, supramolecular interactions, and high ionic conductivity.^{38,39} Pyridinium and pyrrolidinium are also popular for applications requiring specific electrochemical stability or mechanical performance.³⁸ Quaternary ammonium containing monomers are used for bio-compatible or cholinium-based ionic liquids.⁴⁰

Poly(ethylene glycol) methyl ether methacrylate (mPEGMA) is a methacrylate-functionalized, non-linear polyethylene glycol analogue.⁴¹ Upon polymerization, mPEGMA becomes flexible and is soluble in water and many organic solvents.⁴¹ These properties make mPEGMA particularly useful in applications requiring biocompatibility, hydration, and antifouling behaviour. It has been widely explored in hydrogels and tissue engineering, often as a comonomer in systems designed for drug delivery and cartilage regeneration. Additionally, mPEGMA-containing polymers have been used for surface modification to reduce protein adsorption and prevent biofouling.⁴² Its solubility and flexibility make mPEGMA relevant to PIL design, where these properties may help

improve processability, ion mobility, and compatibility with aqueous or biological environments. mPEGMA-based polymers have also been investigated as polyelectrolyte solutions for lithium-ion battery applications, further highlighting their relevance in ion-conducting polymer materials.⁴³

2-(Dimethylamino)ethyl methacrylate (DMAEMA) is a functional methacrylate monomer containing both a methacrylate group and a tertiary amine. The tertiary amine functionality provides opportunities for protonation, quaternization, or other post-polymerization modifications, making DMAEMA especially valuable for the synthesis of charged or stimuli-responsive polymers.^{44,45} DMAEMA-based polymers have been used in water treatment applications, including water clarification and sludge dewatering, as well as in drug delivery due to their tunable charge and reported biocompatibility.⁴⁵ They have also been incorporated into coatings to improve properties such as adhesion, hardness, and water resistance.⁴⁶ For PILs, DMAEMA is particularly significant because its amine group can be converted into an ionic functionality, allowing for the synthesis of PILs with adjustable charge density and ion-exchange behaviour.^{44,45}

Styrene is an aromatic vinyl monomer composed of a vinyl group attached to a benzene ring.⁴⁷ When polymerized, styrene forms polystyrene, a rigid and hydrophobic polymer widely used in plastics, synthetic rubber, insulation materials, fiberglass composites, and food packaging.⁴⁷ The aromatic ring in styrene creates stiffness and improves the thermal stability of the polymer backbone. In the context of PILs, styrene-based monomers are valuable because they can provide mechanical strength, structural rigidity, and control during polymerization.

1.3.2 Synthesis

Nitroxide Mediated Polymerization (NMP) is a controlled radical polymerization (CRP) technique that is used to synthesize polymers with low dispersities and predictable molecular weight.^{48,49} NMP is considered a scalable polymerization method as it does not require transition-metal catalysts, thiol-based chain-transfer agents, or strictly air-free conditions which other CRP approaches like atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) require.^{48,49} NMP is commonly referred to as a pseudo-living polymerization since the growing polymer chains are repeatedly activated and deactivated during propagation through a process known as reversible termination and the persistent radical effect.^{48,50}

In NMP, a unimolecular initiator, such as BlocBuilder-MA, is thermally initiated allowing for the propagating radical and stable free radical to form.^{48,49,51} The propagating radical reacts with the monomer units, while reversible coupling with the stable free radical temporarily deactivates chain growth. This repeated activation/deactivation of growing chains reduces irreversible termination which produces polymers with lower dispersity and preserves active chain ends.^{48,52} As a result, NMP enables synthesis of

well-defined homopolymers, random copolymers, and block copolymers with narrow dispersities of 1-1.5 and predictable molecular weights.^{48,53} The absence of metal catalysts and extensive post-polymerization purification makes NMP well-suited for electronics and biological applications as fewer process steps are required and fewer performance hindering contaminants are present.^{32,48}

Initially, NMP was used for polymerizing styrenics only as the radicals formed on styrene were relatively stable making the activation/deactivation reversible, controlled, and balanced.^{49,52} Advances in initiator design have expanded the range of monomers compatible with NMP to include acrylates and methacrylates.^{50,54–56} Currently, NMP can be used to synthesize homopolymers, random copolymers, and block co-polymers of styrenic, acrylate, acrylamides and methacrylate units.^{45,50,53,57} These advancements in initiator design enable the synthesis of a polymer containing mPEGMA, DMAEMA, and styrene to be easily synthesized via NMP. A small amount of styrene is incorporated to act as a controlling monomer, which allows for a controlled pseudo-living polymerization via NMP.⁴⁸ This versatility enables tunable polymer design, where monomer composition can be adjusted to control properties such as flexibility, polarity, and solubility.^{58,59}

1.4 Metal-insulator-metal (MIM) Capacitors and Electrochemical Impedance Spectroscopy (EIS)

The electrical properties of the PIL coatings are investigated using a metal-insulator-metal (MIM) capacitor configuration so that the resistive (impedance) behaviour of the material can be characterized.^{37,60} In this approach, the dielectric layer of interest is sandwiched between two electrodes deposited on a substrate. A two-probe setup is used for electrochemical impedance spectroscopy (EIS) measurements. The MIM capacitor architecture used for EIS analysis measures a total of 10 capacitor sites (Figure 1.3).

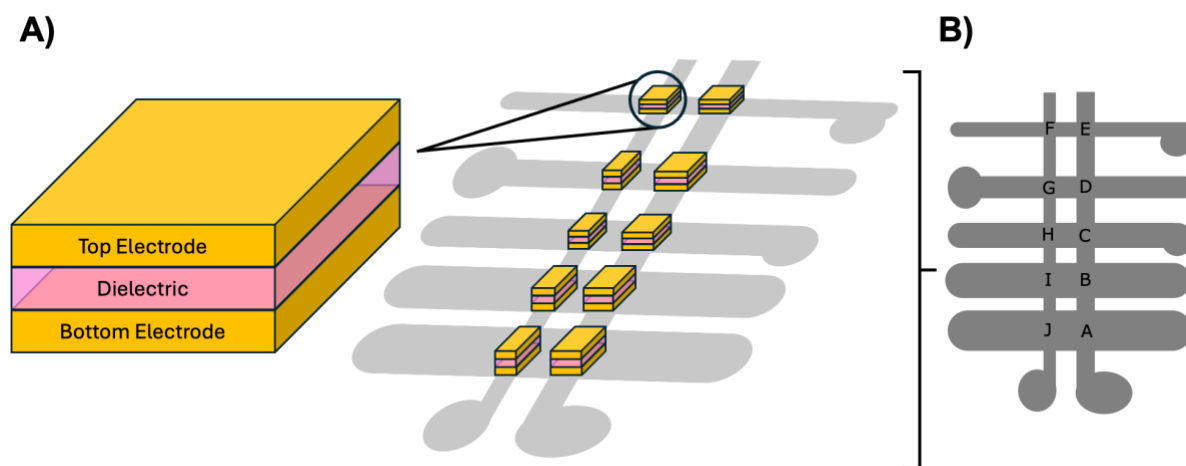


Figure 1.3 MIM capacitor architecture a) stack, b) sites

EIS probes the frequency-dependant electrical response by applying a potential to sweep frequency and measures the resulting impedance signal.^{61,62} The impedance (Z) is defined as the ratio of applied voltage (V) to measured current (I) in Equation 1.1:

$$Z(f) = \frac{V(f)}{I(f)} \quad (1.1)$$

EIS can distinguish between the resistance and capacitance contributions of a system.^{62,63} The capacitive component is frequency dependant, whereas the resistive component remains frequency independent. As a result, EIS provides insight on charge transport, dielectric polarization, intrinsic resistance, and diffusion resistance. EIS data is commonly expressed through a Nyquist plot which shows the real (Z') and imaginary (-Z'') component of the impedance (Figure 1.4). The equation for impedance can be represented by Equation 1.2.^{63,64}

$$Z = Z' + jZ'' \quad (1.2)$$

Bode plots can be used to identify information related to the frequency dependence (Figure 1.4). The Bode plot shows two graphs: phase angle (ϕ) as a function of frequency and $\log |Z|$ as a function of frequency. The frequency is plotted in a log scale on the x-axis while ϕ and $\log |Z|$ are plotted on separate y-axes. Phase angle (ϕ) is determined through Equation 1.3.

$$\phi = \tan^{-1} \left(\frac{Z''}{Z'} \right) \quad (1.3)$$

Nyquist and Bode plots provide a visual representation of EIS data to explain underlying electrical processes.⁶²⁻⁶⁴ For an ideal resistor, the Nyquist plot appears as a single point offset from the origin such that $Z''=0$ and Z represents the measured resistance (Figure 1.4a-c). The corresponding Bode plot exhibits a flat line for phase angle and $\log |Z|$ indicating constant values with respect to frequency (Figure 1.4b). For an ideal capacitor, the Nyquist plot shows a vertical line at the origin, while the Bode plot shows a constant ϕ of -90° and $\log |Z|$ linearly decreasing as frequency increases (Figure 1.4d-f).

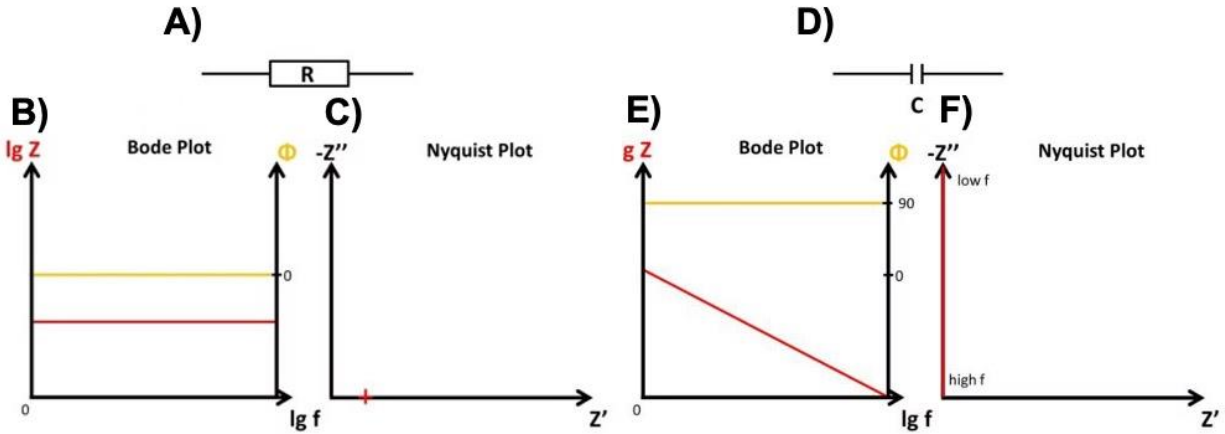


Figure 1.4 Ideal plots for EIS data,⁶³ a) ideal resistor circuit, b) ideal resistor Nyquist plot, c) ideal resistor Bode plot, d) ideal capacitor circuit, e) ideal capacitor Nyquist Plot, f) ideal capacitor. Image reproduced from reference 63 with permission.

In practice, MIM capacitors deviate from ideal behaviour and have both resistive and double layer capacitance contributions. The electrochemical response of MIM capacitors can be represented with Randles equivalent circuit, which includes an ohmic resistance (R_W) associated with the electrode resistance, in series with a capacitor (C_{dl}) and resistor (R_{ct}) in parallel. C_{dl} represents the double layer capacitance formed from the ions migrating to the electrode-dielectric interfaces.^{62,64} R_{ct} represents the charge-transfer resistance that arises from electron transfer across the interface. In many MIM capacitors, a Warburg impedance (Z_W), is also included in the Randles circuit to account for the mass-transfer for the diffusion effects that can be observed.^{62,64} Typically, Z_W appears as a 45° line following the semicircle observed in the Nyquist plot (Figure 1.5).

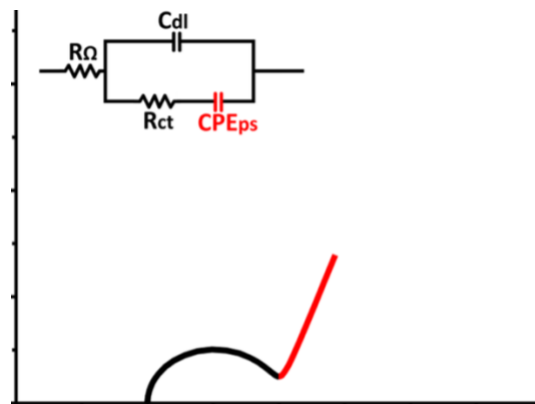


Figure 1.5 Typical experimental response of PIL MIM capacitor characterized with Randles equivalent circuit and related Nyquist plot.⁶² Image reproduced from reference 62 with permission.

These plots provide helpful insight regarding to the electrical processes occurring within the MIM capacitor. By measuring impedance, the resistive contributions associated with the material of interest can be quantified to characterize the electrical properties. The Nyquist and Bode Plots can be used to determine several other important parameters including dielectric constant (κ) capacitance (C), and capacitance density (C_i). Determining these electrical performance characteristics requires measuring the thickness of the dielectric layer and the capacitive site area in which the metal electrodes overlapped. Thickness measurements are obtained using profilometry and capacitive area is measured using an optical microscope. The κ , C , and C_i are calculated using the Z and Z'' portions of impedance, average film thickness (t), capacitor area (A), permittivity of vacuum (ϵ_0), and angular frequency (ω) in Equation 1.4, 1.5, and 1.6 respectively.

$$\kappa = \frac{t}{\omega A \epsilon_0} \left(\frac{Z''}{Z''^2 + Z'^2} \right) \quad (1.4)$$

$$C = \frac{\kappa \epsilon_0 A}{t} \quad (1.5)$$

$$C_i = CA \quad (1.6)$$

Additionally, ionic conductivity for dielectrics can be estimated using EIS-derived Z and Z'' portions of the impedance to calculate the bulk resistance from a circular fit of the semi-circle portion. From this the ionic conductivity (σ) of the films was determined using the average film thickness (t), bulk resistance (R_b), and capacitor area (A) described in Equation 1.7.

$$\sigma = \frac{t}{R_b A} \quad (1.7)$$

1.5 Organic Thin Film Transistors (OTFTs)

Transistors are fundamental components in electronics responsible for controlling the flow of current by functioning as an electrical switch.^{32,65} OTFTs are a type of transistor composed of several layers including a gate electrode, dielectric layer, an organic semiconducting layer, and source/drain electrodes.^{27,32} Applying a bias between the gate and source electrodes (V_{GS}) polarizes the dielectric layer which allows charge transport between the source and drain electrodes when a separate bias is applied across them (V_{SD}).

When characterizing the performance of an OTFT the following parameters are considered: threshold voltage (V_T), On/Off current ($I_{ON/OFF}$), and transconductance (g_m). V_T is described as the bias at which enough carriers are located at the interface of the semiconductor and dielectric for charge transport to occur from source to drain.

Regarding performance of the transistor, typically, a V_T close to zero is desirable. $I_{ON/OFF}$ represents the ratio between the current when the transistor is on and when the transistor is off. A higher $I_{ON/OFF}$ is desired for efficient switching. g_m represents the transistors' ability to efficiently convert input voltage change into an output current change. Maximizing g_m is desirable.

OTFTs are characterized using an output curve and a transfer curve. The output curve plots the V_{SD} to current (I_{SD}) obtained by sweeping V_{SD} while keeping V_{GS} constant. In the linear regime of an output curve I_{SD} increases proportionally with V_{SD} . In the saturation regime the I_{SD} plateaus. Transfer curves are obtained in the linear regime by sweeping V_{GS} and maintaining a constant V_{SD} . Parameters such as g_m , $I_{ON/OFF}$, and V_T were determined using the metal-oxide-semiconductor field-effect transistor (MOSFET) model as seen in Equations 1.8, 1.9, and 1.10.

$$I_{SD} = \frac{W}{L} \mu C_i \left(V_{GS} - V_T - \frac{V_{SD}}{2} \right) V_{SD} \quad (1.8)$$

$$g_m = \frac{dI_{SD}}{dV_{GS}} \quad (1.9)$$

$$I_{ON/OFF} = \frac{I_{ON}}{I_{OFF}} \quad (1.10)$$

When fabricating an OTFT, the architecture and deposition method matter as they can influence interface compatibility, material compatibility, and in turn performance. OTFTs can be fabricated in various device architectures depending on the intended application and the constraints associated with orthogonal processing (Figure 1.6). In multilayer organic devices, each layer is deposited orthogonally. Issues with deposition such as dissolving subsequent layers, or swelling should be considered. Solvent sensitivity is especially important to consider for dielectric layers as incompatibility between the substrate or the semiconductor can cause poor film formation leading to defects at the interface which causes poor performance. Crosslinking the dielectric material can help make layers more resistant to solvents and more compatible with orthogonal processing. Evaporation is another method of deposition which can be used to avoid solvent-related challenges in fabrication; however not all materials can be thermally evaporated.

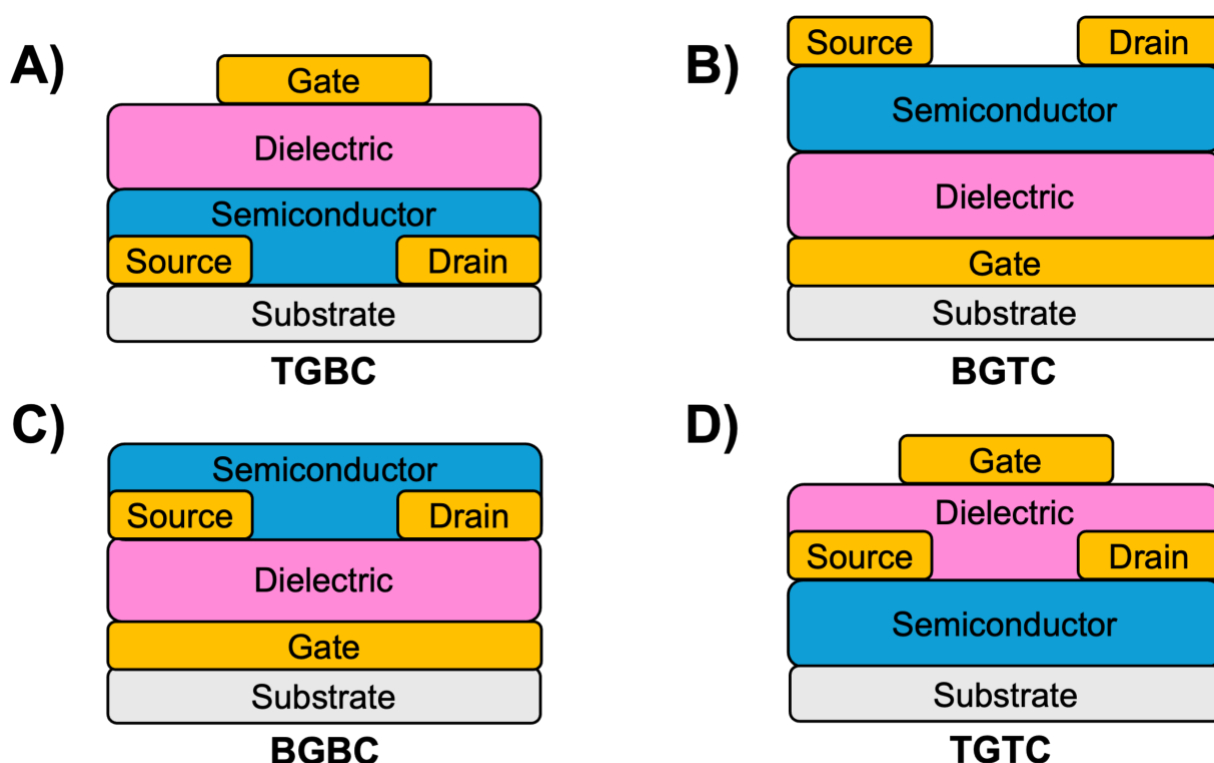


Figure 1.6 OTFT architecture cross-sections A) Top-Gate Bottom-Contact (TGBC), B) Bottom-Gate Top-Contact (BGTC), C) Bottom-Gate Bottom-Contact (BGBC), D) Top-Gate Top-Contact (TGTC).

For effective integration of OTFTs into flexible electronics, we require polymer dielectric materials with high electrical performance which also have the mechanical flexibility needed to allow for wearable and biocompatible applications.^{14,66} The tunability of polymer structure enables high dielectric performance while maintaining the necessary mechanical properties. However, for applications where the OTFTs are in contact with human skin or are expected to degrade into the environment, material selection must also account for health and safety, prioritizing non-toxic and environmentally benign polymers.^{67,68} It is therefore critical that we assess the toxicology of novel polymers as they are synthesized and not just when they are mass produced or after they enter into the environment.

1.6 Toxicology

Assessing the toxicology of new materials helps broaden the understanding of adverse effects on human health and the environment.^{67,69} Understanding the toxicological effect of materials enables informed regulation of new and emerging compounds to determine risks in safe handling, transport, and disposal protocols.^{67,70} Establishing high throughput protocols for toxicological effects allows for a proactive and safe by design approach.^{71,72} Improper disposal can contaminate the soil and

groundwater, air, and ecosystem, negatively impacting plants, animals, and humans.^{3,4} By developing proactive protocols, we will reduce the harm toward the environment as seen through the chlorofluorocarbons in aerosols depletion of the ozone layer.^{73,74} There is a need to move toward informed proactive preventative measures as opposed to the reactive approaches that have defined the past.^{68,75}

Previous methods of assessing toxicology of new materials exist which originally relied on invasive animal testing.^{76,77} A movement toward New Approach Methodologies (NAMs) focuses on modern, cost-effective, rapid screening of materials to provide insights on toxicity.^{68,75} NAMs aims to implement the 3Rs (replacement, reduction, and refinement) framework for minimizing animal testing to reduce pain and distress.^{76,77} Replacement prioritizes the use of use of computational models, in vitro testing via cell cultures, and microphysiological systems, and databases to limit animal use.⁷⁵⁻⁷⁷ When replacement is not possible, reduction can be applied to minimize the number of animals.⁷⁶ Refinement involves lessening or avoiding pain and distress to enhance animal wellbeing by implementing better housing, using humane endpoints, and implementing better anesthesia and analgesia.^{76,77} Using zebrafish embryos as a NAMs for medium-high throughput toxicity testing helps bridge in vivo and in vitro studies.^{68,71,78}

Zebrafish (*Danio rerio*) are a widely used model organism as they share similar genetic homology and biological pathways as humans.^{79,80} Zebrafish embryos are ideal for investigating toxicological effects as the embryo is translucent allowing for real-time observation.^{80,81} The embryo has a permeable membrane which allows direct chemical exposure.^{80,82} Zebrafish embryos can be obtained in large numbers and develop rapidly which allows for high-throughput chemical exposures.^{71,80} Typical growth of a zebrafish occurs rapidly; embryos remain intact within the chorion at 24 and 48 hours post fertilization (hpf). Most vital organs form between 48 and 72 hpf in which hatching is observed by 72 hpf.⁸³ After hatching, the embryos are considered eleutheroembryos that are free swimming but dependent on yolk sac reserves for ~96-120 hpf in which typical development of external structures including normal body axis elongation and defined head and tail structures can be observed (Figure 1.7).^{83,84}

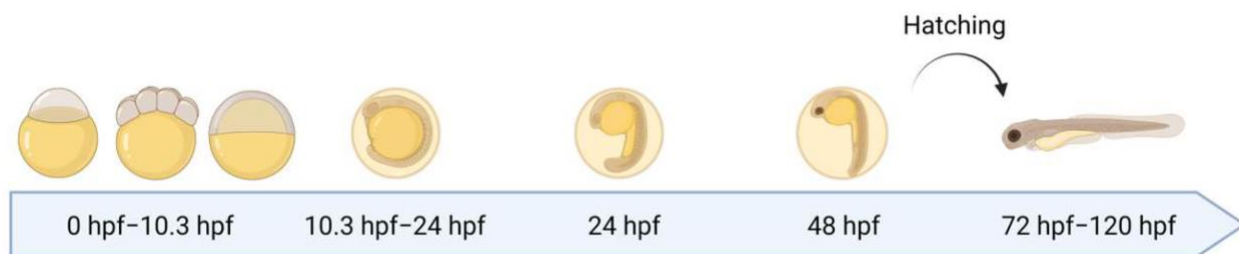


Figure 1.7 Normal Development of a Zebrafish Embryo to 120 hpf.⁸⁵ Image reproduced from reference 85 with permission.

1.6.1 ZFET

The zebrafish embryo acute toxicity (ZFET) test is a reproducible test method for rapidly assessing acute aquatic toxicity and has an established standardized protocol which makes it an efficient screening tool.^{72,86} By using zebrafish embryos, we can observe developmental changes, survival rates, and visible signs of toxicity within a short period of time, allowing for faster and more ethical testing compared to traditional methods that use adult fish.

Cumulative lethality and teratogenic endpoints based on Organisation for Economic Co-operation and Development (OECD) guideline No. 236 can be used to assess a compound's toxicological effects.^{82,86} When evaluating embryotoxicity key lethal endpoints include coagulation of the embryo where the embryo becomes opaque or white, lack of somite formation, and non-detachment of the tail from the yolk sac (Figure 1.8). These lethality endpoints help determine the LC₅₀ which is the concentration in which 50% of the exposed population died.^{86,87} The teratogenic endpoints considered included abnormal development of spine/tail such as tail shortening or tail bending, or presence of edema observed as fluid accumulation in the zebrafish.^{82,87,88} The sublethal indicators can lead to premature death of zebrafish and can be used to determine the EC₅₀ which is the concentration in which 50% of the exposed population were observed to have malformations.^{70,87}



Figure 1.8 Common malformations/lethality observed a) tail malformation, b) edema, c) dead hatched, d) dead unhatched, e) control.

Assessing developmental toxicity is important as embryos are highly sensitive to chemicals which allows for developmental endpoints to be used to reveal sublethal effects that might not be as obvious in adult systems.^{69,85,87} Optical microscopy can be used to directly visualize the development of embryos to identify malformations and score dead and malformed embryos.^{81,82} Typically, the presence or absence of morphological deformities is scored using a binary scoring system where clear structural abnormalities, such as tail curvature or edema, are deemed deformed/effected.^{69,82} A similar system is used to score dead versus alive embryos based on failure to hatch, opacity, and lack of motion are deemed dead.

1.7 Thesis Scope

This thesis will focus on the synthesis and characterization of solution-processed mPEGMA, DMAEMA, and styrene based PIL dielectrics for application in organic electronics specifically capacitors and transistors exploring the effect of monomer composition, alkylation, crosslinking, and counterion on the electrical performance and toxicity in the ZFET test. This thesis demonstrates how polymer design plays a crucial role in the performance of a dielectric as well as the effect on toxicity and demonstrates how standard high-throughput methods for screening new materials help provide information necessary for a safe-by-design approach for new materials.

In Chapter 2, the influence of monomer composition and percent alkylation on PIL dielectric performance was studied in capacitors and transistors using PILs composed of styrene, mPEGMA, and DMAEMA, with varied alkylation of the DMAEMA units. This chapter demonstrates how the monomer composition effected the electrical performance of the PIL through EIS data and film formation. It was determined that a 30:70 ratio of DMAEMA:mPEGMA was most optimal with high capacitance density and high EDL onset frequency. Additionally, this chapter shows how the percent alkylation had a greater impact on electrical performance with a more noticeable effect on EDL onset frequency and maximum capacitance density. In conclusion this chapter highlights the potential of PILs as high performing dielectrics.

In Chapter 3, we used a PIL of 50%, 46%, and 4% mPEGMA, DMAEMA, and styrene respectively to explore the effect of counterion and alkylation percentage on the electrical performance and toxicity. This chapter showed the effect of TFSI versus Br as a free-moving counterion and suggests that free-moving counterion size may explain why less alkylation was needed to achieve similar performance as determined through EIS. Additionally, this chapter studied the toxicity of the starting reagents, crosslinking agent, alkylation agent, and polymers synthesized to provide a complete picture of the toxicological effect. Toxicological effects were assessed using the ZFET method through microscopy and LC₅₀ and EC₅₀ concentrations.

In Chapter 4, the main findings of this thesis are summarized and future work towards automated testing to enhance high-throughput screening is discussed. This work involved adapting the existing OTFT autotester for capacitor-based measurements through redesigned shadow masks, custom substrate adapters, and a LabVIEW-controlled switching and EIS program, enabling 20 capacitor sites to be tested on a single substrate. Preliminary comparisons with manual measurements produced similar dielectric responses, although further validation across a broader range of materials is required before the platform can support reliable high-throughput electrical screening.

1.8 References

- (1) Balde, C. P.; Kuehr, R.; Yamamoto, T.; McDonald, R.; D'Angelo, E.; Althaf, S.; Bel, G.; Deubzer, O.; Fernandez-Cubillo, E.; Forti, V.; Gray, V.; Herat, S.; Honda, S.; Iattoni, G.; Khetriwal, D. S.; Luda di Cortemiglia, V.; Lobuntsova, Y.; Nnorom, I.; Pralat, N.; Wagner, M. *Global E-Waste Monitor 2024*; International Telecommunication Union (ITU) and United Nations Institute for Training and Research (UNITAR): Geneva/Bonn, 2024. https://ewastemonitor.info/wp-content/uploads/2024/12/GEM_2024_EN_11_NOV-web.pdf (accessed 2026-05-07).
- (2) *Electronic Waste (E-Waste)*. [https://www.who.int/news-room/fact-sheets/detail/electronic-waste-\(e-waste\)](https://www.who.int/news-room/fact-sheets/detail/electronic-waste-(e-waste)) (accessed 2026-02-27).
- (3) Parvez, S. M.; Jahan, F.; Brune, M.-N.; Gorman, J. F.; Rahman, M. J.; Carpenter, D.; Islam, Z.; Rahman, M.; Aich, N.; Knibbs, L. D.; Sly, P. D. Health Consequences of Exposure to E-Waste: An Updated Systematic Review. *Lancet Planet. Health* **2021**, 5 (12), e905–e920. [https://doi.org/10.1016/S2542-5196\(21\)00263-1](https://doi.org/10.1016/S2542-5196(21)00263-1).
- (4) Andeobu, L.; Wibowo, S.; Grandhi, S. Environmental and Health Consequences of E-Waste Dumping and Recycling Carried out by Selected Countries in Asia and Latin America. *Sustainability* **2023**, 15 (13), 10405. <https://doi.org/10.3390/su151310405>.
- (5) Elgarahy, A. M.; Eloffy, M. G.; Priya, A. K.; Hammad, A.; Zahran, M.; Maged, A.; Elwakeel, K. Z. Revitalizing the Circular Economy: An Exploration of E-Waste Recycling Approaches in a Technological Epoch. *Sustain. Chem. Environ.* **2024**, 7, 100124. <https://doi.org/10.1016/j.scenv.2024.100124>.
- (6) Das, P.; Gabriel, J.-C. P.; Tay, C. Y.; Lee, J.-M. Value-Added Products from Thermochemical Treatments of Contaminated E-Waste Plastics. *Chemosphere* **2021**, 269, 129409. <https://doi.org/10.1016/j.chemosphere.2020.129409>.
- (7) Castro, G.; Cobo, M.; Rodriguez, I. Identification of Hazardous Organic Compounds in E-Waste Plastic Using Non-Target and Suspect Screening Approaches. *Chemosphere* **2024**, 356, 141946. <https://doi.org/10.1016/j.chemosphere.2024.141946>.
- (8) Butturi, M. A.; Marinelli, S.; Gamberini, R.; Rimini, B. Ecotoxicity of Plastics from Informal Waste Electric and Electronic Treatment and Recycling. *Toxics* **2020**, 8 (4), 99. <https://doi.org/10.3390/toxics8040099>.
- (9) Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z. An Overview of the Uses of Per- and Polyfluoroalkyl Substances (PFAS). *Environ. Sci.: Processes Impacts* **2020**, 22 (12), 2345–2373. <https://doi.org/10.1039/D0EM00291G>.
- (10) Lohmann, R.; Cousins, I. T.; DeWitt, J. C.; Glüge, J.; Goldenman, G.; Herzke, D.; Lindstrom, A. B.; Miller, M. F.; Ng, C. A.; Patton, S.; Scheringer, M.; Trier, X.; Wang, Z. Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? *Environ. Sci. Technol.* **2020**, 54 (20), 12820–12828. <https://doi.org/10.1021/acs.est.0c03244>.
- (11) Duis, K.; Junker, T.; Coors, A. Environmental Fate and Effects of Water-Soluble Synthetic Organic Polymers Used in Cosmetic Products. *Environ. Sci. Eur.* **2021**, 33 (1), 21. <https://doi.org/10.1186/s12302-021-00466-2>.

- (12) *An Act Respecting the Interoperability of Health Information Technology and to Prohibit Data Blocking by Health Information Technology Vendors*; 2026.
<https://www.parl.ca/DocumentViewer/en/45-1/bill/S-5/first-reading> (accessed 2026-04-28).
- (13) Sahle-Demessie, E.; Mezgebe, B.; Dietrich, J.; Shan, Y.; Harmon, S.; Lee, C. C. Material Recovery from Electronic Waste Using Pyrolysis: Emissions Measurements and Risk Assessment. *J. Environ. Chem. Eng.* **2021**, 9 (2), 104943. <https://doi.org/10.1016/j.jece.2020.104943>.
- (14) Yang, Z.; Yue, D.; Yao, Y.; Li, J.; Chi, Q.; Chen, Q.; Min, D.; Feng, Y. Energy Storage Application of All-Organic Polymer Dielectrics: A Review. *Polymers* **2022**, 14 (6), 1160. <https://doi.org/10.3390/polym14061160>.
- (15) Li, H.; Zhou, Y.; Liu, Y.; Li, L.; Liu, Y.; Wang, Q. Dielectric Polymers for High-Temperature Capacitive Energy Storage. *Chem. Soc. Rev.* **2021**, 50 (11), 6369–6400. <https://doi.org/10.1039/D0CS00765J>.
- (16) Zhang, T.; Sun, H.; Yin, C.; Jung, Y. H.; Min, S.; Zhang, Y.; Zhang, C.; Chen, Q.; Lee, K. J.; Chi, Q. Recent Progress in Polymer Dielectric Energy Storage: From Film Fabrication and Modification to Capacitor Performance and Application. *Prog. Mater. Sci.* **2023**, 140, 101207. <https://doi.org/10.1016/j.pmatsci.2023.101207>.
- (17) Neu, J.; Oh, J.; Mukherjee, S.; Kashani, S.; Chen, Z.; Mardiev, S.; Ade, H.; You, W. Tuning the Solubility Parameters of Conjugated Polymers via Side-Chain Engineering for All-Polymer Solar Cells. *Chem. Mater.* **2025**, 37 (10), 3788–3798. <https://doi.org/10.1021/acs.chemmater.5c00515>.
- (18) Ding, J.-F.; Chen, G.-L.; Liu, P.-H.; Tseng, K.-W.; Wu, W.-N.; Lin, J.-M.; Tung, S.-H.; Wang, L.; Liu, C.-L. Enhancing the Thermoelectric Performance of Donor-Acceptor Conjugated Polymers through Dopant Miscibility: A Comparative Study of Fluorinated Substituents and Side-Chain Lengths. *J. Mater. Chem. A* **2024**, 12 (16), 9806–9816. <https://doi.org/10.1039/D4TA00032C>.
- (19) Christmas, B. K. *Understanding Glass Transition Temperature: Part 3*. <https://uvebtech.com/articles/2020/understanding-glass-transition-temperature-part-3/> (accessed 2026-05-07).
- (20) *Polymer (Matrix) Structure - A236*. <https://compositeskn.org/KPC/A236> (accessed 2026-05-07).
- (21) Ma, X.; Yu, J.; Hu, Y.; Texter, J.; Yan, F. Ionic Liquid/Poly(Ionic Liquid)-Based Electrolytes for Lithium Batteries. *Ind. Chem. Mater.* **2023**, 1 (1), 39–59. <https://doi.org/10.1039/D2IM00051B>.
- (22) Singh, M.; Manoli, K.; Tiwari, A.; Ligonzo, T.; Di Franco, C.; Cioffi, N.; Palazzo, G.; Scamarcio, G.; Torsi, L. The Double Layer Capacitance of Ionic Liquids for Electrolyte Gating of ZnO Thin Film Transistors and Effect of Gate Electrodes. *J. Mater. Chem. C* **2017**, 5 (14), 3509–3518. <https://doi.org/10.1039/C7TC00800G>.
- (23) Silvester, D. S.; Jamil, R.; Dobliger, S.; Zhang, Y.; Atkin, R.; Li, H. Electrical Double Layer Structure in Ionic Liquids and Its Importance for Supercapacitor, Battery, Sensing, and Lubrication Applications. *J. Phys. Chem. C* **2021**, 125 (25), 13707–13720. <https://doi.org/10.1021/acs.jpcc.1c03253>.
- (24) Vavra, S.; Ahlberg, E.; Martinelli, A. Charge Transfer and Electrical Double Layer of an Amphiphilic Protic Ionic Liquid in Bulk and When Confined in Nanochannels.

- Phys. Chem. Chem. Phys.* **2022**, 24 (39), 24469–24479.
<https://doi.org/10.1039/D2CP01634F>.
- (25) Neal, J. N.; Wesolowski, D. J.; Henderson, D.; Wu, J. Electric Double Layer Capacitance for Ionic Liquids in Nanoporous Electrodes: Effects of Pore Size and Ion Composition. *J. Mol. Liq.* **2018**, 270, 145–150.
<https://doi.org/10.1016/j.molliq.2017.10.128>.
 - (26) Peltekoff, A. J.; Brixi, S.; Niskanen, J.; Lessard, B. H. Ionic Liquid Containing Block Copolymer Dielectrics: Designing for High-Frequency Capacitance, Low-Voltage Operation, and Fast Switching Speeds. *JACS Au* **2021**, 1 (7), 1044–1056.
<https://doi.org/10.1021/jacsau.1c00133>.
 - (27) Peltekoff, A. J.; Hiller, V. E.; Lopinski, G. P.; Melville, O. A.; Lessard, B. H. Unipolar Polymerized Ionic Liquid Copolymers as High-Capacitance Electrolyte Gates for n-Type Transistors. *ACS Appl. Polym. Mater.* **2019**, 1 (11), 3210–3221.
<https://doi.org/10.1021/acsapm.9b00959>.
 - (28) Shaplov, A. S.; Marcilla, R.; Mecerreyes, D. Recent Advances in Innovative Polymer Electrolytes Based on Poly(Ionic Liquid)s. *Electrochim. Acta* **2015**, 175, 18–34. <https://doi.org/10.1016/j.electacta.2015.03.038>.
 - (29) Elwan, H. A.; Thimmappa, R.; Mamlouk, M.; Scott, K. Applications of Poly Ionic Liquids in Proton Exchange Membrane Fuel Cells: A Review. *J. Power Sources* **2021**, 510, 230371. <https://doi.org/10.1016/j.jpowsour.2021.230371>.
 - (30) Yuan, J.; Mecerreyes, D.; Antonietti, M. Poly(Ionic Liquid)s: An Update. *Prog. Polym. Sci.* **2013**, 38 (7), 1009–1036.
<https://doi.org/10.1016/j.progpolymsci.2013.04.002>.
 - (31) Lebedeva, O.; Kultin, D.; Kustov, L. Polymeric Ionic Liquids: Here, There and Everywhere. *Eur. Polym. J.* **2024**, 203, 112657.
<https://doi.org/10.1016/j.eurpolymj.2023.112657>.
 - (32) Tousignant, M. N.; Ourabi, M.; Niskanen, J.; Mirka, B.; Bodnaryk, W. J.; Adronov, A.; Lessard, B. H. Poly(Ionic Liquid) Dielectric for High Performing P- and N-Type Single Walled Carbon Nanotube Transistors. *Flex. Print. Electron.* **2022**, 7 (3), 034004. <https://doi.org/10.1088/2058-8585/ac928f>.
 - (33) Shim, Y.; Shim, M.; Kim, D. S. A Computer Simulation Study of Thermal and Mechanical Properties of Poly(Ionic Liquid)s. *Membranes* **2022**, 12 (5), 450.
<https://doi.org/10.3390/membranes12050450>.
 - (34) Rhoades, T. C.; Wistrom, J. C.; Johnson, R. D.; Miller, K. M. Thermal, Mechanical and Conductive Properties of Imidazolium-Containing Thiol-Ene Poly(Ionic Liquid) Networks. *Polymer* **2016**, 100, 1–9. <https://doi.org/10.1016/j.polymer.2016.08.010>.
 - (35) Keith, J. R.; Rebello, N. J.; Cowen, B. J.; Ganesan, V. Influence of Counterion Structure on Conductivity of Polymerized Ionic Liquids. *ACS Macro Lett.* **2019**, 8 (4), 387–392. <https://doi.org/10.1021/acsmacrolett.9b00070>.
 - (36) Niskanen, J.; Tousignant, M. N.; Peltekoff, A. J.; Lessard, B. H. Poly(Ethylene Glycol)-Based Poly(Ionic Liquid) Block Copolymers through 1,2,3-Triazole Click Reactions. *ACS Appl. Polym. Mater.* **2022**, 4 (3), 1559–1564.
<https://doi.org/10.1021/acsapm.1c01678>.
 - (37) McKillop, S.; Dickson, L. E.; Cho, H.; Ourabi, M.; Manion, J. G.; DiPalo, V.-A.; Lessard, B. H. High Conductivity Poly(Ionic Liquid)-Based Crosslinked Dielectrics.

- J. Mater. Chem. C* **2025**, *13* (39), 20085–20093.
<https://doi.org/10.1039/D5TC02087E>.
- (38) Shaplov, A. S.; Vlasov, P. S.; Lozinskaya, E. I.; Ponkratov, D. O.; Malyskhina, I. A.; Vidal, F.; Okatova, O. V.; Pavlov, G. M.; Wandrey, C.; Bhide, A.; Schönhoff, M.; Vygodskii, Y. S. Polymeric Ionic Liquids: Comparison of Polycations and Polyanions. *Macromolecules* **2011**, *44* (24), 9792–9803.
<https://doi.org/10.1021/ma2014518>.
- (39) Cao, W.; Tan, L.; Wang, H.; Yuan, J. Dual-Cationic Poly(Ionic Liquid)s Carrying 1,2,4-Triazolium and Imidazolium Moieties: Synthesis and Formation of a Single-Component Porous Membrane. *ACS Macro Lett.* **2021**, *10* (1), 161–166.
<https://doi.org/10.1021/acsmacrolett.0c00784>.
- (40) Isik, M.; Gracia, R.; Kollnus, L. C.; Tomé, L. C.; Marrucho, I. M.; Mecerreyes, D. Cholinium-Based Poly(Ionic Liquid)s: Synthesis, Characterization, and Application as Biocompatible Ion Gels and Cellulose Coatings. *ACS Macro Lett.* **2013**, *2* (11), 975–979. <https://doi.org/10.1021/mz400451g>.
- (41) Hussain, H.; Mya, K. Y.; He, C. Self-Assembly of Brush-Like Poly[Poly(Ethylene Glycol) Methyl Ether Methacrylate] Synthesized via Aqueous Atom Transfer Radical Polymerization. *Langmuir* **2008**, *24* (23), 13279–13286.
<https://doi.org/10.1021/la802734e>.
- (42) Yang, W. J.; Neoh, K.-G.; Kang, E.-T.; Teo, S. L.-M.; Rittschof, D. Stainless Steel Surfaces with Thiol-Terminated Hyperbranched Polymers for Functionalization via Thiol-Based Chemistry. *Polym. Chem.* **2013**, *4* (10), 3105–3115.
<https://doi.org/10.1039/C3PY00009E>.
- (43) Kang, Y.; Kim, H. J.; Kim, E.; Oh, B.; Cho, J. H. Photocured PEO-Based Solid Polymer Electrolyte and Its Application to Lithium–Polymer Batteries. *Journal of Power Sources* **2001**, *92* (1), 255–259. [https://doi.org/10.1016/S0378-7753\(00\)00546-2](https://doi.org/10.1016/S0378-7753(00)00546-2).
- (44) Lee, S. B.; Russell, A. J.; Matyjaszewski, K. ATRP Synthesis of Amphiphilic Random, Gradient, and Block Copolymers of 2-(Dimethylamino)Ethyl Methacrylate and n-Butyl Methacrylate in Aqueous Media. *Biomacromolecules* **2003**, *4* (5), 1386–1393. <https://doi.org/10.1021/bm034126a>.
- (45) Wang, Z. J.; Lessard, B. H.; Maric, M. Thermo-Responsive, UV-Active Poly(Phenyl Acrylate)-b-Poly(Diethyl Acrylamide) Block Copolymers. *eXPRESS Polym. Lett.* **2013**, *7* (12), 1020–1029. <https://doi.org/10.3144/expresspolymlett.2013.100>.
- (46) Stawarczyk, B.; Egli, R.; Roos, M.; Özcan, M.; Hämmerle, C. H. F. The Impact of in Vitro Aging on the Mechanical and Optical Properties of Indirect Veneering Composite Resins. *The Journal of Prosthetic Dentistry* **2011**, *106* (6), 386–398.
[https://doi.org/10.1016/S0022-3913\(11\)60153-4](https://doi.org/10.1016/S0022-3913(11)60153-4).
- (47) PubChem. *Styrene*. <https://pubchem.ncbi.nlm.nih.gov/compound/7501> (accessed 2026-05-28).
- (48) Lamontagne, H. R.; Lessard, B. H. Nitroxide-Mediated Polymerization: A Versatile Tool for the Engineering of Next Generation Materials. *ACS Appl. Polym. Mater.* **2020**, *2* (12), 5327–5344. <https://doi.org/10.1021/acsapm.0c00888>.
- (49) Maric, M. History of Nitroxide Mediated Polymerization in Canada. *Can. J. Chem. Eng.* **2021**, *99* (4), 832–852. <https://doi.org/10.1002/cjce.23989>.

- (50) Lessard, B. H.; Guillaneuf, Y.; Mathew, M.; Liang, K.; Clement, J.-L.; Gigmès, D.; Hutchinson, R. A.; Maric, M. Understanding the Controlled Polymerization of Methyl Methacrylate with Low Concentrations of 9-(4-Vinylbenzyl)-9H-Carbazole Comonomer by Nitroxide-Mediated Polymerization: The Pivotal Role of Reactivity Ratios. *Macromolecules* **2013**, *46* (3), 805–813. <https://doi.org/10.1021/ma3023525>.
- (51) Van Steenberge, P. H. M.; D'Hooge, D. R.; Reyniers, M. F.; Marin, G. B.; Cunningham, M. F. 4-Dimensional Modeling Strategy for an Improved Understanding of Miniemulsion NMP of Acrylates Initiated by SG1-Macroinitiator. *Macromolecules* **2014**, *47* (22), 7732–7741. <https://doi.org/10.1021/ma501746r>.
- (52) Lessard, B.; Marić, M. Nitroxide-Mediated Synthesis of Poly(Poly(Ethylene Glycol) Acrylate) (PPEGA) Comb-Like Homopolymers and Block Copolymers. *Macromolecules* **2008**, *41* (21), 7870–7880. <https://doi.org/10.1021/ma800603a>.
- (53) Lessard, B. H.; Savelyeva, X.; Maric, M. Smart Morpholine-Functional Statistical Copolymers Synthesized by Nitroxide Mediated Polymerization. *Polymer* **2012**, *53* (25), 5649–5656. <https://doi.org/10.1016/j.polymer.2012.10.020>.
- (54) Schmidt, A. C.; Turgut, H.; Le, D.; Beloqui, A.; Delaittre, G. Making the Best of It: Nitroxide-Mediated Polymerization of Methacrylates via the Copolymerization Approach with Functional Styrenics. *Polym. Chem.* **2020**, *11* (2), 593–604. <https://doi.org/10.1039/C9PY01458F>.
- (55) Tran, J.; Guegain, E.; Ibrahim, N.; Harrisson, S.; Nicolas, J. Efficient Synthesis of 2-Methylene-4-Phenyl-1,3-Dioxolane, a Cyclic Ketene Acetal for Controlling the NMP of Methyl Methacrylate and Conferring Tunable Degradability. *Polym. Chem.* **2016**, *7* (26), 4427–4435. <https://doi.org/10.1039/C6PY00778C>.
- (56) Ballard, N.; Aguirre, M.; Simula, A.; Agirre, A.; Leiza, J. R.; Asua, J. M.; Van Es, S. New Class of Alkoxyamines for Efficient Controlled Homopolymerization of Methacrylates. *ACS Macro Lett.* **2016**, *5* (9), 1019–1022. <https://doi.org/10.1021/acsmacrolett.6b00547>.
- (57) Ballard, N.; Aguirre, M.; Simula, A.; Leiza, J. R.; Van Es, S.; Asua, J. M. High Solids Content Nitroxide Mediated Miniemulsion Polymerization of N-Butyl Methacrylate. *Polym. Chem.* **2017**, *8* (10), 1628–1635. <https://doi.org/10.1039/C7PY00067G>.
- (58) Vancoillie, G.; Van Guyse, J. F. R.; Voorhaar, L.; Maji, S.; Frank, D.; Holder, E.; Hoogenboom, R. Understanding the Effect of Monomer Structure of Oligoethylene Glycol Acrylate Copolymers on Their Thermoresponsive Behavior for the Development of Polymeric Sensors. *Polym. Chem.* **2019**, *10* (42), 5778–5789. <https://doi.org/10.1039/C9PY01326A>.
- (59) Tajbakhsh, S.; Hajiali, F.; Maric, M. Nitroxide-Mediated Miniemulsion Polymerization of Bio-Based Methacrylates. *Ind. Eng. Chem. Res.* **2020**, *59* (19), 8921–8936. <https://doi.org/10.1021/acs.iecr.0c00840>.
- (60) DiPalo, V.-A.; Dickson, L. E.; Cruz, M.; Cho, H.; Lessard, B. H. Synthesis of Semibatch Copoly(Ionic Liquid) Solid-State Electrolytes for Organic Thin-Film Transistors. *ACS Appl. Polym. Mater.* **2025**, *7* (21), 14541–14549. <https://doi.org/10.1021/acsapm.5c02870>.
- (61) O'Rourke, M.; Duffy, N.; Marco, R. D.; Potter, I. Electrochemical Impedance Spectroscopy-A Simple Method for the Characterization of Polymer Inclusion

- Membranes Containing Aliquat 336. *Membranes* **2011**, 1 (2), 132–148.
<https://doi.org/10.3390/membranes1020132>.
- (62) Lazanas, A.; Prieto Simon, B. A Guide to Recognizing Your Electrochemical Impedance Spectra: Revisions of the Randles Circuit in (Bio)Sensing. *Sensors* **2025**, 25 (19), 6260. <https://doi.org/10.3390/s25196260>.
- (63) *Bode and Nyquist Plot*. <https://www.palmsens.com/knowledgebase-article/bode-and-nyquist-plot/> (accessed 2026-05-07).
- (64) Metrohm. *Electrochemical Impedance Spectroscopy (EIS) Part 4 - Equivalent Circuit Models*; Application Note AN-EIS-004.
<https://www.metrohm.com/content/dam/metrohm/shared/documents/application-notes/an-e/AN-EIS-004.pdf> (accessed 2026-05-07).
- (65) Rice, N. A.; Bodnaryk, W. J.; Mirka, B.; Melville, O. A.; Adronov, A.; Lessard, B. H. Polycarbazole-Sorted Semiconducting Single-Walled Carbon Nanotubes for Incorporation into Organic Thin Film Transistors. *Adv. Electron. Mater.* **2019**, 5 (1), 1800539. <https://doi.org/10.1002/aelm.201800539>.
- (66) Fang, L.; Zhou, Y.; Huang, Q. Ionic Conductive Textiles for Wearable Technology. *Adv. Mater.* **2025**, 2502140. <https://doi.org/10.1002/adma.202502140>.
- (67) Schuijt, L. M.; Peng, F.-J.; van den Berg, S. J. P.; Dingemans, M. M. L.; Van den Brink, P. J. (Eco)Toxicological Tests for Assessing Impacts of Chemical Stress to Aquatic Ecosystems: Facts, Challenges, and Future. *Sci. Total Environ.* **2021**, 795, 148776. <https://doi.org/10.1016/j.scitotenv.2021.148776>.
- (68) Tanguay, R. L. ToxPoint: The Indispensable Role of Zebrafish as a New Approach Methodology (NAM) in Toxicology. *Toxicol. Sci.* **2025**, 208 (1), 40–41.
<https://doi.org/10.1093/toxsci/kfaf121>.
- (69) Ball, J. S.; Tochwin, A.; Winter, M. J.; Trznadel, M.; Currie, R.; Wolton, K.; French, J. M.; Hetheridge, M. J.; Tyler, C. R. Determination of the Zebrafish Embryo Developmental Toxicity Assessment (ZEDTA) as an Alternative Non-Mammalian Approach for the Safety Assessment of Agrochemicals. *Reprod. Toxicol.* **2025**, 132, 108837. <https://doi.org/10.1016/j.reprotox.2025.108837>.
- (70) EFSA Scientific Committee; Hardy, A.; Benford, D.; Halldorsson, T.; Jeger, M. J.; Knutsen, K. H.; More, S.; Mortensen, A.; Naegeli, H.; Noteborn, H.; Ockleford, C.; Ricci, A.; Rychen, G.; Silano, V.; Solecki, R.; Turck, D.; Aerts, M.; Bodin, L.; Davis, A.; Edler, L.; Gundert-Remy, U.; Sand, S.; Slob, W.; Bottex, B.; Abrahantes, J. C.; Marques, D. C.; Kass, G.; Schlatter, J. R. Update: Use of the Benchmark Dose Approach in Risk Assessment. *EFSA J.* **2017**, 15 (1), e04658.
<https://doi.org/10.2903/j.efsa.2017.4658>.
- (71) Truong, L.; Simonich, M. T.; Tanguay, R. L. Better, Faster, Cheaper: Getting the Most Out of High-Throughput Screening with Zebrafish. In *High-Throughput Screening Assays in Toxicology*; Zhu, H., Xia, M., Eds.; Springer: New York, NY, 2016; pp 89–98. https://doi.org/10.1007/978-1-4939-6346-1_10.
- (72) Busquet, F.; Strecker, R.; Rawlings, J. M.; Belanger, S. E.; Braunbeck, T.; Carr, G. J.; Cenijn, P.; Fochtman, P.; Gourmelon, A.; Huebler, N.; Kleensang, A.; Knoebel, M.; Kussatz, C.; Legler, J.; Lillicrap, A.; Martinez-Jeronimo, F.; Polleichtner, C.; Rzodeczko, H.; Salinas, E.; Schneider, K. E.; Scholz, S.; van den Brandhof, E.-J.; van der Ven, L. T. M.; Walter-Rohde, S.; Weigt, S.; Witters, H.; Halder, M. OECD Validation Study to Assess Intra- and Inter-Laboratory Reproducibility of the

- Zebrafish Embryo Toxicity Test for Acute Aquatic Toxicity Testing. *Regul. Toxicol. Pharmacol.* **2014**, 69 (3), 496–511. <https://doi.org/10.1016/j.yrtph.2014.05.018>.
- (73) Mackenzie, J. S.; Jeggo, M. The One Health Approach-Why Is It So Important? *Trop. Med. Infect. Dis.* **2019**, 4 (2), 88. <https://doi.org/10.3390/tropicalmed4020088>.
- (74) Zhang, H.; Jiang, J.; Wang, H.; Zhou, Z.; Xie, Y.; Chen, Q.; Long, T. Early Warning of Aquatic Ecological Risks for Trifluoromethanesulfonimide: Oxidative Stress-Driven Adverse Outcome Pathways and Toxicity Thresholds. *J. Hazard. Mater.* **2025**, 499, 140246. <https://doi.org/10.1016/j.jhazmat.2025.140246>.
- (75) *Use of New Approach Methods (NAMs) in Risk Assessment*. <https://www.canada.ca/en/health-canada/services/chemical-substances/fact-sheets/use-new-approach-methods-risk-assessment.html> (accessed 2026-05-07).
- (76) Stokes, W. S. Animals and the 3Rs in Toxicology Research and Testing: The Way Forward. *Hum. Exp. Toxicol.* **2015**, 34 (12), 1297–1303. <https://doi.org/10.1177/0960327115598410>.
- (77) *Animal Use Alternatives (3Rs)*. <https://www.nal.usda.gov/animal-health-and-welfare/animal-use-alternatives> (accessed 2026-05-07).
- (78) Zhao, W.; Chen, Y.; Hu, N.; Long, D.; Cao, Y. The Uses of Zebrafish (*Danio Rerio*) as an in Vivo Model for Toxicological Studies: A Review Based on Bibliometrics. *Ecotoxicol. Environ. Saf.* **2024**, 272, 116023. <https://doi.org/10.1016/j.ecoenv.2024.116023>.
- (79) Gut, P.; Reischauer, S.; Stainier, D. Y. R.; Arnaout, R. Little Fish, Big Data: Zebrafish as a Model for Cardiovascular and Metabolic Disease. *Physiol. Rev.* **2017**, 97 (3), 889–938. <https://doi.org/10.1152/physrev.00038.2016>.
- (80) Ali, S.; Champagne, D. L.; Spaink, H. P.; Richardson, M. K. Zebrafish Embryos and Larvae: A New Generation of Disease Models and Drug Screens. *Birth Defects Res., Part C* **2011**, 93 (2), 115–133. <https://doi.org/10.1002/bdrc.20206>.
- (81) Volkov, M.; Machikhin, A.; Bukova, V.; Khokhlov, D.; Burlakov, A.; Krylov, V. Optical Transparency and Label-Free Vessel Imaging of Zebrafish Larvae in Shortwave Infrared Range as a Tool for Prolonged Studying of Cardiovascular System Development. *Sci. Rep.* **2022**, 12 (1), 20884. <https://doi.org/10.1038/s41598-022-25386-w>.
- (82) Hong, T.; Park, J.; Song, G.; Lim, W. Brief Guidelines for Zebrafish Embryotoxicity Tests. *Mol. Cells* **2024**, 47 (8), 100090. <https://doi.org/10.1016/j.mocell.2024.100090>.
- (83) Kimmel, C. B.; Ballard, W. W.; Kimmel, S. R.; Ullmann, B.; Schilling, T. F. Stages of Embryonic Development of the Zebrafish. *Dev. Dyn.* **1995**, 203 (3), 253–310. <https://doi.org/10.1002/aja.1002030302>.
- (84) Nipu, N.; Wei, L.; Hamilton, L.; Lee, H.; Thomas, J.; Mennigen, J. A. Methylene Blue at Recommended Concentrations Alters Metabolism in Early Zebrafish Development. *Commun. Biol.* **2025**, 8 (1), 120. <https://doi.org/10.1038/s42003-025-07471-8>.
- (85) Bondue, T.; Princiero Berlingiero, S.; van den Heuvel, L.; Levchenko, E. The Zebrafish Embryo as a Model Organism for Testing mRNA-Based Therapeutics. *Int. J. Mol. Sci.* **2023**, 24 (13), 11224. <https://doi.org/10.3390/ijms241311224>.
- (86) OECD. *Test No. 236: Fish Embryo Acute Toxicity (FET) Test*; OECD Guidelines for the Testing of Chemicals, Section 2; OECD Publishing: Paris, 2013.

https://www.oecd.org/content/dam/oecd/en/publications/reports/2013/07/test-no-236-fish-embryo-acute-toxicity-fet-test_g1g34036/9789264203709-en.pdf (accessed 2026-02-27).

- (87) Hedgpeth, B. M.; Redman, A. D.; Alyea, R. A.; Letinski, D. J.; Connelly, M. J.; Butler, J. D.; Zhou, H.; Lampi, M. A. Analysis of Sublethal Toxicity in Developing Zebrafish Embryos Exposed to a Range of Petroleum Substances. *Environ. Toxicol. Chem.* **2019**, 38 (6), 1302–1312. <https://doi.org/10.1002/etc.4428>.
- (88) Duan, J.; Yu, Y.; Shi, H.; Tian, L.; Guo, C.; Huang, P.; Zhou, X.; Peng, S.; Sun, Z. Toxic Effects of Silica Nanoparticles on Zebrafish Embryos and Larvae. *PLoS One* **2013**, 8 (9), e74606. <https://doi.org/10.1371/journal.pone.0074606>.

2. High Conductivity Poly(ionic liquid)-Based Crosslinked Dielectrics

This chapter was published in the journal “Journal of Materials Chemistry C”: Sophia McKillop, Laura E. Dickson, Hyungjun Cho, May Ourabi, Joseph G. Manion, Vittoria DiPalo, Benoît H. Lessard* High Conductivity Poly(ionic liquid)-Based Crosslinked Dielectrics

2.1 Context

Our group has previously investigated how polymer architecture can influence EDL formation and lower threshold voltage in OTFTs. We explored the use of random copolymers and block copolymers as a way to tune the mechanical properties of the polymers. Crosslinking is another versatile strategy to increase mechanical stiffness which can be easier to troubleshoot and optimize through tuning ratios/amounts. In this work we characterize a new series of crosslinkable poly(mPEGMA-DMAEMA-Styrene) copolymer based PILs in MIM and OTFTs. We demonstrated how monomer composition, percentage of alkylation, and amount of crosslinker can impact film formation, EDL onset frequency, ionic conductivity, and maximum capacitance density in capacitors.

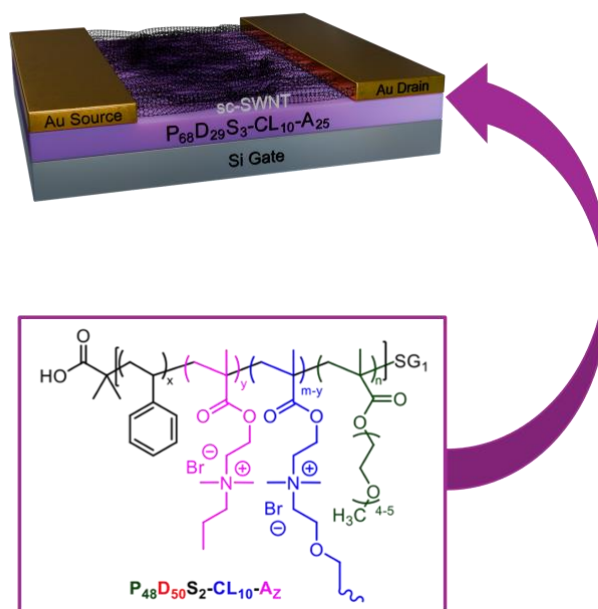
2.2 Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. S.M: Conceptualization, Investigation, Formal Analysis, Writing-Original Draft. S.M. conducted experimental work and data analysis, as well as wrote the initial draft of the manuscript. L.E.D: Investigation, Methodology, Data Curation, Writing-Review and Editing. L.E.D assisted in the OTFT and Raman spectroscopy experiments and analysis. H.C: Investigation, Writing-Review and Editing. H.C assisted in synthesis. M.O: Investigation, Writing-Review and Editing. M.O. assisted in Raman spectroscopy experiments, and SWCNT preparation. J.G.M: Visualization, Writing-Review and Editing. J.G.M created OTFT figures. V.D: Analysis, Writing-Reviewing and Editing. V.D contributed to Raman spectroscopy analysis and manuscript editing. B.H.L: Funding acquisition, Supervision, Project administration, Conceptualization, Writing-Review and Editing. B.H.L. acquired funding, managed supervision, directed the study, and assisted in editing the manuscript.

2.3 Abstract

A wide range of emerging applications, from organic electronics to batteries, require dielectrics that offer high ionic conductivity while preventing hazards associated with dielectric leakage. Poly(ionic liquids) (PILs) are a promising class of materials which combine the high ionic conductivity of ionic liquids with the desirable mechanical properties of polymers. When developing thin film devices, the deposition of multiple layers may necessitate orthogonal processing, limiting the choice of processing solvents and device designs. We developed a PIL that can be crosslinked with bis(2-bromoethyl)

ether (BBEE) for use as a high performing dielectric. Electrochemical impedance spectroscopy was used to establish structure-property relationships. We investigated the effect of poly(ethylene glycol) methacrylate ion conducting monomers (mPEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) composition in the PIL, the alkylation percentage in the PIL, and amount of BBEE to PIL on corresponding metal-insulator-metal capacitor performance. A balance between polymer composition and BBEE composition was identified to produce a robust PIL dielectric with a high electrical double layer (EDL) onset frequency and high capacitance density that is a solid at room temperature. The optimized PIL dielectric was then successfully integrated into a proof-of-concept solution-processed organic thin-film transistor (OTFT).



2.4 Introduction

Flexible and lightweight electronics for smart packaging offer considerable potential for addressing pressing global issues, such as reducing the estimated 1.3 billion tonnes of food wasted annually.¹ Realizing the widespread application of these technologies hinges on optimizing both the design of the electronic components, such as transistors, and the materials from which they are made. Organic thin-film transistors (OTFTs) are logic-gate operators or electrical switches that use carbon-based semiconductors such as conjugated polymers or small molecules in place of traditional inorganic semiconductors. OTFTs enable the design of complex circuits and sensors that can be integrated into flexible substrates and have the potential for low energy processing and large area manufacturing. For lightweight electronics and smart packaging, low operating voltage devices with reduced power consumption are critical to reduce the size

of the required batteries.^{2,3} Electrolyte-based or ionic liquid-based dielectric materials, where mobile ions can migrate during device operation to form electrical double layers (EDLs), enable thickness-independent capacitance that reduces device operating voltage (V_T).⁴ However, during OTFT operation, the ions will diffuse into the semiconductor, slowing their return to the dielectric and leading to slow operating speed in a phenomenon known as electrochemical doping.^{5,6} Electrolytes are also often toxic and can leak or leach into the environment upon device damage or at their end of life, limiting their use in applications where the device is in contact with skin or food.⁶⁻⁸

Poly(ionic liquids) (PILs) combine solid-state operation at room temperature with high ionic conductivity. In OTFTs they also limit electrochemical doping as the ions are bound to the polymer chain, preventing their diffusion into the semiconductor.⁹⁻¹¹ It is known that a PIL's molecular structure and architecture influence both the electrical and mechanical properties of the resulting thin film.¹² Block copolymer-based PILs can be an effective strategy to optimize switching speed, ionic conductivity, capacitance density, and mechanical stability by utilizing one block as a soft ion conducting domain while another provides a mechanically stable matrix.^{13,14} While promising, many of the monomers and block copolymers used to create these dielectrics require multi-step, overly-complex synthetic routes. Additionally, PIL dielectrics can be limited by moisture sensitivity, suboptimal dielectric constants, and challenges with interfacial adhesion.

In previous work by Tousignant et al., we prepared poly(2-(methacryloyloxy)ethyl trimethylammonium bis(trifluoromethylsulfonyl)azanide) based PILs for use in OTFTs through a simple quaternization and subsequent counterion exchange at copolymers prepared with commercially available 2-(dimethylamino)ethyl methacrylate (DMAEMA) monomers.¹⁵ By varying the copolymer composition, we could influence the frequency-dependent EDL formation which would dictate the operating frequency of the corresponding OTFTs. The corresponding devices were promising but suffered from low conductivity due to the polymers' high glass transition temperatures (T_g). Furthermore, these polymers required orthogonal solvent processing to minimize redissolution and washing off of the PIL during semiconductor deposition.

To overcome these issues, we designed a new PIL composed of poly(ethylene glycol) methyl ether methacrylate (mPEGMA) ion-conducting monomers and DMAEMA. We synthesized a series of statistical copolymers containing styrene and different ratios of mPEGMA and DMAEMA to enable optimization of both the T_g and ionic conductivity. The incorporation of mPEGMA reduces the T_g of the resulting polymers and confers ion transport capabilities to the PIL. DMAEMA contributes reactive sites which can undergo quaternization with di-bromo alkanes, leading to ionically charged species and enables crosslinking of the deposited film. Styrene was used to improve control of the polymerization.¹⁶ The mPEGMA:DMAEMA ratios deployed in polymer syntheses were 10/90, 30/70, 50/50, 70/30 and 90/10. A portion of Poly(mPEGMA-DMAEMA-Sty) was

partially alkylated by reacting the DMAEMA functional groups with n-propyl bromide for an alkylation range of 0 to 95%.

Abbasi et al. recently investigated the crosslinking of copolymers with 50 mol% of DMAEMA comonomer content, using bis(2-bromoethyl) ether (BBEE) in quaternation reactions. They found that a BBEE to DMAEMA ratio of 0.1 was sufficient to provide a high degree of crosslinking.¹⁷ In this study we leveraged this crosslinking reaction to form robust PIL dielectrics for applications in organic electronics. BBEE content and mPEGMA:DMAEMA ratios in the copolymers were correlated to demonstrate that crosslinking of the thin films is directly related to EDL formation and conductivity of the capacitors. The crosslinked dielectrics were then integrated into bottom-gate top-contact (BGTC) OTFTs using semiconducting single-walled carbon nanotubes (sc-SWCNTs) as an air-stable semiconductor.

2.5 Results and Discussion

2.5.1 Synthesis and Crosslinking Poly(mPEGMA-DMAEMA-Sty)

A series of poly(mPEGMA-DMAEMA-Sty) copolymers, denoted by P_vD_wS_x-CL_y-A₀, were synthesized via nitroxide-mediated polymerization (NMP) using BlocBuilder-MA and styrene with different compositions of mPEGMA and DMAEMA (**Table 2.1**). NMP is an effective technique for the synthesis of well-defined polymers, providing narrow molecular weight distribution which can be integrated into organic electronics without the need for excessive purification beyond precipitation.^{15,18–21} Using unimolecular initiators, NMP can synthesize a wide range of styrenics, acrylamides, acrylates and even methacrylates under specific conditions.^{22–26} Copolymer composition and molecular weight characteristics such as number average molecular weight (M_n) and polymer dispersity ($\bar{D}$) are in **Table S1 and S2, Figure S1-S3**. The polymers were synthesized to a M_n of 31 to 67 kg/mol with a $\bar{D}$ between 1.6–2.2, which is typical for NMP of methacrylates when copolymerized with a small amount of styrene (**Table 2.1, Figure 2.1**).^{17,27,28} Similar crosslinking chemistry with poly(mPEGMA-DMAEMA-Sty) was performed within the range of 0 to 0.5 molar equivalents of BBEE to DMAEMA.

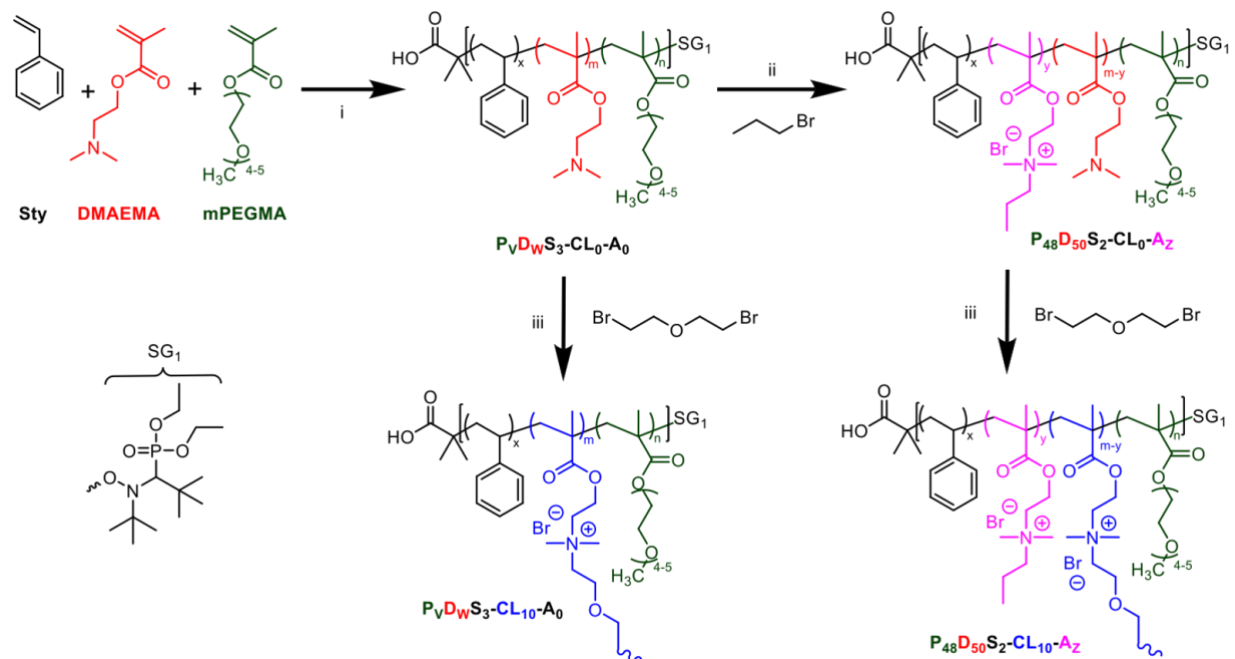


Figure 2.1 Synthesis pathway of poly(mPEGMA-DMAEMA-Sty), i) dissolved in toluene SG1 (BlocBuilder-MA) and put in an ice bath for 15 min bubbled with N_2 then heated and stirred at $90^\circ C$ for 60 min, ii) alkylation reaction of $P_{50} D_{48} S_2 - CL_0 - A_0$ by adding desired molar equivalent of n-propyl bromide in acetonitrile stirring at room temperature overnight, iii) crosslinking reaction of polymer with desired molar equivalent of BBEE to DMAEMA coated and annealed at $80^\circ C$ overnight and increased to $100^\circ C$ for 1 hour.

Raman spectroscopy was used to study the crosslinked films of $P_{50} D_{48} S_2 - CL_Y - A_0$. The polymer was dissolved in acetonitrile (ACN) and combined with 0 to 0.9 molar equivalents of BBEE per DMAEMA unit (**Figure 2.1iii**). The polymer/BBEE solution was used to cast films and then heated to crosslink the polymer chains. The Raman spectra between 2700 to 3200 cm^{-1} was examined as the methyl and methylene functional groups associated with the quaternization reaction are found within this region.²⁹⁻³¹ The extent of crosslinking in the films upon quaternization with BBEE was monitored through the $-CH_3$ vibration in the $-N(CH_3)_2$ group of DMAEMA.³¹ The Raman peak associated with this group has been assigned to the peak occurring at $\sim 2825\text{ cm}^{-1}$ which is within the known literature range.^{29,31} In the films of $P_{50} D_{48} S_2 - CL_0 - A_0$, which have 0 molar equivalents of BBEE there is a peak at $\sim 2825\text{ cm}^{-1}$ that downshifts to 2820 cm^{-1} with increasing crosslinker content (**Figure 2.2F**). This peak shift is consistent with a change in the environment and with a mix of species (reacted/unreacted).

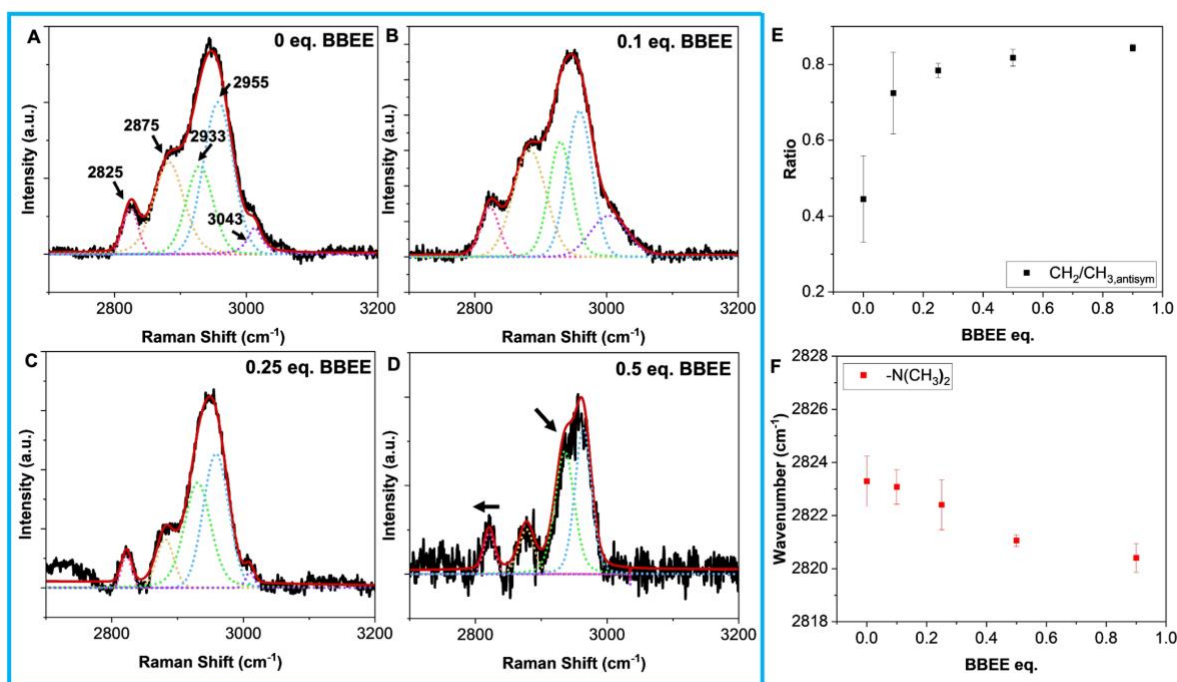


Figure 2.2 (A–D) Raman spectra $P_{50}D_{48}S_2\text{-CL}_Y\text{-A}_0$ crosslinking (black) together with the results of fitted peak analysis (red) of five mixed Lorentz-Gaussian functions (pink, yellow, green, blue, and purple) for 0, 0.1, 0.25, and 0.5 molar eq. BBEE to DMAEMA monomer units. (E) $-\text{CH}_2/-\text{CH}_3$, antisymmetric ratio and (F) $-\text{N}(\text{CH}_3)_2$ Raman peak wavenumber plotted against BBEE molar equivalent to DMAEMA monomer units.

Other notable Raman signals appear at 2875 cm^{-1} and 2965 cm^{-1} , corresponding to the $-\text{CH}_3$ symmetric and antisymmetric vibrations of the DMAEMA monomer, respectively. Weaker bands are observed at 2933 cm^{-1} and 3043 cm^{-1} , associated with $-\text{CH}$ and $-\text{CH}_2$ vibrations.^{29–31} In particular, the $-\text{CH}_2$ vibration was monitored because the quaternization reaction is expected to increase the Raman intensity of this signal due to the methylene units of the BBEE crosslinker. Consistent with this, increasing crosslinker content produces a shoulder near 2933 cm^{-1} , suggesting a growing concentration of these units upon quaternization (**Figure 2.2A–D**). This trend is further supported by the rising intensity ratio of the $-\text{CH}_2$ to $-\text{CH}_3$ antisymmetric stretches, which increases with BBEE content until plateauing at 0.5 equivalents of BBEE per DMAEMA monomer unit (**Figure 2.2E**).³³ As the films are vacuum annealed above the boiling point of BBEE prior to their evaluation we anticipate that any residual, unreacted crosslinker should be removed and therefore the observed increase in methylene signal is likely due to increased crosslinking or partial alkylation by BBEE.

Increasing the molar equivalent BBEE content past 0.5 appears to result in stabilization of the $-\text{N}(\text{CH}_3)_2$ peak wavenumber and $-\text{CH}_2/-\text{CH}_3$, antisymmetric ratio, indicating that the degree of crosslinking is limited to this molar equivalent of crosslinker

(**Figure S4**). Indeed, exceeding 0.5 eq. crosslinker can result in crosslinking suppression due to the bifunctionality of BBEE. Therefore, we surmise the high degree of quaternization associated with high crosslinker content inhibits further quaternization, resulting in minimal shifts to the Raman spectra.

2.5.2 Crosslinked PIL Dielectrics Integration in MIM Capacitors

MIM capacitors were fabricated on glass substrates using $P_vD_wS_x-CL_y-A_z$ sandwiched between gold electrodes and were characterized by impedance spectroscopy over a frequency range of 10^6 to 0.01 Hz. **Figure 2.3A** demonstrates the capacitance density as a function of frequency as well as the phase angle as a function of frequency. The mPEGMA:DMAEMA ratio in the polymer ranges from 10/90, 30/70, 50/50, 70/30, and 90/10. Each film was crosslinked with 0.1 equivalent of BBEE to DMAEMA present in the polymer for film formation. $P_{87}D_{10}S_3-CL_{10}-A_0$ (~90% mPEGMA) had poor film formation which led to non-functional sites which is why it is not presented in **Figure 2.3A**.

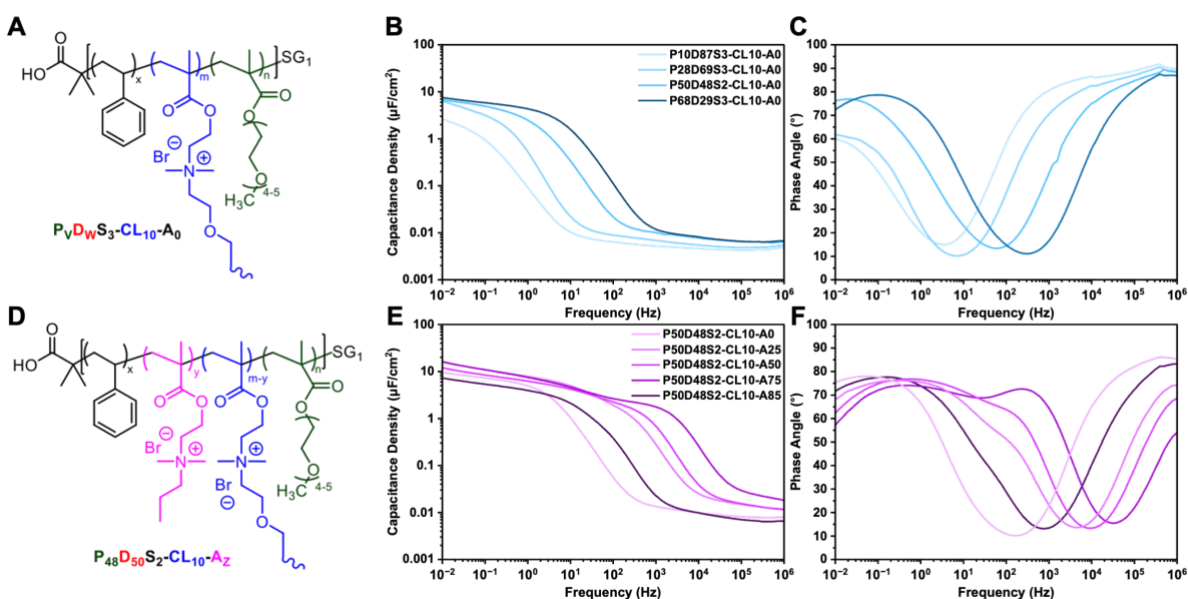


Figure 2.3 Electrochemical impedance spectroscopy (EIS) results of the effect of changing mPEGMA to DMAEMA ratio in $P_vD_w-CL_{10}-A_0$ and effect of alkylation of $P_{48}D_{50}S_2-CL_{10}-A_z$. A) chemical structure of $P_vD_wS_x-CL_{10}-A_0$, B) capacitance density vs frequency of mPEGMA to DMAEMA ratio in $P_vD_wS_x-CL_{10}-A_0$, C) phase angle vs frequency of mPEGMA to DMAEMA ratio in $P_vD_wS_x-CL_{10}-A_0$. The legend used in B) is the same for C). Results for $P_{87}D_{10}S_3-CL_{10}-A_0$ was not included due to poor film formation. D) chemical structure of $P_{50}D_{48}S_2-CL_{10}-A_z$, E) capacitance density vs frequency of effect of alkylation of $P_{50}D_{48}S_2-CL_{10}-A_z$, F) phase angle vs frequency of effect of alkylation of $P_{50}D_{48}S_2-CL_{10}-A_z$. The legend used in E) is the same for F).

Electrolytic dielectric material performance is characterized by EDL formation and the frequency at which the EDL onset occurs. The initial decrease in the phase angle, from 90° to 45°, is indicative of the dipolar relaxation regime where the polymer chains start aligning with the applied electric field. This was used to identify when the EDL began to form and was reported as the EDL onset frequency.³⁴ As the phase angle decreases below 45° the ionic relaxation regime is entered, in which mobile ions begin migrating towards the positively or negatively charged electrodes.³⁴ The phase angle increases above 45° again, which is considered the EDL formation regime, and the EDL is considered fully formed once the phase angle curve plateaus.³⁴ This phenomenon was used to evaluate the corresponding PILs. An overall trend was observed: as the mPEGMA content increased the capacitance density and the EDL onset frequency both increased (**Figure 2.3A**). The EDL onset was found to shift from 1.26×10^1 to 7.94×10^2 Hz as the mPEGMA content increased in the polymers (**Table 2.1**). Additionally, the maximum capacitance density at 0.01 Hz was found to increase from 2.63 to 7.57 $\mu\text{F}/\text{cm}^2$ as the mPEGMA content increased (**Table 2.1, Figure 2.3**). The capacitance density of P₁₀D₈₇S₃-CL₁₀-A₀, P₂₈D₆₉S₃-CL₁₀-A₀, P₅₀D₄₈S₂-CL₁₀-A₀, and P₆₈D₂₉S₃-CL₁₀-A₀ are comparable to other PIL MIM capacitors, as previously reported by our group, where Tousignant et al. investigated PILs containing 35 and 62 mol% DMAEMA in copolymers with methyl methacrylate resulting in capacitance densities of 1.15 and 1.78 $\mu\text{F}/\text{cm}^2$, respectively.¹⁵ In another study by our group, Peltekoff et al. explored PIL block copolymers of poly(styrene)-*b*-poly(1-(4-vinylbenzyl)-3-butyylimidazolium-*random*-poly(ethylene glycol) methyl ether methacrylate) (poly(S)-*b*-poly(VBBI⁺[X]-*r*-PEGMA)) with varying PEGMA/VBBI⁺ ratios and three different mobile anions (where X = TFSI⁻, PF₆⁻ or BF₄⁻), and reported capacitance densities between 0.02 to 10 $\mu\text{F}/\text{cm}^2$. Similarly, Peltekoff et al. found that capacitance density and EDL onset frequency increased with mPEGMA content.¹³ PILs with higher mPEGMA content stored more charge and were better able to align the dipoles in response to an electric field, allowing for ions to move quickly and easily through the film.¹³ The same is thought to explain the results presented in **Table 2.1**, however, increasing the mPEGMA content past 70% led to non-functional devices highlighting the tradeoff between high performance and overall device reliability.

Table 2.1 Summary of characteristics of capacitors of P_vD_wS_x-CL_y-A_z including EDL onset, capacitance density at 0.01 Hz and 10 Hz, and conductivity.

Film ID	EDL onset (Hz)	C _i at 10 Hz (μF/cm ²)	C _i at 0.01 Hz (μF/cm ²)	Conductivity (S/cm)
P ₁₀ D ₈₇ S ₃ -CL ₀ -A ₀	12.589	0.01±0.003	2.63±1.86	2.26 × 10 ⁻¹⁰
P ₂₈ D ₆₉ S ₃ -CL ₁₀ -A ₀	25.116	0.02±0.013	6.34±2.67	1.12 × 10 ⁻⁹
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₀	501.19	1.02±0.201	9.35±1.31	1.50 × 10 ⁻⁸
P ₆₈ D ₂₉ S ₃ -CL ₁₀ -A ₀	794.33	1.57±0.762	7.57±1.39	2.68 × 10 ⁻⁸
P ₈₇ D ₁₀ S ₃ -CL ₁₀ -A ₀	—	—	—	—
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₂₅	15849	4.89±0.779	15.49±2.93	3.33 × 10 ⁻⁷
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₅₀	31623	4.15±0.817	11.90±2.24	8.20 × 10 ⁻⁷
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₇₅	125890	4.56±0.760	16.08±3.08	1.58 × 10 ⁻⁵
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₈₅	2511.9	2.08±0.822	7.18±1.39	7.03 × 10 ⁻⁸
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₉₅	—	—	—	—

The ionic conductivity of P₁₀D₈₇S₃-CL₁₀-A₀, P₂₈D₆₉S₃-CL₁₀-A₀, P₅₀D₄₈S₂-CL₁₀-A₀, and P₆₈D₂₉S₃-CL₁₀-A₀ was determined using parallel resistance of the circular fit from the semi-circle portion of the Nyquist plot from EIS (**Figure S5**). The conductivities were determined to be between 2.26×10⁻¹⁰ to 2.68×10⁻⁸ S/cm (**Table 2.1**). The results presented in this work are comparable to other previously reported results by Tousignant et al. with conductivities between 3.47×10⁻¹¹ to 1.78×10⁻⁹ S/cm and Peltekoff et al. with conductivities ranging from 5.8×10⁻¹¹ to 3.4×10⁻⁷ S/cm.^{13,15}

The amount of BBEE to DMAEMA was investigated to optimize the crosslinker to DMAEMA in the copolymer through integration into capacitors (**Figure S6, Table S4**). Various ratios of BBEE to DMAEMA, from 0, 0.1, 0.25, and 0.5 molar equivalents of BBEE, were explored. The capacitance density at 10 Hz was found to be 0.02 and 2.08 μF/cm², for 0 and 0.1 molar equivalents of BBEE respectively. Molar equivalents of BBEE ≥0.25 led to poor film formation and significant roughness (**Tables S2 and S3**) resulting in inconsistent and non-functional devices. Therefore, the optimal amount of crosslinker was determined to be 0.1 molar equivalents of BBEE relative to DMAEMA for all samples.

2.5.3 Pre-Alkylation of DMAEMA Containing Polymers

We surmised that with 0.1 molar equivalents of BBEE to DMAEMA, not all the DMAEMA units are being reacted and would still be available for functionalization. Therefore, we performed an alkylation step to P₅₀D₄₈S₂-CL₀-A₀ by quaternization of the initial polymer with n-propyl bromide prior to crosslinking in the films (**Table 2.1, Figure 2.1**). The ratio of n-propyl bromide was calculated to different molar ratios relative to the available DMAEMA sites. The percentage of alkylation to DMAEMA in the polymers ranges from 0, 25, 50, 75, and 85%. We wanted to only partially alkylate copolymers to ensure that DMAEMA sites were still available for crosslinking with BBEE. For example,

P₅₀D₄₈S₂-CL₁₀-A₉₅, alkylation of 95% was attempted and did not produce functional devices which we associated to full quaternization and in turn a lack of crosslinking sites available in the polymers, leading to soft sticky films. Capacitors were therefore fabricated with the alkylated series of polymers, with the addition of 0.1 molar equivalent of BBEE (**Figure 2.3B**, **Table 2.1**). Overall, the pre-alkylation led to an increase in capacitance density, EDL onset frequency, and conductivity compared to the non-alkylated polymers with identical compositions (**Table 2.1**). The EDL onset was found to range from 5.01×10^2 to 1.26×10^5 Hz and the maximum capacitance density at 0.01 Hz was found to be 16.08 $\mu\text{F}/\text{cm}$ for P₅₀D₄₈S₂-CL₁₀-A₇₅; which is roughly 9 times greater than previous reports using alkylated P(DMAEMA-*ran*-MMA) PIL dielectrics and roughly 54 times greater than poly(S)-*b*-poly(VBBI⁺[X]-*r*-PEGMA), block copolymers with TFSI⁻.^{13,15}

The ion conductivity for P₅₀D₄₈S₂-CL₁₀-A_x was determined from a circular fit of the semi-circle portion of the Nyquist plot from EIS. Ionic conductivity was determined to be as high as 1.59×10^{-5} S/cm for P₅₀D₄₈S₂-CL₁₀-A₇₅, which is roughly 8000 times greater than previous reports using alkylated P(DMAEMA-*ran*-MMA) PIL dielectrics and roughly 46 times greater than poly(S)-*b*-poly(VBBI⁺[X]-*r*-PEGMA), block copolymers with TFSI⁻; clearly demonstrating the importance of alkylation of the pre-polymer prior to crosslinking (**Table 2.1**).^{13,15} An overall trend was observed: an increase in alkylation up to 75% of the DMAEMA repeat units led to an increase in ion conductivity, capacitance density, and EDL onset frequency. This suggests that the increase in alkylation up to this point allows for more ions to be present within the film, which leads to more ions moving through the film. This enables the film to form the EDL at higher frequencies and possess higher conductivity. The alkylation of the prepolymer leads to the quaternization of the crosslinkable DMAEMA repeat units and as a result minimal crosslinking occurs. This may give the film the high conductivity desired as well as flexibility due to crosslinking suppression due to the alkylation. Moreover, the capacitance density of devices made with P₅₀D₄₈S₂-CL₁₀-A₈₅ decreased dramatically, suggesting that the resulting films were too soft and there were insufficient DMAEMA sites for the crosslinking reaction to take place. Beyond the performance metrics, the film's properties differ in that its polymer matrix contains fewer partially crosslinked crosslinkers and presumably little to no free DMAEMA sites. The tertiary amine groups of free DMAEMA are electron-donating moieties known to impact OTFT device performance.³⁵

2.5.4 Crosslinked PIL Dielectric Integration into Organic Thin Film Transistors

Proof-of-concept *n*-type bottom gate top contact (BGTC) OTFTs were fabricated on Si substrates with P₆₈D₂₉S₃-CL₁₀-A₂₅ as the dielectric layer combined with sc-SWCNT as the semiconducting layer. Sc-SWCNTs were selected due to their good mechanical properties, solution processability, and high current carrying capacity leading to OTFTs with high transconductance even when paired with polymer dielectrics.^{18,35–39} Recently, we integrated sc-SWCNTs into proof-of-concept OTFTs using bio-based dielectrics such

as chitosan.^{40,41} Building on this, the crosslinked PILs from this work were integrated into OTFTs, with characteristic output and transfer curves reported in **Figure 2.4**.

When operating in the linear regime, device performance from 5 devices was found to have an average $I_{ON/OFF}$ of 25, a V_T of $1.65 \text{ V} \pm 0.10$, and a transconductance of $0.72 \mu\text{S} \pm 0.41$ (**Table S6**). The devices showed negligible hysteresis, but significant leakage current is observed, which is attributed to the high conductivity of the $\text{P}_{68}\text{D}_{29}\text{S}_3\text{-CL}_{10}\text{-A}_{25}$ dielectric.⁴² The V_T of the $\text{P}_{68}\text{D}_{29}\text{S}_3\text{-CL}_{10}\text{-A}_{25}$ with sc-SWCNT OTFTs presented in this work is comparable to other PIL dielectrics integrated into OTFTs, reporting operating voltages of 1.1 to 2.7 V for P(METATFSI-MMA) PILs when paired with sc-SWCNTs.¹⁵ Similarly, when 1-butyl-3-methylimidazolium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethanesulfonyl)imide and mPEGMA based block copolymers are paired in a device with sc-SWCNTs, a threshold voltage of 1.1 V can be achieved.⁴³ However, in both cases, device architecture was top gate bottom contact while this study integrates the material in a bottom gate top contact architecture. This highlights the orthogonal processability of these dielectric materials and illustrates that incorporating crosslinking in the dielectric layer enables more flexibility in the fabrication of OTFTs.

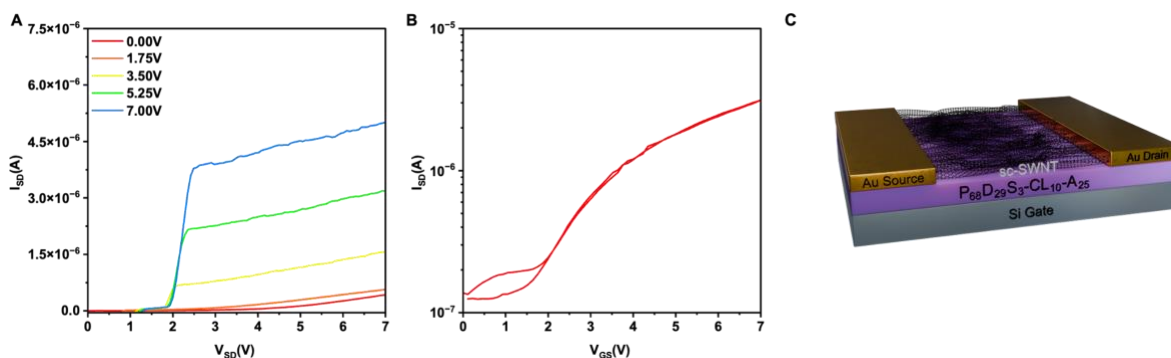


Figure 2.4 Characteristic a) output, b) transfer curves for BGTC OTFTs prepared using $\text{P}_{68}\text{D}_{29}\text{S}_3\text{-CL}_{10}\text{-A}_{25}$ with sc-SWCNTs. The transfer curve was operated at a V_{SD} of 3V, and the average of the last measurement of five transfer curves is presented to ensure the film is appropriately charged. c) BGTC device architecture.

2.6 Experimental

2.6.1 Materials

Styrene (S4972, $\geq 99\%$), poly(ethylene glycol) methyl ether methacrylate (mPEGMA, 447935, $\leq 100\%$), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 234907, 98%), acetonitrile (ACN, 271004, $\geq 99.8\%$), aluminum oxide (199443, Brockmann I, activated, basic with $<0.03\%$ Fe_2O_3 , $<0.4\%$ Na_2O), hexanes (227064, $\geq 99\%$), and dichloromethane (DCM, 270997, $\geq 99.8\%$) were purchased from Millipore-Sigma. BlocBuilder-MA (HES1179) was kindly donated by Marc Dubé (University of Ottawa), who received it from Arkema. Toluene (92030-2-10, $\geq 99.5\%$) was purchased from Caledon.

N,N-Dimethylformamide (DMF, 99.9% HPLC grade), Bis(2-bromoethyl) ether (BBEE, 005451, 97%) and n-propyl bromide (BR1117, 99%) were purchased from Oakwood Chemical. Plasma torch carbon nanotubes were purchased from Raymor NanoIntegris (RNB781-120). Poly(9,9'-didodecyl-fluorene-co-N-(2'-decyltetradecane)-carbazole) (PCPF) was received from the Adronov Research Group at McMaster University. All chemicals and reagents were used as received unless otherwise specified.

2.6.2 Preparation of sc-SWCNT Dispersion

Pure dispersions of semiconducting single-walled carbon nanotubes were prepared using conjugated polymer sorting, as reported in our previous work.¹⁸ Briefly, the conjugated polymer, PCPF, and raw nanotubes were added to 20 mL of toluene in a 0.8:1 ratio and sonicated for 90 minutes. The dispersions were then centrifuged, and the supernatants were combined to create a stock solution.

2.6.3 Synthesis of Poly(mPEGMA-DMAEMA-Sty)

Poly(mPEGMA-DMAEMA-Sty) was synthesized through nitroxide mediated polymerization (NMP) following previously reported synthesis procedures for NMP.^{19–21,44,45} The molar ratio of BlocBuilder-MA and of mPEGMA, DMAEMA, and styrene was calculated to provide a target number average molecular weight of $M_{n,Target} = 67$ kg/mol. As an example, for P₅₀D₄₈S₂-CL₁₀-A₀ BlocBuilder-MA (0.07 g, 0.19 mmol), mPEGMA (5.70 g, 19.00 mmol), DMAEMA (2.99 g, 19.00 mmol), and styrene (0.12 g, 1.14 mmol) were added to 8.25 mL toluene and bubbled with N₂ in an ice bath for 15 minutes (**Table S1**). The solution was then heated in a sand bath at 90°C for 60 minutes to allow for polymerization to occur. An aliquot of polymerization mixture was taken for analysis with ¹H-NMR to determine monomer conversion for each polymer before precipitation and isolation of the polymer (**Figure S1**). The polymer was isolated by precipitation in 100 mL hexanes, decanted, then redissolved in 2.5 mL DCM, this was repeated 3 times. The polymer dissolved in DCM was dried and analyzed through size exclusion chromatography (SEC) and ¹H-NMR. Analysis by SEC including M_n and $\bar{D}$ for each polymer is presented in **Table S2**. The polymer size and size dispersity were analyzed by gel permeation chromatography (GPC) with DMF as the eluent. The eluent was pumped by Malvern Omnisec Resolve at a flow rate of 1.0 mL/min. at 40 °C. The sample passed through a guard column (DGuard, Org Guard, 10×4.6 mm) and then two analytical columns in series (two D6000M, General mixed org, 300×8.0 mm). The sample was analyzed using a MALS detector, (Malvern Viscotek SEC-MALS 20), RI & UV/vis detectors (Malvern Omnisec Reveal). PS standards (105 kDa and 245 kDa) were used to perform multi-detector calibration. The ¹H-NMR analysis showed peaks at 4.0–3.3 ppm (HC-O-R from mPEGMA), 2.0–2.7 ppm (O-CH₂ from DMAEMA), and 6.9–7.25 ppm aromatic rings from styrene were used to determine the polymer molar composition (F_s , F_{DMAEMA} and F_{mPEGMA}). The styrene peaks at 6.9–7.3 ppm was assumed to represent 3

repeats for 3 mol% composition since styrene conversion was complete, thus, integration value of 15 was assigned. The ^1H -NMR spectra were obtained by using a Bruker AVANCE II 400 MHz spectrometer. The ^1H -NMR spectrum and SEC results are presented in **Figures S1 and S2**. For $\text{P}_{50}\text{D}_{48}\text{S}_2\text{-CL}_{10}\text{-A}_0$ the polymerization conversion was 54% with a final $M_n = 67$ kg/mol, $\bar{D} = 1.5$ and $F_{\text{DMAEMA}} = 0.48$, $F_{\text{mPEGMA}} = 0.50$.

2.6.4 Alkylation of Poly(mPEGMA-DMAEMA-Sty)

The polymer (0.5 g) was dissolved in ACN (3 mL) equipped with a stir bar. The percentage (25%, 50%, 75%, 85%, 95%) per DMAEMA molar ratio of n-propyl bromide to DMAEMA units was added to the flask containing the polymer solution (**Table S3**). The solution was left stirring at room temperature overnight. The stir bar was removed, the excess solvent was rotovapped, and the sample was dried *in vacuo* overnight and analyzed by ^1H -NMR. Broad peaks that appeared at 4.5 ppm indicated successful alkylation. ^1H -NMR spectra are presented in **Figure S3**. Sample composition has been abbreviated as $\text{P}_V\text{D}_W\text{S}_X\text{-CL}_Y\text{-A}_Z$, where V, W, X represent the percentage of mPEGMA, DMAEMA, and styrene respectively, Y represents the percentage of crosslinking, and Z represents the percentage of alkylation.

2.6.5 Preparation of Dielectric Solution

Each component of the dielectric solution including the polymer, ACN, and crosslinker were filtered through a 0.45 μm polytetrafluorethylene syringe filter prior to mixing. The dielectric solution was composed of 150 mg/mL of $\text{P}_V\text{D}_W\text{S}_X\text{-CL}_Y\text{-A}_Z$ dissolved in ACN and 0.1 molar equivalent of the crosslinker, BBEE, per DMAEMA was added.

2.6.6 Fabrication and Characterization of Metal-Insulator-Metal (MIM) Capacitors

25 mm $\times$ 25 mm glass substrates were submerged in the following sequence: detergent solution, DI water, acetone, and methanol for 5 minutes each and placed in an ultrasonication bath to be cleaned. The substrates were dried with a flow of nitrogen gas and transferred into the glovebox for the physical vapour deposition of the bottom electrodes. 2 nm of Cr followed by 50 nm of Au were patterned onto the substrates to create bottom electrodes using custom shadow masks. The dielectric solution was prepared as previously described. The dielectric layer was fabricated by coating the solution on top of the bottom electrodes via spin-coating. 300 μL of dielectric solution was dispensed onto the substrate and spin-coated at 2000 rpm for 90 s. Once spin-coated, the substrates were annealed in an oven under vacuum at 80°C overnight. The following morning, the oven temperature was increased to 100°C for 1 hour and then cooled to room temperature before being removed from the oven. 50 nm of Au top electrodes were deposited on the substrates through a shadow mask. Each substrate contained 10 capacitor sites with different areas, and each polymer sample used as a dielectric layer was fabricated in duplicates, resulting in a total of 20 capacitor sites per sample ($n=20$).

2.6.7 Electrochemical Impedance Spectroscopy (EIS)

EIS was used to obtain the dielectric properties of the films which was achieved by sweeping frequency from 10^6 Hz to 0.01 Hz at 10 mV using a Metrohm PGSTAT204 potentiostat/galvanostat. An average film thickness and root mean square roughness was calculated from six different measurements taken on each film using a Dektak XT profilometer (Bruker) (**Table S5**). Equations 2.1 and 2.2 describe the dielectric constant (κ) and capacitance density (C_i) for each site which was calculated using the real (Z') and imaginary (Z'') portions of impedance, average film thickness (t), capacitor area (A), permittivity of vacuum (ϵ_0), and angular frequency (ω).

$$\kappa = \frac{t}{\omega A \epsilon_0} \left(\frac{Z''}{Z''^2 + Z'^2} \right) \quad (2.1)$$

$$C_i = \frac{\kappa \epsilon_0 A}{t} \quad (2.2)$$

EIS-derived real (Z') and imaginary (Z'') portions of impedance were used to calculate the parallel resistance from a circular fit of the semi-circle portion. This fit obtained the value of bulk resistance which was used to obtain ionic conductivity (σ) of the films using average film thickness (t), bulk resistance (R_b), and capacitor area (A) seen in Equation 2.3.

$$\sigma = \frac{t}{R_b A} \quad (2.3)$$

2.6.8 Raman Spectroscopy of Poly(mPEGMA-DMAEMA-Sty)

Raman spectra were recorded using Renishaw inVia InSpec confocal Raman microscope with a Leica Microsystems bright-field microscope with a DM2700 light source. A 500 mW 532 nm wavelength laser with a 2400 L/mm grading was used to measure the 2700–3500 cm^{-1} spectral range using 100 $\times$ objective. Calibration was performed against a 520 cm^{-1} silicon reference peak within 0.5 cm^{-1} . Films for Raman spectroscopy were prepared on 20 mm $\times$ 15 mm Si wafers and were cleaned beforehand by sonication in detergent, DI water, acetone, and methanol for 5 minutes each. Films were fabricated as described previously. Raman spectra were taken in the middle of the sample with 10% laser power, an exposure time of 10 seconds, and 10 accumulations. The spectra were baseline corrected, and peak position was determined through the WiRE curve fitting software. Each spectrum was normalized between 0 and 1 to show the change in intensity between the various spectra.

2.6.9 Fabrication of OTFTs

OTFTs were fabricated on 20 mm × 15 mm Si wafers (WaferPro), cleaned as previously described for MIM capacitors. The dielectric used for MIM capacitors was used as the dielectric in the OTFT following the same spin coating and annealing procedure but instead onto an Si wafer and using 200 µL for spin coating. After annealing, SWCNTs were dropcast onto the substrate manually using a prepatterned guide for drop placement. 0.3 µL of SWCNT dispersions were drop-cast onto the substrate in each of the 20 prepatterned channel positions. After each drop of SWCNTs, the substrate was rinsed with 1 mL of toluene four times and dried with nitrogen between each rinse. This was repeated three times such that each OTFT channel received 3 drops of SWCNTs. Substrates were then annealed at 100°C for 2 hours under vacuum. Gold top electrodes were deposited via PVD at 0.5 Å/s to a thickness of 50 nm through prepatterned Ossila shadow masks.

OTFTs were tested using a custom designed autotester connected to a Keithley 2614B source meter. The output and transfer curves for all 20 sites on the substrate were obtained using this autotester and a LabVIEW program.⁴⁶ Output curves were obtained by sweeping the source-drain voltage (V_{SD}) while maintaining a constant source-gate voltage (V_{GS}). Transfer curves were obtained in the linear regime by sweeping V_{GS} and maintaining a constant V_{SD} . Transconductance (g_m) and V_T were modelled using the metal-oxide-semiconductor field-effect transistor (MOSFET) model as seen in Equations 2.4 and 2.5.

$$I_{SD} = \frac{W}{L} \mu C_i \left(V_{GS} - V_T - \frac{V_{SD}}{2} \right) V_{SD} \quad (2.4)$$

$$g_m = \frac{dI_{SD}}{dV_{GS}} \quad (2.5)$$

2.7 Conclusion

Crosslinking with BBEE and the tertiary amine present in the DMAEMA of the PIL was used to fabricate robust PILs for orthogonal solution processed bilayer devices with tunable capacitance and ionic conductivity. Raman spectroscopy showed a drop in wavenumber with increased BBEE content, suggesting increased crosslinking. PIL MIM capacitors were fabricated with the resulting robust films and demonstrated high capacitance density, high frequency EDL formation, and ionic conductivity. Moreover, increasing the ratio of mPEGMA in the PIL dielectric demonstrated an increase in capacitance density and EDL onset. Additionally, the pre-alkylation of the DMAEMA units of the PIL polymers led to a 3-order of magnitude increase in EDL onset formation and conductivity, as well as a 4× increase in capacitance density when pre-alkylating 75% of the DMAEMA monomers prior to crosslinking in the film.

The PIL was also incorporated into preliminary bottom gate top contact, solution processed OTFTs with sc-SWCNT semiconductors, achieving a threshold voltage of <1.6 V and performance characteristics comparable to other PIL dielectrics incorporated into OTFTs. Overall, this study demonstrates an effective strategy to develop robust highly conductive dielectrics for use in robust solution processed organic electronics.

2.8 Acknowledgements

This work was supported by NSERC CGS to L.E.D. and M.O. The authors acknowledge financial support from NSERC Discovery grant program (B.H.L.). The authors thank the Adronov Research Group from McMaster University for the synthesis of the PCPF polymer. Professor Marc Dubé from University of Ottawa for donating the BlocBuilder-MA from Arkema.

2.9 Supporting Information

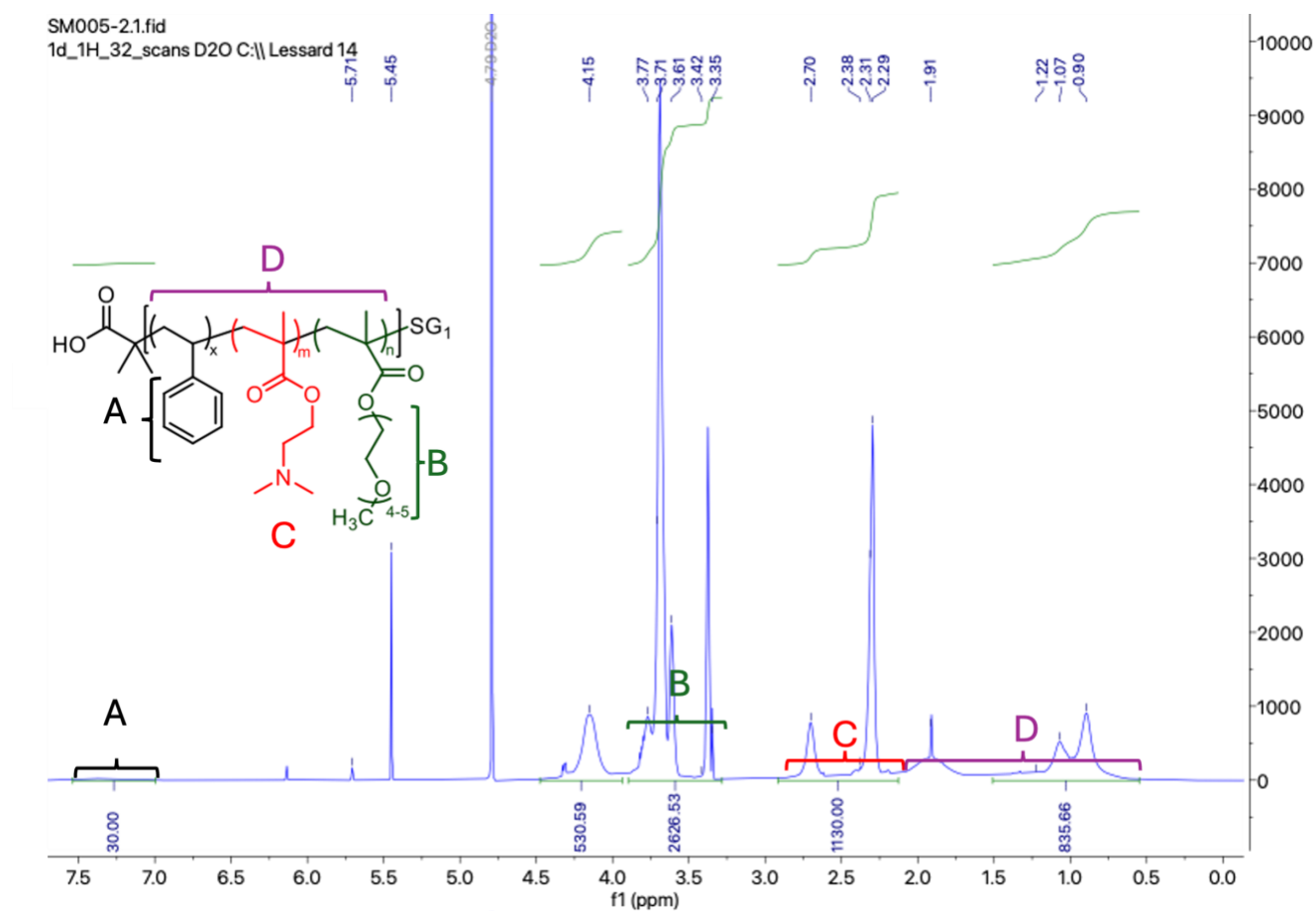


Figure S1. ^1H -NMR of $P_{50}D_{48}S_2-CL_{10}-A_0$

The molar ratio of Styrene, mPEGMA, and DMAEMA was calculated:

Styrene: mPEGMA: DMAEMA

$$\frac{I_A}{6} : \frac{I_B}{17.78} : \frac{I_C}{8}$$

Styrene was assumed to have a value of 30 (based on 6 styrene repeat units per chain).

The composition of the entire polymer was calculated:

$$F_{Styrene} = \frac{Styrene}{Styrene + PEGMA + DMAEMA}$$

$$F_{PEGMA} = \frac{PEGMA}{Styrene + PEGMA + DMAEMA}$$

$$F_{DMAEMA} = \frac{DMAEMA}{Styrene + PEGMA + DMAEMA}$$

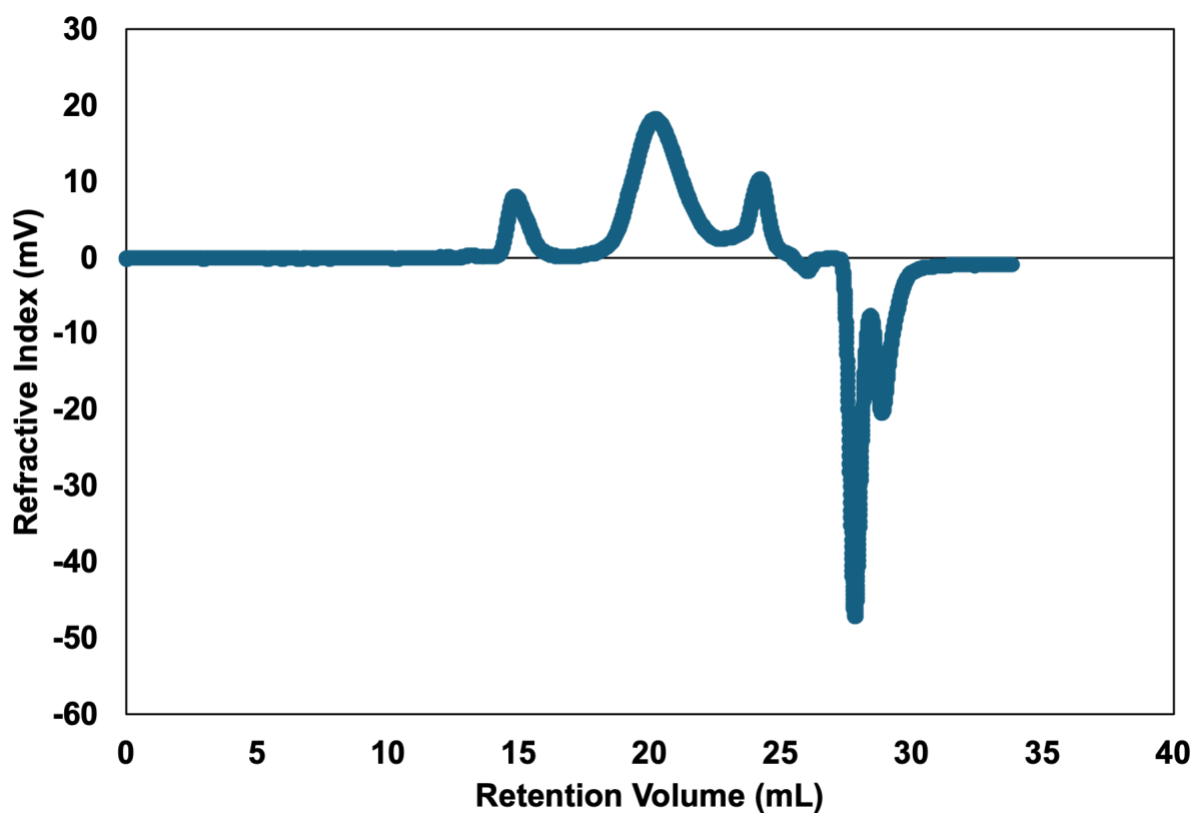


Figure S2. GPC of P₅₀D₄₈S₂-CL₁₀-A₀

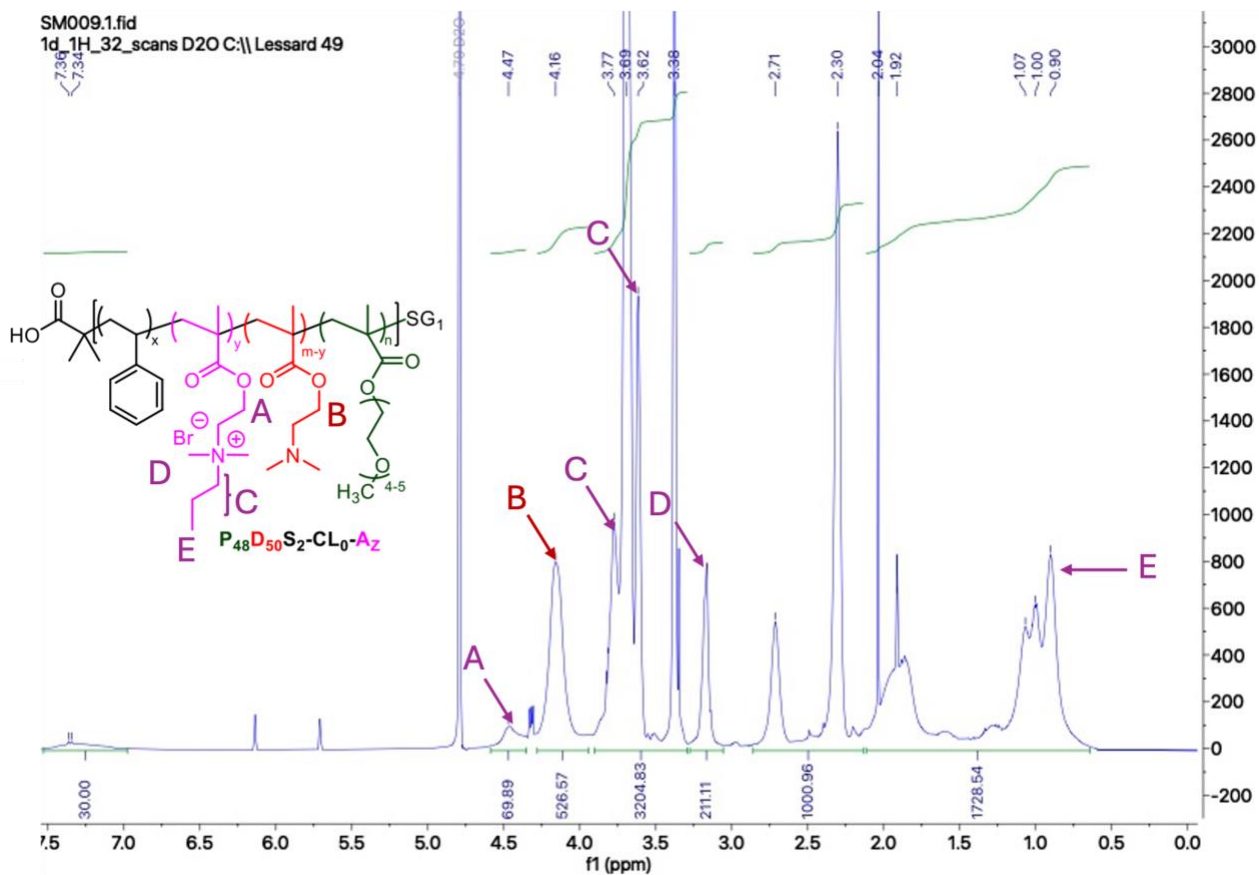


Figure S3. ^1H -NMR of $\text{P}_{50}\text{D}_{48}\text{S}_2\text{-CL}_{10}\text{-A}_{25}$

Styrene, mPEGMA, and DMAEMA components were calculated as seen in Figure S1.

Peaks A, C, D, E are specific to alkylation of the PIL, the molar ratio of DMAEMA alkylated was calculated:

DMAEMA alkylated

$$\frac{\left(\frac{I_A}{2} + \frac{I_C}{4} + \frac{I_D}{6}\right)}{3}$$

The composition of the entire polymer was calculated:

$$F_{\text{Styrene}} = \frac{\text{Styrene}}{\text{Styrene} + \text{PEGMA} + \text{DMAEMA} + \text{DMAEMA alkylated}}$$

$$F_{\text{PEGMA}} = \frac{\text{PEGMA}}{\text{Styrene} + \text{PEGMA} + \text{DMAEMA} + \text{DMAEMA alkylated}}$$

$$F_{DMAEMA} = \frac{DMAEMA}{Styrene + PEGMA + DMAEMA + DMAEMA \text{ alkylated}}$$

$$F_{DMAEMA \text{ alkylated}} = \frac{DMAEMA}{Styrene + PEGMA + DMAEMA + DMAEMA \text{ alkylated}}$$

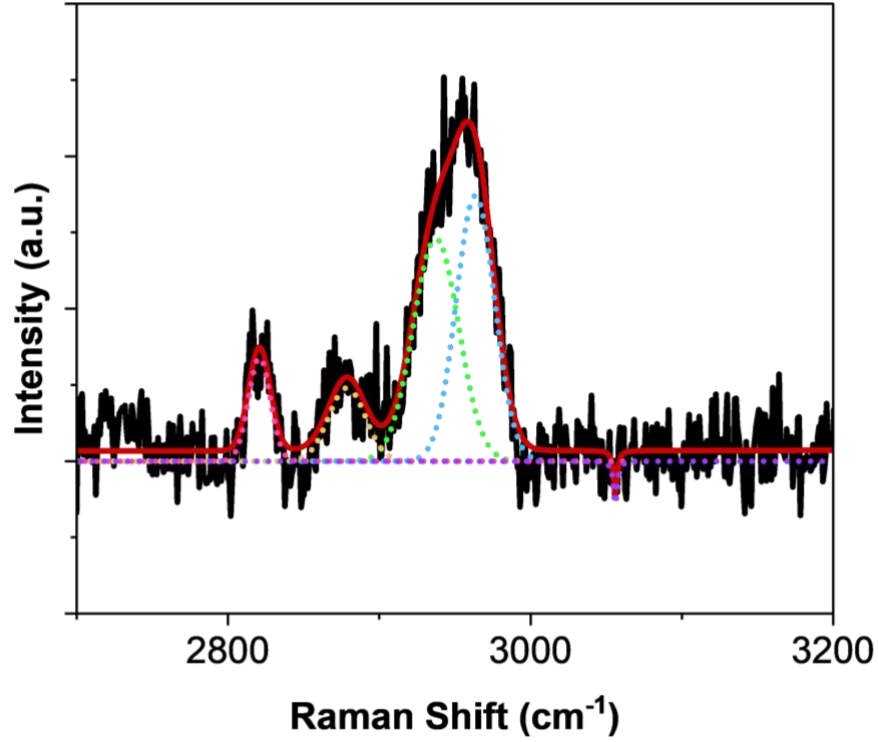


Figure S4. Raman spectra P₅₀D₄₈S₂-CL_Y-A₀ crosslinking (black) together with the results of fitted peak analysis (red) of five mixed Lorentz-Gaussian functions (pink, yellow, green, blue, and purple) for 0.9 BBEE molar equivalent to DMAEMA monomer units.

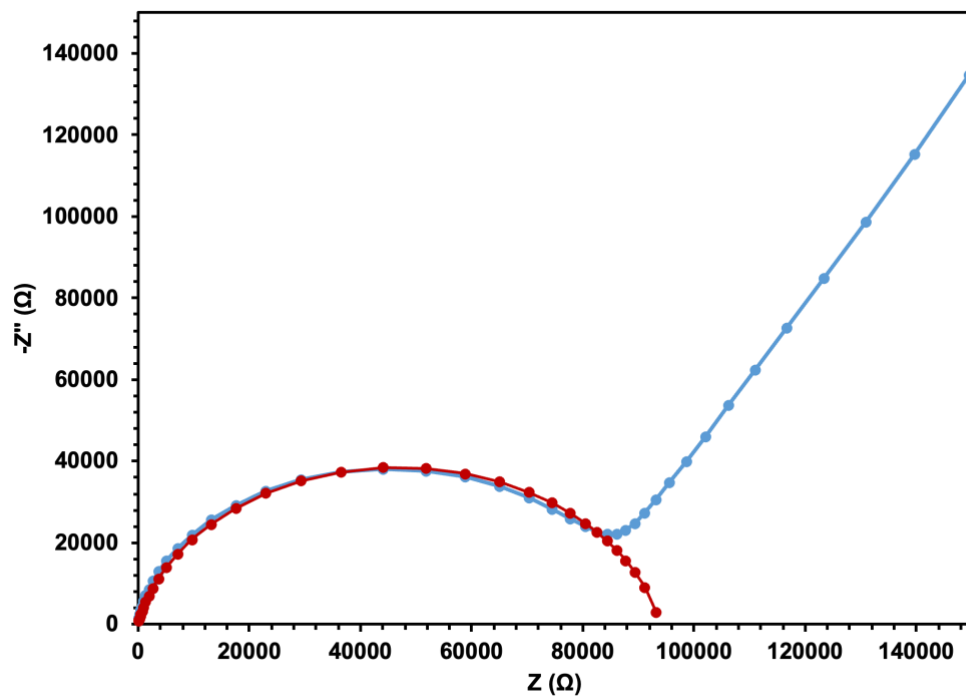


Figure S5. Representative Nyquist plot from MIM capacitor. Ionic conductivity was determined by performing a circular fit from the semi-circle portion seen in red.

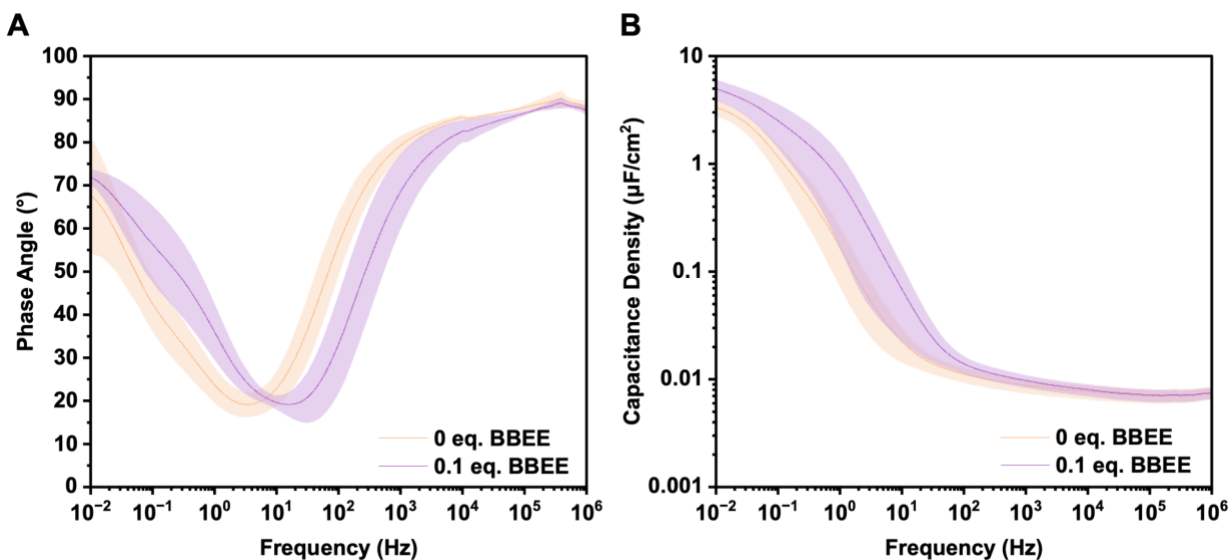


Figure S6. EIS results of the effect of BBEE content to $P_{48}D_{45}S_7\text{-CLY-A}_0$ a) phase angle vs frequency and b) capacitance density vs frequency.

Table S1. PIL synthesis deployed molar equivalents. P_VD_WS_X-CL_Y-A_Z describes a short form of polymer composition where V, W, X, Y, and Z represents the amount of mPEGMA, DMAEMA, Styrene, Crosslinker (BBEE), and percentage of alkylation respectively.

ID	BlocBuilder	Deployed Molar Eq.		
		Styrene	DMAEMA	mPEGMA
P ₁₀ D ₈₇ S ₃ -CL ₀ -A ₀	1	6	180	20
P ₂₈ D ₆₉ S ₃ -CL ₀ -A ₀	1	6	140	60
P ₅₀ D ₄₈ S ₂ -CL ₀ -A ₀	1	6	100	100
P ₆₈ D ₂₉ S ₃ -CL ₀ -A ₀	1	6	60	140
P ₉₀ D ₈₇ S ₃ -CL ₀ -A ₀	1	6	20	180

Table S2. PIL synthesis summary. P_VD_WS_X-CL_Y-A_Z describes a short form of polymer composition where V, W, X, Y, and Z represents the amount of mPEGMA, DMAEMA, Styrene, Crosslinker (BBEE), and percentage of alkylation respectively. Đ represents dispersity (M_n/M_w). F_S, F_{DMAEMA}, and F_{mPEGMA} represent the frequency of monomer in the polymer. SEC was used to obtain M_n and Đ. NMR was used to determine monomer conversion and composition in the polymer.

ID	M _n	Đ	F _S	F _{DMAEMA}	F _{mPEGMA}	Conversion (%)	Yield (%)
P ₁₀ D ₈₇ S ₃ -CL ₀ -A ₀	31000	1.7	0.03	0.1	0.87	32	26
P ₂₈ D ₆₉ S ₃ -CL ₀ -A ₀	33000	1.5	0.03	0.28	0.69	48	45
P ₅₀ D ₄₈ S ₂ -CL ₀ -A ₀	67000	1.5	0.02	0.50	0.48	54	39
P ₆₈ D ₂₉ S ₃ -CL ₀ -A ₀	46000	2.1	0.03	0.65	0.32	60	59
P ₉₀ D ₈₇ S ₃ -CL ₀ -A ₀	50000	2.2	0.03	0.81	0.15	56	59

Table S3. PIL synthesis deployed molar equivalents. P_VD_WS_X-CL_Y-A_Z describes a short form of polymer composition where V, W, X, Y, and Z represents the amount of mPEGMA, DMAEMA, Styrene, Crosslinker (BBEE), and percentage of alkylation respectively.

ID	Deployed Molar Eq.		Number of Units DMAEMA	% of DMAEMA Units
	P ₅₀ D ₄₈ S ₂ -CL ₀ -A ₀	n-propyl bromide		
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₂₅	1	35.25	141	25
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₅₀	1	70.5	141	50
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₇₅	1	105.75	141	75
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₈₅	1	119.85	141	85
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₉₅	1	133.95	141	95

Table S4. MIM capacitor EIS results summary

Film ID	EDL onset (Hz)	κ at 10 Hz	C_i at 10 Hz ($\mu\text{F}/\text{cm}^2$)	κ at 0.01 Hz	C_i at 0.01 Hz ($\mu\text{F}/\text{cm}^2$)	Conductivity (S/cm)
P ₁₀ D ₈₇ S ₃ -CL ₀ -A ₀	12.589	11.95±3.37	0.01±0.003	3055±2165	2.63±1.86	2.26×10^{-10}
P ₂₈ D ₆₉ S ₃ -CL ₁₀ -A ₀	25.116	29.68±17.74	0.02±0.013	6937±4108	6.34±2.67	1.12×10^{-9}
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₀	501.19	924.58±213.57	1.02±0.201	8483±1331	9.35±1.31	1.50×10^{-8}
P ₆₈ D ₂₉ S ₃ -CL ₁₀ -A ₀	794.33	1477.26±714.53	1.57±0.762	7105±1302	7.57±1.39	2.68×10^{-8}
P ₈₇ D ₁₀ S ₃ -CL ₁₀ -A ₀	-	-	-	-	-	-
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₂₅	15849	3651.12±588.54	4.89±0.779	11570±2272	15.49±2.93	3.33×10^{-7}
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₅₀	31623	3783.80±728.98	4.15±0.817	10850±2049	11.90±2.24	8.20×10^{-7}
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₇₅	125890	3654.99±543.99	4.56±0.760	12892±2245	16.08±3.08	1.58×10^{-5}
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₈₅	2511.9	2664.74±1121.53	2.08±0.822	9201±2148	7.18±1.39	7.03×10^{-8}
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₉₅	-	-	-	-	-	-
P ₄₈ D ₄₅ S ₇ -CL ₀ -A ₀	19.953	16.60±6.24	0.02±0.008	2485±450	3.32±0.54	-
P ₄₈ D ₄₅ S ₇ -CL ₁₀ -A ₀	158.49	56.79±38.40	0.07±0.045	4108±901	4.93±1.07	-
P ₄₈ D ₄₅ S ₇ -CL ₂₅ -A ₀	-	-	-	-	-	-
P ₄₈ D ₄₅ S ₇ -CL ₅₀ -A ₀	-	-	-	-	-	-

Table S5. MIM capacitor profilometry and film information summary

Film ID	Thickness (nm)	Roughness (nm)	n
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₀	803±121	33±23	15
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₂₅	654±94	17±12	12
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₅₀	808±71	15±5	13
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₇₅	720±92	18±10	4
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₈₅	1111±153	21±8	18
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₉₅	-	-	0
P ₁₀ D ₈₇ S ₃ -CL ₀ -A ₀	1023±38	19±16	15
P ₂₈ D ₆₉ S ₃ -CL ₁₀ -A ₀	1104±192	59±30	8
P ₅₀ D ₄₈ S ₂ -CL ₁₀ -A ₀	803±121	33±23	15
P ₆₈ D ₂₉ S ₃ -CL ₁₀ -A ₀	832±10	19±9	17
P ₄₈ D ₄₅ S ₇ -CL ₀ -A ₀	661±56	10±4	17
P ₄₈ D ₄₅ S ₇ -CL ₁₀ -A ₀	734±31	7±7	18
P ₄₈ D ₄₅ S ₇ -CL ₂₅ -A ₀	690±186	472±197	0
P ₄₈ D ₄₅ S ₇ -CL ₅₀ -A ₀	308±191	287±450	0

Table S6. OTFT characteristic parameters of BGTC P₆₈D₂₉S₃-CL₁₀-A₂₅ dielectric with sc-SWCNT operating in the linear regime. Values are presented as an average of the last 4 of 5 measurements, (n=5).

I _{ON} /OFF	Threshold Voltage (V)	Transconductance (μS)	Hysteresis (V)
25	1.65±0.10	0.72±0.41	0.15±0.06

2.10 References

- 1 Food and Agriculture Organization of the United Nations (FAO), Global initiative on food loss and waste reduction, Rome, 2016.
- 2 S. Jakher and R. Yadav, *Microelectron. Eng.*, 2024, 290, 112193.
- 3 Z. Hao, Z. Wu, S. Liu, X. Tang, J. Chen and X. Liu, *J. Mater. Chem. C*, 2024, 12, 9427–9454.
- 4 H. Kim, Y. Won, H. W. Song, Y. Kwon, M. Jun and J. H. Oh, *Adv Sci (Weinh)*, 2023, 11, 2306191.
- 5 L. G. Kaake, Y. Zou, M. J. Panzer, C. D. Frisbie and X.-Y. Zhu, *J. Am. Chem. Soc.*, 2007, 129, 7824–7830.
- 6 J. D. Yuen, A. S. Dhoot, E. B. Namdas, N. E. Coates, M. Heeney, I. McCulloch, D. Moses and A. J. Heeger, *J. Am. Chem. Soc.*, 2007, 129, 14367–14371.
- 7 S. Jin, D. Mu, Z. Lu, R. Li, Z. Liu, Y. Wang, S. Tian and C. Dai, *J. Clean. Prod.*, 2022, 340, 130535.
- 8 K. Du, E. H. Ang, X. Wu and Y. Liu, *Energy Environ. Mater.*, 2022, 5, 1012–1036.
- 9 J. Li, W. Tang, Q. Wang, W. Sun, Q. Zhang, X. Guo, X. Wang and F. Yan, *Mater. Sci. Eng. R Rep.*, 2018, 127, 1–36.
- 10 B. Nketia-Yawson and Y.-Y. Noh, *Adv. Funct. Mater.*, 2018, 28, 1802201.
- 11 T. Fujimoto and K. Awaga, *Phys. Chem. Chem. Phys.*, 2013, 15, 8983–9006.
- 12 L. G. T. Gaines, *Am. J. Ind. Med.*, 2023, 66, 353–378.
- 13 A. J. Peltekoff, S. Bixi, J. Niskanen and B. H. Lessard, *JACS Au*, 2021, 1, 1044–1056.
- 14 J. Niskanen, M. N. Tousignant, A. J. Peltekoff and B. H. Lessard, *Polymer*, 2021, 212, 123144.
- 15 M. N. Tousignant, M. Ourabi, J. Niskanen, B. Mirka, W. J. Bodnaryk, A. Adronov and B. H. Lessard, *Flex. Print. Electron.*, 2022, 7, 034004.
- 16 J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes and B. Charleux, *Progress in Polymer Science*, 2013, 38, 63–235.
- 17 R. Abbasi, A. Mitchell, P. G. Jessop and M. F. Cunningham, *RSC Appl. Polym.*, 2024, 2, 214–223.

- 18 N. A. Rice, W. J. Bodnaryk, B. Mirka, O. A. Melville, A. Adronov and B. H. Lessard, *Adv. Electron. Mater.*, 2019, 5, 1800539.
- 19 H. R. Lamontagne and B. H. Lessard, *ACS Appl. Polym. Mater.*, 2020, 2, 5327–5344.
- 20 B. H. Lessard, X. Savelyeva and M. Marić, *Polymer*, 2012, 53, 5649–5656.
- 21 M. Marić, *Can. J. Chem. Eng.*, 2021, 99, 832–852.
- 22 B. Lessard and M. Marić, *Macromolecules*, 2010, 43, 879–885.
- 23 G. Delaittre, J. Rieger and B. Charleux, *Macromolecules*, 2011, 44, 462–470.
- 24 B. King and B. H. Lessard, *Macromol. React. Eng.*, 2017, 11, 1600073.
- 25 B. Lessard and M. Marić, *Macromolecules*, 2008, 41, 7870–7880.
- 26 A. Moayeri, B. Lessard and M. Maric, *Polym. Chem.*, 2011, 2, 2084–2092.
- 27 B. Lessard, C. Tervo, S. De Wahl, F. J. Clerveaux, K. K. Tang, S. Yasmine, S. Andrelić, A. D'Alessandro and M. Marić, *Macromolecules*, 2010, 43, 868–878.
- 28 C. Zhang, B. Lessard and M. Maric, *Macromol. React. Eng.*, 2010, 4, 415–423.
- 29 N. B. Colthup, L. H. Daly and S. E. Wiberley, in *Introduction to Infrared and Raman Spectroscopy* (Third Edition), eds. N. B. Colthup, L. H. Daly and S. E. Wiberley, Academic Press, San Diego, 1990, pp. 215–233.
- 30 D. A. Long, *Journal of Raman Spectroscopy*, 2005, 36, 271–271.
- 31 J.-Y. Wang, F. Jin, X.-Z. Dong, J. Liu, M.-X. Zhou, T. Li and M.-L. Zheng, *Small*, 2023, 19, 2303166.
- 32 N. J. Overall, in *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Ltd, 2006.
- 33 Ch. Hirschl, L. Neumaier, W. Mühleisen, M. Zauner, G. Oreski, G. C. Eder, S. Seufzer, Ch. Berge, E. Rüland and M. Kraft, *Sol. Energy Mater. Sol. Cells*, 2016, 152, 10–20.
- 34 O. Larsson, E. Said, M. Berggren and X. Crispin, *Adv. Funct. Mater.*, 2009, 19, 3334–3341.
- 35 B. Ronnasi, B. King, S. Bixi, S. Swaraj, J. Niskanen and B. H. Lessard, *Adv. Electron. Mater.*, 2024, 10, 2300810.
- 36 B. Mirka, N. A. Rice, P. Williams, M. N. Tousignant, N. T. Boileau, W. J. Bodnaryk, D. Fong, A. Adronov and B. H. Lessard, *ACS Nano*, 2021, 15, 8252–8266.
- 37 B. Mirka, D. Fong, N. A. Rice, O. A. Melville, A. Adronov and B. H. Lessard, *Chem. Mater.*, 2019, 31, 2863–2872.

- 38 M. N. Tousignant, N. A. Rice, J. Niskanen, C. M. Richard, D. Ritaine, A. Adronov and B. H. Lessard, *Adv. Electron. Mater.*, 2021, 7, 2100700.
- 39 M. N. Tousignant, Z. S. Lin, J. Brusso and B. H. Lessard, *ACS Appl. Mater. Interfaces*, 2023, 15, 3680–3688.
- 40 M. N. Tousignant, B. Ronnasi, V. Tischler and B. H. Lessard, *Adv. Mater. Interfaces*, 2023, 10, 2300079.
- 41 B. Ronnasi, S. P. McKillop, M. Ourabi, M. Perry, H. A. Sharp and B. H. Lessard, *ACS Appl. Mater. Interfaces*, 2024, 16, 65425–65435.
- 42 B. Ronnasi, M. N. Tousignant and B. H. Lessard, *J. Mater. Chem. C*, 2023, 11, 3197–3205.
- 43 L. E. Dickson, S. Bixi, C. L. Radford, J. G. Manion, T. L. Kelly and B. H. Lessard, *J. Mater. Chem. C*, 2024, 12, 17902–17912.
- 44 D. R. Nosov, B. Ronnasi, E. I. Lozinskaya, D. O. Ponkratov, L. Puchot, P. Grysan, D. F. Schmidt, B. H. Lessard and A. S. Shaplov, *ACS Appl. Polym. Mater.*, 2023, 5, 2639–2653.
- 45 B. H. Lessard, E. J. Y. Ling and M. Marić, *Macromolecules*, 2012, 45, 1879–1891.
- 46 A. J. Peltekoff, V. E. Hiller, G. P. Lopinski, O. A. Melville and B. H. Lessard, *ACS Appl. Polym. Mater.*, 2019, 1, 3210–3221.

3. Designing Safer Crosslinked Poly(ionic liquid)s through High-Throughput Toxicological Screening

This chapter has been adapted from work published in the journal “Environmental Science: Advances”: Sophia McKillop, Vittoria-Ann DiPalo, Lai Wei, Joseph G. Manion, Jan A. Mennigen*, and Benoît H. Lessard*: Designing Safer Crosslinked Poly(ionic liquid)s through High-Throughput Toxicological Screening

3.1 Context

This work builds upon the findings of the previous chapter by using the same baseline PIL while investigating the influence of counterion identity on dielectric performance. Secondly, we characterize the toxicological effects of the mPEGMA-DMAEMA-styrene polymer, its alkylated derivatives containing either Br⁻ or TFSI⁻ counterions and all the starting materials were assessed using a zebrafish embryo toxicity assay to evaluate the impact to the environment and human health. This provides an opportunity to evaluate the material properties and the toxicity, which provides a way to screen and select the most promising materials in terms of toxicity and performance.

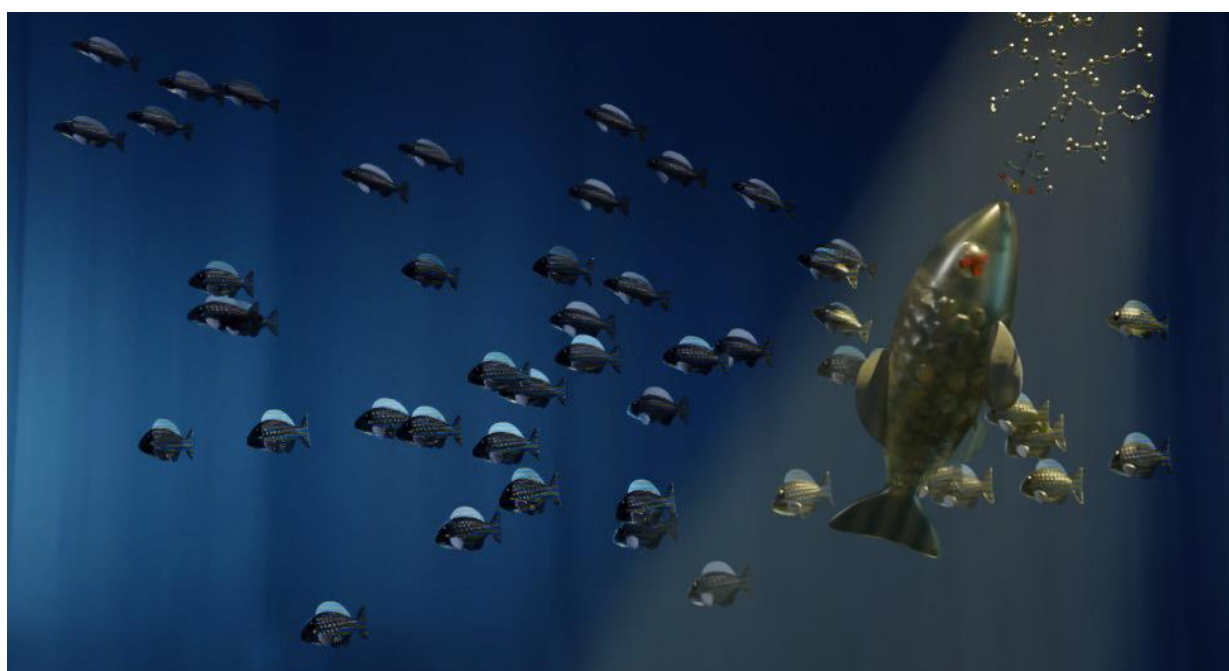
3.2 Contributions

The manuscript was written by contributions from all authors who have given approval to the final version. S. M: conceptualization, investigation, formal analysis, writing - original draft. S. M. conducted experimental work and data analysis and wrote the initial draft of the manuscript. V. D.: analysis, writing - reviewing and editing. V. D. contributed to NMR analysis and manuscript editing. L. W. writing - reviewing and editing. L. W. contributed to the training of zebrafish related experiments and manuscript editing. J. G. M.: writing - review and editing. J. A. M.: funding acquisition, writing - review and editing. J. A. M. acquired funding and assisted in editing the manuscript. B. H. L.: funding acquisition, supervision, project administration, conceptualization, writing - review and editing. B. H. L. acquired funding, managed supervision, directed the study, and assisted in editing the manuscript.

3.3 Abstract

Next-generation electronics require materials that are flexible while also achieving high performance. Polymer dielectrics make this achievable by maintaining high capacitive energy storage while providing more desirable mechanical properties. New polymer materials for electronics continue to be proposed yet their ecotoxicological profiles remain largely uncharacterized at the development stage. This study investigates the effect of counterion identity, bromide (Br⁻) versus bis(trifluoromethanesulfonyl)imide (TFSI⁻), on both the dielectric properties and environmental toxicity in poly(mP-D-S). Dielectric performance was evaluated using electrochemical impedance spectroscopy (EIS) in a metal-insulator-metal capacitor, to determine electrical double layer (EDL) onset

frequency, maximum capacitance density, and ionic conductivity. Environmental toxicity was assessed using the Organisation for Economic Co-operation and Development test guideline 236 (OECD TG 236) zebrafish embryo toxicity test (ZFET), monitoring survival over 120 hours. TFSI⁻-bearing polymers showed similar dielectric performance relative to their Br⁻ counterparts while requiring less alkylation. Toxicological findings revealed comparable embryotoxicity between the two counterion systems, providing insights into the safety of counterions in polymers. This is the first study to evaluate counterion effects on both electrochemical performance and ecotoxicity in a PIL-based dielectric, establishing a characterization framework for responsible next-generation polymer dielectric development.



3.4 Introduction

Electronics are increasingly treated as consumables, driven by rapid technological advancements and consumer demand for the latest devices. Consequently, global electronic manufacturing continues to expand each year, accompanied by a parallel rise in electronic waste (e-waste). 62 million tonnes of e-waste was generated in 2022 and only 22.3% of that was collected for recycling.¹ Improper disposal of e-waste can lead to the release of hazardous chemicals that leach into the surrounding environment.^{2,3} Polymer materials in electronic devices constitute a significant fraction of e-waste, yet their contribution to chemical leaching into aquatic environments remains poorly characterized.^{2,3} Despite the scale of the e-waste problem, the environmental impact of

polymeric material used in electronics remain a growing but not fully explored area of research.

Polymer dielectrics are key components in electronic devices, enabling high capacitive energy storage and electrical insulation. They additionally offer flexibility, high breakdown strength, high dielectric constant and compatibility with low-cost fabrication.^{4,5} The dielectric performance of a polymer is governed by its dielectric constant (ϵ_r) which relate to the polymer's molecular structure, chain architecture, and the nature of its polar functional groups.^{6,7} Poly(ionic liquid) (PIL) systems are particularly attractive because the incorporation of ionic moieties enhances electrical energy storage and responsiveness. In addition, counterion selection provides a versatile handle to tune both the electrical and mechanical properties of the resulting films.^{6–10} These features have enabled PILs to function as polymer electrolytes for energy storage devices,^{11,12} fuel cells,¹³ and organic electronic applications.¹⁴ While optimizing has been the main objective, the lack of early stage toxicological and environmental studies may limit commercialization or lead to significant environmental and health consequences if overlooked at the production stage.^{9,10,15,16}

Toxicity testing is necessary for assessing exposure effects of pollutants on the ecosystem and human health.^{17,18} Zebrafish (*Danio rerio*) are a widely used model organism because the embryos share similar genetic homology and biological pathways to humans. Briefly, zebrafish embryos can be obtained in large numbers, are translucent, have a permeable membrane, and develop quickly, with most major organs forming and functional between 48-72 hpf, allowing for direct chemical exposure, real-time observation, and high-throughput assessment.^{19–27} Together with its exempt status with regard to vertebrate experimental protocols prior to fully exogenous feeding at 120 hpf, this makes zebrafish embryos an excellent ethically and economically viable New Approach Methodology for medium-high throughput in vivo toxicity testing.^{19–21,24,28–30} This reliability and ease of use has enabled the development of standardized testing guidelines.²⁰ In this work we applied the FET Test outlined in the OECD guidelines for the testing of chemicals (OECD TG 236), to assess chemical risks associated with PILs used in organic electronic devices.²¹

Previously we demonstrated high performing PILs based on poly(poly(ethylene glycol) methyl ether methacrylate -ran-(dimethylamino)methyl methacrylate-ran-styrene) (poly(mP-D-S)) copolymers which could be crosslinked in a film and used in capacitors and organic transistors.³¹ This study builds on these findings by exploring the effect of counterion on both device performance and on environmental toxicity. Specifically, in this work we investigate the substitution of bromide (Br^-) with bis(trifluoromethanesulfonyl)amide (TFSI^-) as the counterion. TFSI^- has several advantages to the physical and electrical properties of the PIL and high charge delocalization. TFSI^- can also act as an internal plasticizer due to its bulky, flexible

structure.^{22,23} This high charge delocalization and bulky structure reduces glass transition temperature (T_g) and enhances segmental chain mobility, which improves ionic conductivity.^{22,23} TFSI⁻ increases electrical double layer (EDL) capacitance and enables faster switching speeds compared to smaller anions.³² Counterion identity can influence not only the physical and electrical properties but may also have a substantial impact on environmental toxicity.^{9,10} We know that ions play a role in the performance of a dielectric but there is a gap in literature regarding the toxicity of PILs and the effect of anions on the toxicological profiles.^{9,10,33} There is a lack of research on the toxicity PILs as a standard method for assessing toxicity has not been established. This is the first study to evaluate counterion effects on both electrochemical/dielectric properties and the environmental toxicity of the poly(mP-D-S) PIL. This work establishes a framework for evaluation of polymers through OECD-standard toxicological assessments and EIS-based capacitor characterization. This approach supports the responsible design of next-generation polymer dielectrics by assessing both material performance and environmental impact at the development stage.

3.5 Materials and Methods

3.5.1 Materials

Styrene (S4972, ≥99%), poly(ethylene glycol) methyl ether methacrylate (mPEGMA, 447935, ≤100%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 234907, 98%), acetonitrile (ACN, 271004, ≥99.8%), aluminum oxide (199443, Brockmann I, activated, basic with <0.03% Fe₂O₃, <0.4% Na₂O), hexanes (227064, ≥99%), dimethyl sulfoxide (D1435, > 99.9 %) and dichloromethane (DCM, 270997, ≥99.8%) were purchased from Millipore-Sigma. N-(2-Methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxyprop-2-yl) hydroxylamine (BlocBuilder-MA, HES1179) was kindly donated by Marc Dubé (University of Ottawa), who received it from Arkema. Toluene (92030-2-10, ≥99.5%) was purchased from Caledon. N,N-Dimethylformamide (DMF, 99.9% HPLC grade), bis(2-bromoethyl) ether (BBEE, 005451, 97%), n-propyl bromide (BR1117, 99%), and lithium bis(trifluoromethanesulfonyl)amide (010326, 99%) were purchased from Oakwood Chemical. Transparent 96-well plates were purchased from Ultident Scientific. Fluorescence-based assay 96-well plates were purchased from (Invitrogen). Tricaine Methanesulfonate Soluble Powder 100% w/w (MS-222) was purchased from Syndel. All chemicals and reagents were used as received unless otherwise specified.

3.5.2 Zebrafish husbandry

3.5.2.1 Maintenance

Procedures followed Canadian Council on Animal Care (CCAC) guidelines and were approved by the University of Ottawa Animal Care and Veterinary Service (ACVS) under protocol BL-4324. The fish used for this study were adult wild-type zebrafish (*Danio*

erio) from AB line fish originally procured from the Zebrafish Core Facility, Life Science Research Institute (LSRI) at Dalhousie University, Halifax, NS, Canada in 2023. Zebrafish were housed in a recirculating system (Tecniplast, Montreal, QC, Canada) with a 14:10 light:dark (L:D) cycle in the University of Ottawa's Aquatics Facility. Recirculating water conditions were maintained at 28 °C, a pH of 7.4, and a conductivity of 400 µS. Zebrafish were fed Gemma micro 300 (Skretting, Westbrook, ME, USA) at 9 am, and brine shrimp were fed at 1 pm.

3.5.2.2 Zebrafish breeding and embryo generation

Adult zebrafish (a breeding ratio consisting of 1 male: 2 female) were transferred to 3 L breeding trap tanks (Techniplast). Embryos were collected in a fine nylon strainer (700 microns) 1 h after breeding and rinsed gently with system water until debris was removed. Viable, translucent embryos were placed in a 10 cm diameter petri dish, and system water was removed and replaced with E3 media (NaCl, KCl, CaCl₂ 2H₂O, MgCl₂ 6H₂O (all Millipore-Sigma, Oakville, ON, Canada, in Type I ultra-pure water) kept at 28°C. Embryos were then seeded into 96-well plates at 6 hours post-fertilization (hpf) in 100 µL E3 media.

3.5.3 Zebrafish Embryo Toxicity Test (ZFET)

The embryotoxicity was performed in accordance with the Fish Embryo Acute Toxicity test (OECD guideline No. 236) intended for zebrafish.²¹ Stock solutions at twice the concentration (2X) were prepared for each exposure concentration using E3 media as solvent. Exposures were performed in 96-well plates where columns 1-2 contained the vehicle control (E3 media with 0.1 % DMSO) and columns 3-4, 5-6, 7-8, 9-10, 11-12 contained dose exposures of 5 concentrations (with 0.1 % DMSO) increasing from left to right. Exposures were performed in duplicates for a total of n=32 embryos per exposure concentration. 100 µL of 2x stock solution was added to wells containing individual embryos seeded in 100 µL E3 medium at 12 hpf to obtain nominal exposure concentrations. Plates were then incubated at 28°C with parafilm cover. Solutions were renewed by removal of 100 µL and replacement with 100 µL of 1X stock solution at 24, 48, 72 and 96 hpf (static renewal design). Cumulative lethality (based on characteristics specified in OECD guideline No. 236) and cumulative teratogenic endpoints were assessed at 120 hpf to quantify zebrafish embryo lethality (LC₅₀) and teratogenicity (EC₅₀). Briefly, zebrafish embryos develop quickly with most major organs forming and functional between 48-72 hpf.³⁰ Once the embryos have hatched at ~48-72 hpf, they are considered eleutheroembryos that are free swimming but dependent on yolk sac reserves (~96-120 hpf). When evaluating embryotoxicity according to OECD guideline No. 236, the key lethal endpoints considered are i) coagulation of the embryo and/or the embryo becoming opaque or white; ii) a lack of somite formation; iii) non-detachment of the tail from the yolk sac and iv) lack of heartbeat. Teratogenic endpoints assessed were abnormal development of the spine/tail (curvatures/axis malformations) and the presence

of generalized or specialized (pericardial, brain, yolk sac) edemas.^{21,34–38} These sublethal indicators often lead to premature death of the zebrafish. An upright microscope (Olympus SZ61 with Infinity 2 camera and Infinity Analyze software) was used to assess embryos for the presence or absence of morphological deformities using a binary scoring system. Embryos were classified as deformed when clear structural abnormalities, such as tail curvature or edema, were observed. Minor variations that were not clearly distinguishable from normal biological variability were not scored as deformities.

3.5.3.1 Statistical analysis

Dead and malformed embryos were scored at 120 hpf and used to determine 120 hpf LC₅₀ and EC₅₀ respectively. This data was used to plot the ZFET concentration based on the cumulative number of dead and malformed embryos as a fraction of initially plated embryos per concentration (n=32) at each concentration at 120 hpf. LC₅₀ and EC₅₀ were determined using the European Food Safety Authority (EFSA's) BMC assessment tool that incorporates PROAST v70.0.³⁹ LC₅₀ and EC₅₀ were calculated based upon fitting to the following models: two-stage, log-logistic, Weibull, log-probit, 3-parameter exponential, 3-parameter Hill, and gamma.³⁹ LC₅₀ and EC₅₀ were determined based on the model that gave the lowest Akaike's Information Criterion (AIC) as recommended by the EFSA Scientific Committee.³⁹ Datapoints were plotted in OriginLab Graphing and Analysis Software (2026). Error bars are shown as 95% confidence intervals and calculated using the Wilson score method.

3.5.4 Imaging of embryos

To obtain representative imaging of lethality and malformations observed in exposures, we conducted a ZFET exposure including 0.1% DMSO vehicle control and 1-1000mg/L logarithmically spaced exposure groups with poly(mP-D-S) as previously described. The exception was the use of black-walled microplates (Invitrogen, Burlington, ON, Canada) to improve imaging and avoiding light interference from other wells.

Imaging was performed using a BioTek Cytation 5 Cell Imaging Multimode Reader (Agilent, Mississauga, ON, Canada) with brightfield microscopy with 4X PL FL using the Gen5 3.17 software. Embryos were imaged prior to media refresh on 24, 48, 72, 96, and 120 hpf. Imaging at 96 and 120 hpf required application of 0.04%w/v pH of 7.2 MS-222 (Syndel) to stabilize eleutheroembryos for imaging. Images were taken with illumination intensity of 10, integration time of 5 ms, and camera gain set at 12 and final magnification of 4X.

3.5.5 Synthesis of poly(mP-D-S)

Poly(mP-D-S) was synthesized by nitroxide mediated polymerization (NMP) as previously reported. BlocBuilder-MA (0.725 g, 1.9 mmol), mPEGMA (57.00 g, 190.0 mmol), DMAEMA (29.87 g, 190.0 mmol), and styrene (1.187 g, 11.4 mmol) were dissolved

in 82.5 mL of toluene and bubbled with N₂ in an ice bath for 30 minutes ($M_{n,Target} = 46 \text{ kg mol}^{-1}$, Table S1). The solution was then heated in a sand bath at 90°C for 90 minutes reaching a conversion of 54%. The start of the reaction was recorded when the target temperature was reached ($t = 0 \text{ min}$). The reaction was stopped, cooled to room temperature and the polymer was purified through precipitation in excess hexanes from 5-10 mL of DCM which was repeated 3 times. The DCM present in the polymer solution was removed via rotary evaporation and dried overnight under vacuum. Analysis was performed using ¹H-NMR.

The ¹H-NMR spectra were obtained using a Bruker AVANCE II 400 MHz spectrometer. Samples were prepared by dissolving 10-15 mg in 0.5mL of CDCl₃. The ¹H-NMR analysis showed peaks at 3.3–4.0 ppm (HC–O–R from mPEGMA), 2.0–2.7 ppm (O–CH₂ from DMAEMA), and 6.9–7.25 ppm (aromatic protons from styrene) were used to determine the polymer molar composition ($F_{P(Sty)}$, F_{DMAEMA} and F_{mPEGMA}). The styrene peaks at 6.9–7.3 ppm was assumed to represent 6 repeats since styrene conversion was complete, thus, an integration value of 30 was assigned. The abbreviated term poly(mP-D-S) represents the synthesized polymer with 50%, 46%, 4% of mPEGMA, DMAEMA, and styrene respectively. The ¹H-NMR spectrum results are presented in Fig. S1.

3.5.6 Alkylation

The polymer, poly(mP-D-S) (2 g), was stirred in ACN (10 mL) at 600 rpm until dissolved. The percentage (25%, 50%, 75%, 85%, 95%) per DMAEMA molar ratio of *n*-propyl bromide to DMAEMA units was added to the flask containing the polymer solution. The solution was left stirring at 600 rpm at room temperature overnight.³¹ The stir bar was removed, the excess solvent was rotovapped, and the sample was dried under vacuum overnight, and prepared by dissolving 10-15 mg in 0.5mL of D₂O. and analyzed by ¹H-NMR. Broad peaks at 4.5 ppm indicated successful alkylation. ¹H-NMR spectra are presented in Fig. S2. The alkylated polymer has been abbreviated as poly(mP-D-S)-Br.

3.5.7 Counterion exchange

The alkylated polymer, poly(mP-D-S)-Br (2 g), was stirred in ACN (10 mL) at 600 rpm until dissolved. Ion exchange was performed with 4 mol eq. of Li-TFSI to alkylated DMAEMA and added to the polymer solution.⁴⁰ Solutions were stirred at 600 rpm at room temperature overnight. The resulting PIL was precipitated three times into diethyl ether from DCM. The excess solvent was rotovapped, and the sample was dried under vacuum overnight, and prepared for NMR by dissolving 10-15 mg in 0.5mL of D₂O. ¹H-NMR and ¹⁹F-NMR were taken before and after counterion exchange. The alkylated polymer with TFSI[−] counterions has been abbreviated as poly(mP-D-S)-TFSI.

3.5.8 Preparation of dielectric solutions

Each component of the dielectric solution including the polymer, ACN, and crosslinker were filtered through a 0.45 µm polytetrafluorethylene syringe filter prior to mixing. The dielectric solution was composed of 150 mg mL⁻¹ of the polymer dissolved in ACN in which 0.1 molar equivalent of the crosslinker, BBEE, per DMAEMA was added.^{31,41}

3.5.9 Fabrication and characterization of metal–insulator–metal (MIM) capacitors

25 mm × 25 mm glass substrates were cleaned by sequential sonication (VWR Ultrasonic cleaner, 97043-964) in detergent solution (Contrex AL alkaline liquid detergent), DI water, acetone, and methanol for 5 minutes each before drying with a stream of N₂. Electrodes were deposited using physical vapour deposition (PVD) of 2 nm of Cr followed by 50 nm of Au and were patterned onto the substrates using custom shadow masks. PVD was performed using Angstrom Engineering EvoVac at a pressure of no more than 10⁻⁶ Torr at a rate of 0.05nm/s. The dielectric solution was deposited *via* static spin-coating. 300 µL of dielectric solution was dispensed onto the substrate at 2000 rpm for 90 s. Substrates were then annealed in an oven under vacuum at 80°C overnight. The following morning, the oven temperature was increased to 100°C for 1 hour and then cooled to room temperature. PVD was used to deposit 50 nm of Au on the substrates through a shadow mask. Each substrate contained 10 capacitor sites with different areas, and each polymer sample used as a dielectric layer was fabricated in duplicates, resulting in a total of 20 capacitor sites per sample ($n = 20$).

3.5.10 Electrochemical Impedance Spectroscopy (EIS)

EIS was used to characterize the dielectric properties of the films by sweeping from 10⁶ Hz to 0.05 Hz at 10 mV using a Metrohm PGSTAT204 potentistat/galvanostat. An average film thickness and root mean square roughness was calculated from six different locations taken on each film using a Bruker Dektak XT profilometer (Table S3). The dielectric constant (k) and capacitance density (C_i) for each site were calculated using the real (Z) and imaginary (Z'') portions of the impedance, average film thickness (t), capacitor area (A), permittivity of vacuum (ϵ_0), and angular frequency (ω) described in Equations 3.1 and 3.2.

$$\kappa = \frac{t}{\omega A \epsilon_0} \left(\frac{Z''}{Z'^2 + Z''^2} \right) \quad (3.1)$$

$$C_i = \frac{\kappa \epsilon_0 A}{t} \quad (3.2)$$

EIS-derived real (Z') and imaginary (Z'') portions of the impedance were used to calculate the bulk resistance from a circular fit of the semi-circle portion. The ionic conductivity (σ) of the films was determined using the average film thickness (t), bulk resistance (R_b), and capacitor area (A) described in Equation 3.3.

$$\sigma = \frac{t}{R_b A} \quad (3.3)$$

3.6 Results and Discussion

3.6.1 Synthesis, alkylation, and counterion exchange

Poly(mP-D-S)) random copolymer was synthesized via NMP alkylated with *n*-propyl bromide and subjected to counterion exchange with TFSI⁻ (Fig. 1). NMP was employed for its simple purification process, and for the ability to synthesize different acrylamides, acrylates, styrenics, and methacrylates using the same unimolecular initiator.^{42–46} Prior investigations of poly(mP-D-S) determined the optimal monomer and crosslinking ratios and evaluated the impact of alkylation on its properties.^{42,47} Therefore, the poly(mP-D-S) was alkylated with 25%, 50%, 75%, 85% and 95% *n*-propyl bromide relative to DMAEMA (poly(mP-D-S)-Br) followed by counterion exchange to obtain poly(mP-D-S) alkylated with TFSI⁻ anions (poly(mP-D-S)-TFSI). Completion of alkylation and ion exchange was monitored by ¹H-NMR and ¹⁹F-NMR (Fig. S3 & S4). The resulting polymers were purified for use in electronic device fabrication.

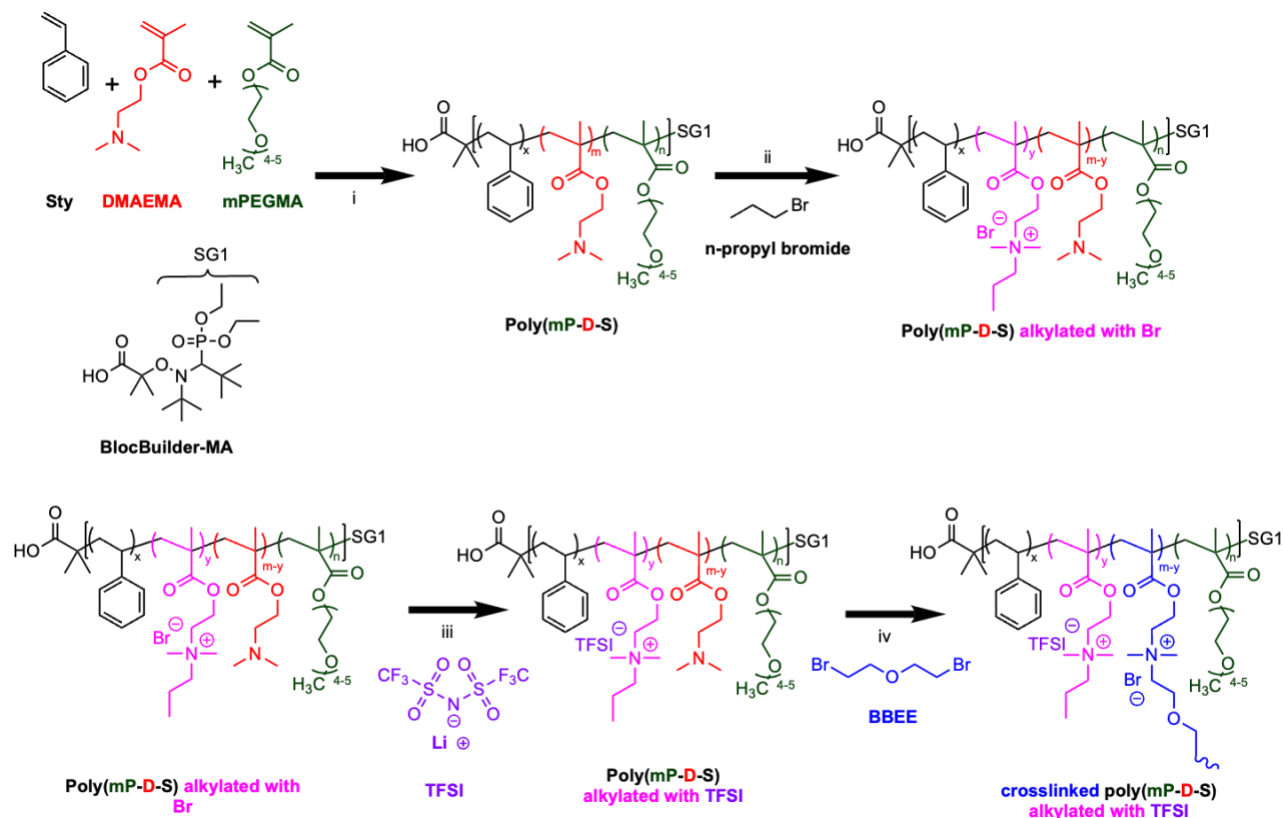


Figure 3.1 Synthesis pathway of poly(mP-D-S), (i) BlocBuilder-MA, mPEGMA, DMAEMA, and styrene are dissolved in toluene and put in an ice bath for 30 min bubbled with N₂ then heated and stirred at 90°C for 90 min, (ii) alkylation reaction of poly(mP-D-S) by adding desired molar equivalent of n-propyl bromide in ACN stirring at room temperature overnight, (iii) counterion exchange of Br⁻ with TFSI⁻ in ACN stirring at room temperature overnight, (iv) crosslinking reaction of polymer with desired molar equivalent of BBEE to DMAEMA, spincoated and annealed at 80°C overnight and increased to 100°C for 1 hour.

3.6.2 PIL integrated into MIM capacitors

Poly(mP-D-S)-TFSI, crosslinked with 0.1 equivalents of BBEE (relative to DMAEMA), was employed as the insulating layer between two gold electrodes in MIM capacitors, which were characterized using EIS. The frequency was swept from 10⁶ to 0.05 Hz to investigate capacitance density and phase angle as a function of frequency. Alkylation percentages of 25, 50, 75, 85, and 95 were investigated with TFSI⁻ as the counterion (Fig. 2). The dielectric performance can be determined based on the EDL onset frequency and capacitance density. When the phase angle begins to decrease this indicates the beginning of the formation of the EDL where the polymer chains begin to align as a function of the applied electric field. The mobile ions, in this case TFSI⁻ from the counterion exchange and Br⁻ from the crosslinking agent, migrate toward the positively charged electrode. Once enough mobile ions have migrated, the EDL is fully formed indicated by a plateau in the capacitance density curve. The EDL onset frequency indicates how fast a dielectric material can form an EDL, so a higher frequency means the mobile ions are able to form an EDL more quickly.^{14,31,45} Additionally, capacitance density is indicative of the packing efficiency of the material.^{47,48} A higher capacitance density means that a large capacitance can be achieved in a smaller area which is ideal when developing high performance dielectrics.

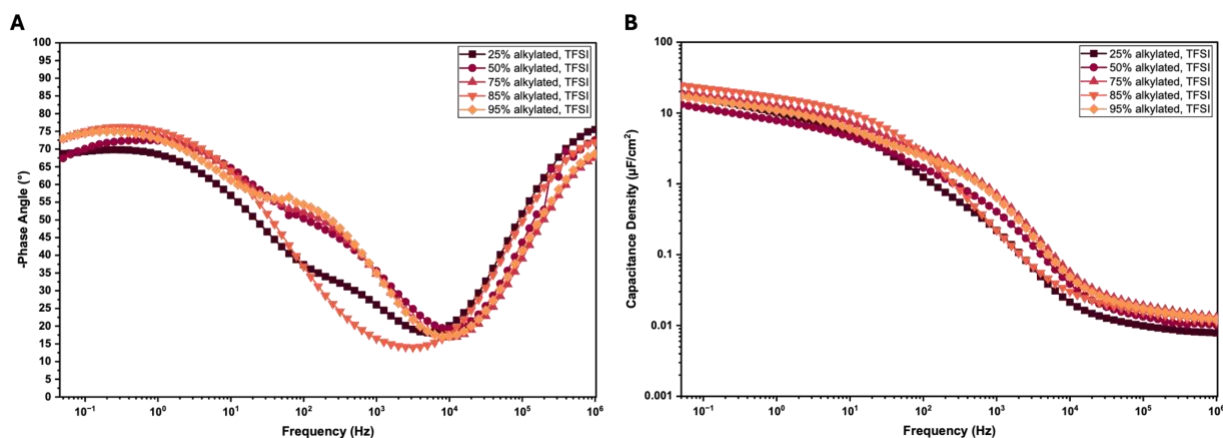


Figure 3.2 EIS results of alkylated poly(mP-D-S) with TFSI⁻ counterions, (A) phase angle vs. frequency, (B) capacitance density vs. frequency.

The EIS results of the crosslinked poly(mP-D-S)-TFSI show that there is almost no difference in performance when increasing alkylation (Table S4, Fig. 2). The EDL onset frequency for poly(mP-D-S)-TFSI ranges from 1.3×10^4 Hz to 5×10^4 Hz when alkylated between 25% and 95%. Minimal difference is observed in the maximum capacitance density achieved which ranged from $13.10 \mu\text{F}/\text{cm}^2$ to $24.67 \mu\text{F}/\text{cm}^2$ at 0.05 Hz for the same samples. This minimal difference in performance when using TFSI⁻ as the counterion is interesting since previously the amount of alkylation had a greater impact on dielectric performance with Br⁻ as the counterion. Previously, the best performance when using Br⁻ as the counterion required 75% alkylation achieving a maximum capacitance density of $11.92 \mu\text{F}/\text{cm}^2$ at 0.05 Hz and an EDL onset frequency of 1.3×10^5 Hz. In this work, similar performance is achievable with 25% alkylation. We believe this can be attributed to the counterion size, TFSI⁻ is larger and able to achieve faster EDL formation,^{45,49–51} and higher capacitance density^{14,31,32,45} with a smaller amount of TFSI⁻ present.

The ionic conductivity of poly(mP-D-S)-TFSI was determined from the Nyquist plot using bulk resistance circular fitting from the semi-circle portion (Fig. S5, Table S4). The ionic conductivities ranged from $3.32 \times 10^{-7} \text{ S cm}^{-1}$ to $7.62 \times 10^{-7} \text{ S cm}^{-1}$. These results are comparable to other previously reported PIL conductivities.^{9,10,31,32,45} Overall, these results highlight a robust crosslinked PIL system with promising potential for integration into solid electrolyte-based electronics and energy technologies. In light of this potential, early-stage toxicity assessment is essential to determine whether this class of materials may present environmental or health concerns during future development and deployment.^{9,10,52}

3.6.3 PIL toxicity

Although PEG materials are frequently described as biocompatible and having low toxicity, limited information is available regarding the developmental/in vivo toxicity of these copolymers or structurally related systems.^{53–55} Incorporating high-throughput toxicological screening at the polymer development stage using an ethically and economically viable NAM in toxicology testing³⁵ that addresses to policy changes such as the Canadian Bill-S5 and others,^{34,56} enables systematic evaluation of how variations in monomer composition, structure, and counterion influence biological response.^{9,52,57} This approach will enable rational design and guide future PIL development. Therefore, we assessed the toxicity of the individual components as well as the fully assembled polymer. This allows us to determine whether the toxicity of the complete material exceeds or is below the sum of its constituent parts (additivity, synergism or antagonism), and if specific compound may drive the compounds overall toxicity. Since the polymers used in this work are composed of 50% mPEGMA they are water soluble and therefore compatible with the water exposure-based ZFET assay. This study investigated several starting materials including mPEGMA, DMAEMA, BlocBuilder-MA, the alkylating agent

(*n*-propyl bromide), the crosslinking agent (BBEE), and the polymers of interest including poly(mP-D-S), poly(mP-D-S)-Br alkylated 25%, and poly(mP-D-S)-TFSI⁻ alkylated 25%, to comprehensively evaluate the effect on the environment from synthesis to application.

3.6.4 Representative Imaging of zebrafish embryos

In addition to lethal endpoints, sublethal indicators of teratogenicity can contribute to delayed mortality at larval or adult stages. Representative brightfield microscopy images from the ZFET assay show observed developmental endpoints for embryos exposed to five concentrations of poly(mP-D-S) (Fig. 3.3). Normal growth and morphology were observed in the control group throughout the exposure period. Embryos remained intact within the chorion at 24 and 48 hpf, followed by hatching by 72 hpf and typical development of external structures including normal body axis elongation and defined head and tail structures at 72, 96, and 120 hpf (Fig. 3.3, Control). Embryos exposed to 1 mg/L poly(mP-D-S) showed comparable development to the control group, with no clear evidence of coagulation, edema, axial curvature, or other malformations (Fig. 3.3, 1mg/L).

At 10 mg/L, embryos remained viable; however, mild yolk-sac edema was observed at 120 hpf, indicating the onset of sublethal developmental toxicity (Fig. 3.3, 10mg/L). At higher concentrations of poly(mP-D-S) (≥ 100 mg/L), embryo development was most severely affected. Embryos exposed to 100 mg/L showed more pronounced toxicity, disrupted morphology and edema near the anterior/yolk-sac region, as indicated by the red arrow in Figure 3. These malformations were associated with subsequent mortality observed in these embryos exposed to 100 mg/L. At 1000 mg/L, embryos exhibited lethality, appeared darkened, and poorly developed across the exposure period, with no normal larval structures evident at 72 hpf and later timepoints (Fig. 3.3, 1000 mg/L). These observations show a representative observation of the exposure to poly(mP-D-S) and related material which resulted in sublethal edema and mortality at high concentrations.

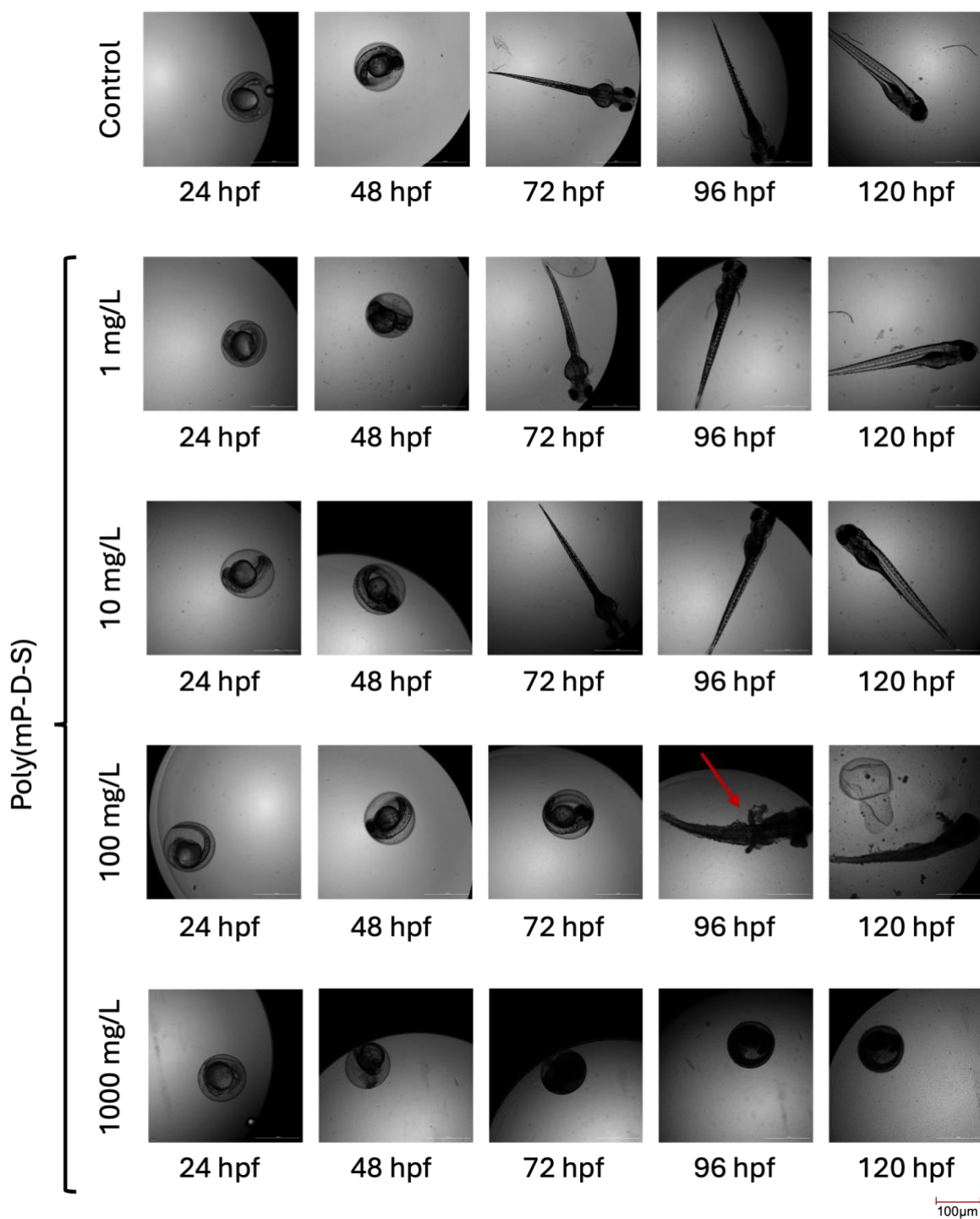


Figure 3.3 Representative images of zebrafish morphology imaging of control and increasing concentrations of poly(mP-D-S) from 1 mg/L to 1000 mg/L. A scale bar of 100µm with 4X magnification was used.

Hatching was assessed by determining whether embryos had exited the chorion by 120 hpf. At the highest exposure concentrations, 100% of embryos died and remained unhatched following treatment with poly(mP-D-S), n-propyl bromide, poly(mP-D-S)-Br, and BBEE (Table S5). The highest concentrations of DMAEMA, poly(mP-D-S)-TFSI, mPEGMA, and BlocBuilder resulted in 50.00%, 46.88%, 53.13%, and 46.88% unhatched embryos, respectively (Table S5).

The lethal endpoints and sublethal developmental effects observed in the exposure of poly(mP-D-S) are consistent with the standard signs of mortality and teratogenicity used in the ZFET. Based on these findings we surmise that PEG-related components may contribute to edema formation through osmotic dysregulation and increased fluid retention in embryonic tissues. The hydrophilic nature of PEG-containing materials may promote water accumulation, while additional toxic constituents in the exposure material may impair normal developmental processes, including cardiovascular and osmoregulatory function. This combined mechanism may explain the observed transition from sublethal edema to mortality with increasing poly(mP-D-S) concentration.

Acrylates and methacrylates are known to cause zebrafish embryo mortality through coagulation and development delays.^{58–62} Other sublethal effects, most notably pericardial edemas have been reported previously.^{58–62} DMAEMA may have contributed to developmental abnormalities such as edemas, given its reported aquatic toxicity in fish and invertebrates and prior observations of pericardial edema in methacrylate-exposed zebrafish embryos.^{52,63,64} Screening materials using the ZFET for potential environmental effects prior to commercialization provides valuable insight within a relatively short timeline. Evaluating the toxicological effect of new polymers, including the monomers and initiators used in their synthesis, during the design phase supports a safer-by-design approach that considers both aquatic life and broader vertebrate development. This approach provides toxicity findings relevant to aquatic toxicology, human toxicology, and One Health frameworks helping for reshaping how new materials in next generation technologies can be advanced.⁶⁵

3.6.4.1 PILs evaluated with ZFET

In addition to observing morphology effects, toxicity tests are a useful method for assessing exposure effects of pollutants on the environment by quantifying exposure limits. In ZFET, acute toxicity is expressed as LC₅₀, representing the concentration in which 50% of the embryos exposed died. Developmental or sublethal toxicity is expressed as EC₅₀, representing the concentration in which 50% of the embryos are observed to have visible malformities. LC₅₀ and EC₅₀ are a useful way to compare pollutant risk and can provide insight to help form policies. The ZFET included exposing embryos to a range of five concentrations of each sample to then plot the concentration response of each sample (Fig. 3.4, Fig. S6). Styrene was not included as it only comprises

4% of the polymer, is insoluble in water, and is already known to be moderately toxic to aquatic life. Li-TFSI⁻ was not included as previous literature in ZFET has been reported of combined threshold EC_{10,overall} was derived as 1154.48 ng/L.⁶⁶ The LC₅₀ and EC₅₀ of each compound has been derived from the concentration responses and presented in Table 1.

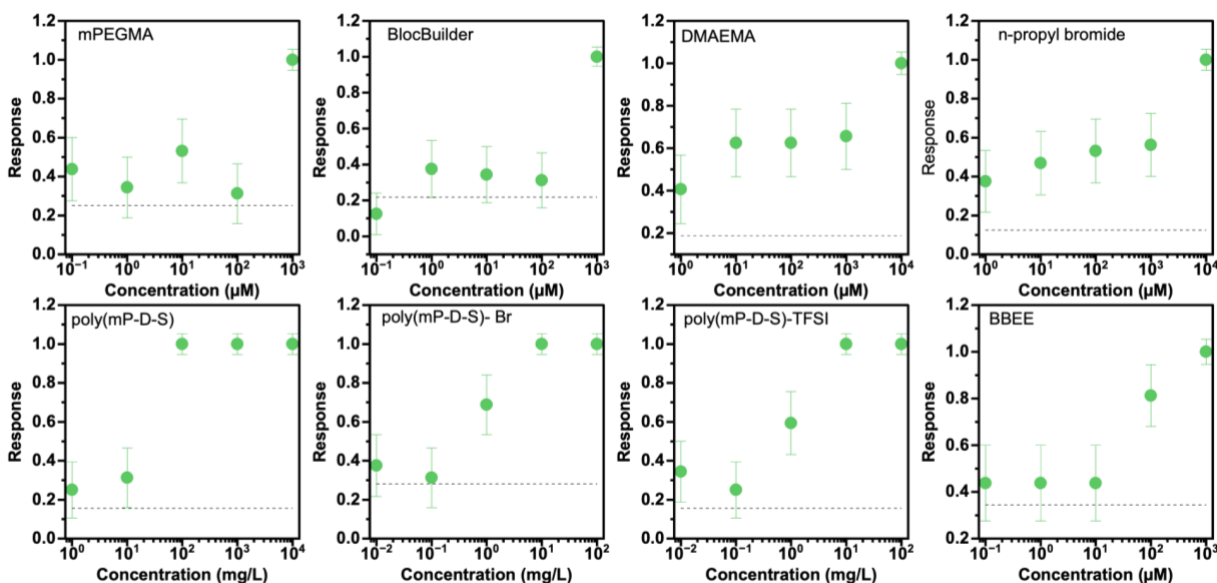


Figure 3.4. ZFET results of reactants, alkylating agent, crosslinking agent, and polymers. Lethal concentration response curve of each sample where the X-axis is the concentration and Y-axis is the response meaning how many embryos did not survive. n=32 for each data point. Error bars represent the 95% confidence interval; dotted line represents control.

Table 3.1 LC₅₀ and EC₅₀ and 95% confidence interval (CI) of the compounds tested in ZFET.

Compound	LC ₅₀ (mg/L)	LC ₅₀ CI	EC ₅₀ (mg/L)	EC ₅₀ CI
mPEGMA	60.6	(27.78, 100.5)	0.102	(0.001, 1.86)
DMAEMA	1.33	(0.057, 9.134)	0.080	(0.0006, 1.041)
BlocBuilder	46.54	(38.145, 361.991)	0.427	(0.020, 3.174)
BBEE	5.032	(0.257, 19.991)	0.257	(0.0002, 4.569)
n-propyl bromide	6.96	(1.070, 35.051)	0.357	(0.012, 2.435)
poly(mP-D-S)	11.5	(10, 80.8)	3.83	(1.05, 9.63)
poly(mP-D-S)-Br	0.781	(0.133, 0.992)	0.144	(0.0258, 0.906)
poly(mP-D-S)-TFSI	0.671	(0.252, 1.46)	0.0834	(0.0145, 0.279)

When categorizing the toxicity of a compound a lower LC₅₀ or EC₅₀ indicates higher toxicity as less of the compound is required to elicit the toxic effect. The ZFET results indicated that of the monomers used, DMAEMA was the most toxic. The results for the polymers showed that poly(mP-D-S) is toxic with an LC₅₀ and an EC₅₀ of 11.50 mg/L and 3.83 mg/L respectively. Interestingly, alkylation seems to increase the toxicity as seen in the results for poly(mP-D-S)-Br. The toxicity is even further increased when the counterion TFSI⁻ is used as seen in poly(mP-D-S)-TFSI. The alkylation agent, *n*-propyl bromide, is less toxic than the monomer DMAEMA which comprises 46% of the polymer, however, when the polymer is alkylated both the DMAEMA and *n*-propyl bromide increase the toxicity dramatically seen by the results of poly(mP-D-S)-Br. The toxicity of poly(mP-D-S)-TFSI is expected to be more than that of poly(mP-D-S)-Br since TFSI⁻ itself is a known toxic compound especially to aquatic life with an 96h-LC₅₀ of 67.20 mg/L from OECD TG 203.⁶⁶ Notably, the final PIL copolymers are more toxic than any of the individual components used in their synthesis. While a common misconception is that diluting more toxic monomers with less toxic ones would reduce the LC₅₀, this trend is not observed. These concentrations, LC₅₀ and EC₅₀, are important for risk assessment and help identify a compound's toxicity. This is increasingly important when it comes to regulation of new and emerging compounds as it helps regulatory agencies refer to values to determine safe handling, transport, and disposal protocols for chemicals.

3.7 Conclusion

In this work we synthesized a series of novel copolymer PILs where the counterion exchange of Br⁻ for TFSI⁻ demonstrated the importance in anion selection towards the resulting electrical properties and environmental toxicity. EIS data showed comparable maximum capacitance density, ionic conductivity, and EDL onset frequency to previous work.³¹ The effect of alkylation with TFSI⁻ as the counterion had a less dramatic on EDL onset than when Br⁻ was used meaning that less alkylation was required to achieve similar performance previously reported when using Br⁻ as the counterion. The toxicity of monomers and PILs was investigated using ZFET to explore the effect on morphology and the toxicological dose descriptors (LC₅₀ and EC₅₀). The morphology of the zebrafish for poly(mP-D-S) were imaged to show the effect of increasing polymer concentration on development. At high concentrations of poly(mP-D-S) hatching is delayed and malformations are observed. The ZFET method was used to plot the lethal and effect concentration response to determine the LC₅₀ and EC₅₀ of several starting materials, crosslinking agent, alkylation agent, and polymers, poly(mP-D-S)-Br and poly(mP-D-S)-TFSI⁻ were both toxic with poly(mP-D-S)-TFSI demonstrating the highest toxicity.

These findings demonstrate how both performance and environmental impact should be considered when developing new polymer materials. High-throughput screening offers an approach that can help reduce environmental risk during material development which can help mitigate the contribution to e-waste on the environment. Identifying potential

toxic compounds early in the development process allows researchers to make informed decisions about investing resources, time, and money into new materials. This approach supports environmental protection and innovation by ensuring that research into safer, promising materials are explored to create an efficient and risk-aware development process.

3.8 Acknowledgements

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3.9 Supplemental Information

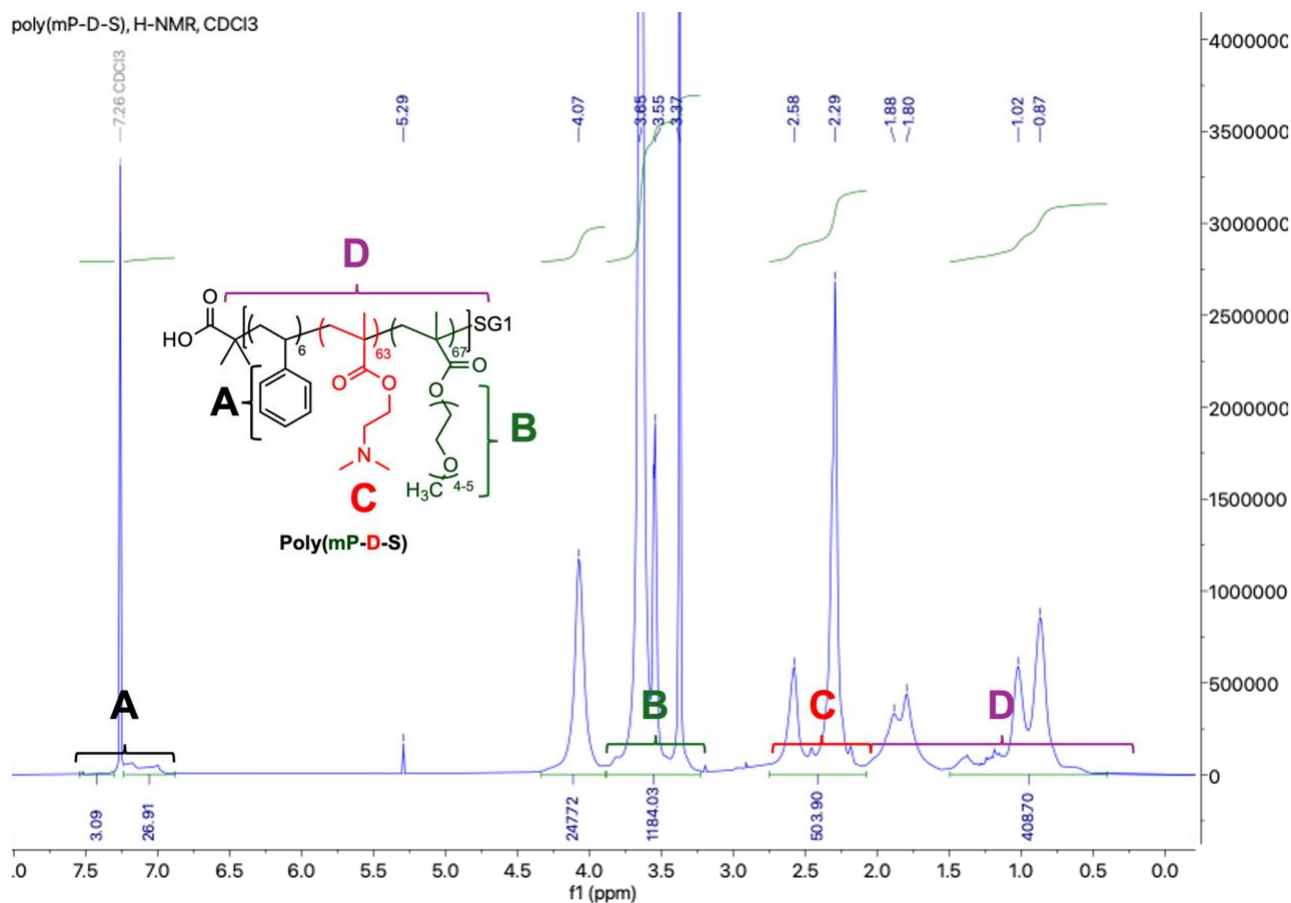


Figure S1. ¹H-NMR of poly(mP-D-S)

The molar ratio of Styrene, mPEGMA, and DMAEMA was calculated:

Styrene: mPEGMA: DMAEMA

$$\frac{I_A}{5} : \frac{I_B}{17.78} : \frac{I_C}{8}$$

Styrene was assumed to have a value of 30 (based on 6 styrene repeat units per chain).

The composition of the entire polymer was calculated:

$$F_{\text{Styrene}} = \frac{\text{Styrene}}{\text{Styrene} + \text{PEGMA} + \text{DMAEMA}}$$

$$F_{\text{PEGMA}} = \frac{\text{PEGMA}}{\text{Styrene} + \text{PEGMA} + \text{DMAEMA}}$$

$$F_{DMAEMA} = \frac{DMAEMA}{Styrene + PEGMA + DMAEMA}$$

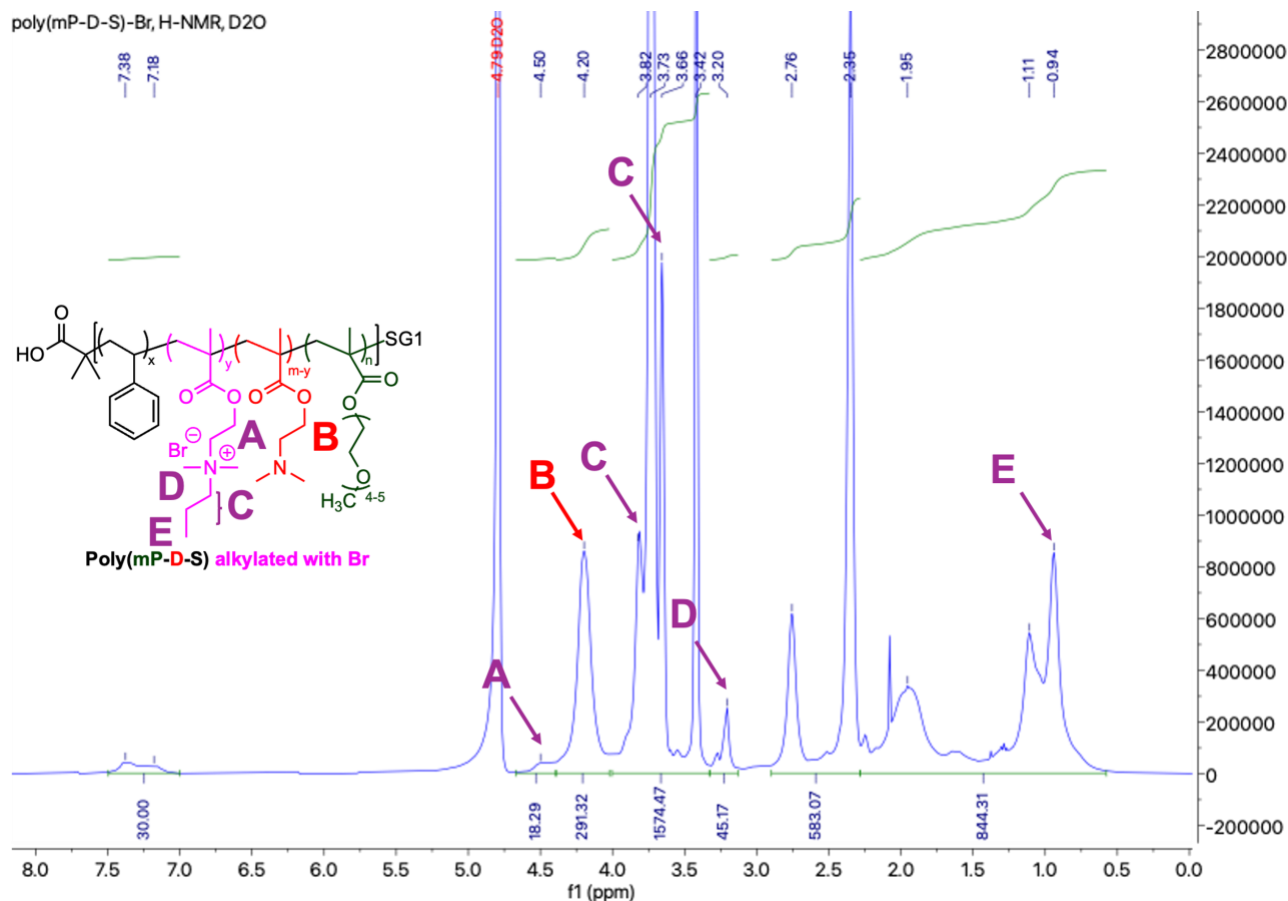


Figure S2. ^1H -NMR of poly(mP-D-S)-Br (25% alkylation)

Styrene, mPEGMA, and DMAEMA components were calculated as seen in Figure S1.

Peaks A, C, D, E are specific to alkylation of the PIL, the molar ratio of DMAEMA alkylated was calculated:

DMAEMA alkylated

$$\frac{\left(\frac{I_A}{2} + \frac{I_C}{4} + \frac{I_D}{6}\right)}{3}$$

The composition of the entire polymer was calculated:

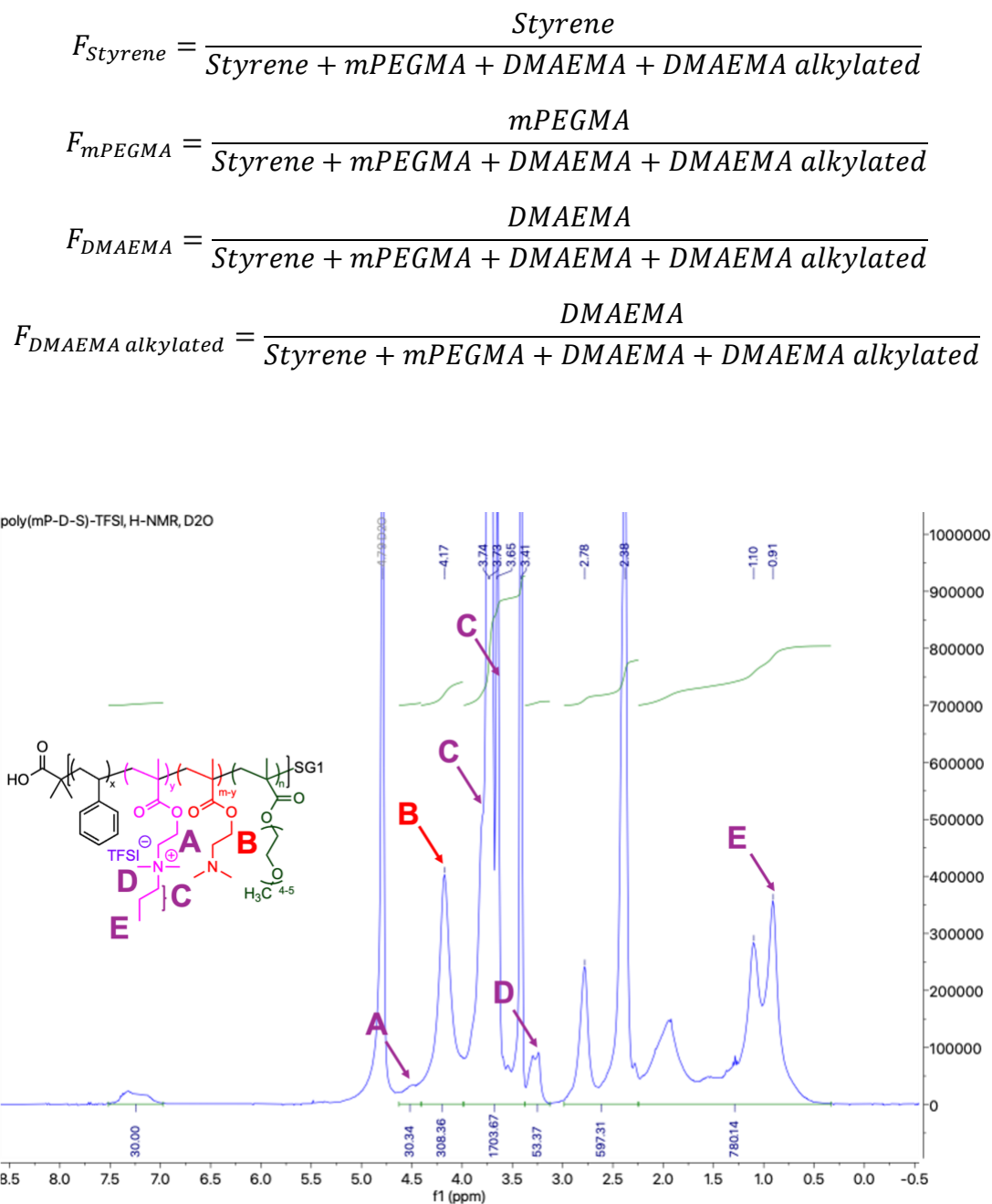


Figure S3. ^1H -NMR of poly(mP-D-S)-TFSI (25% alkylation)

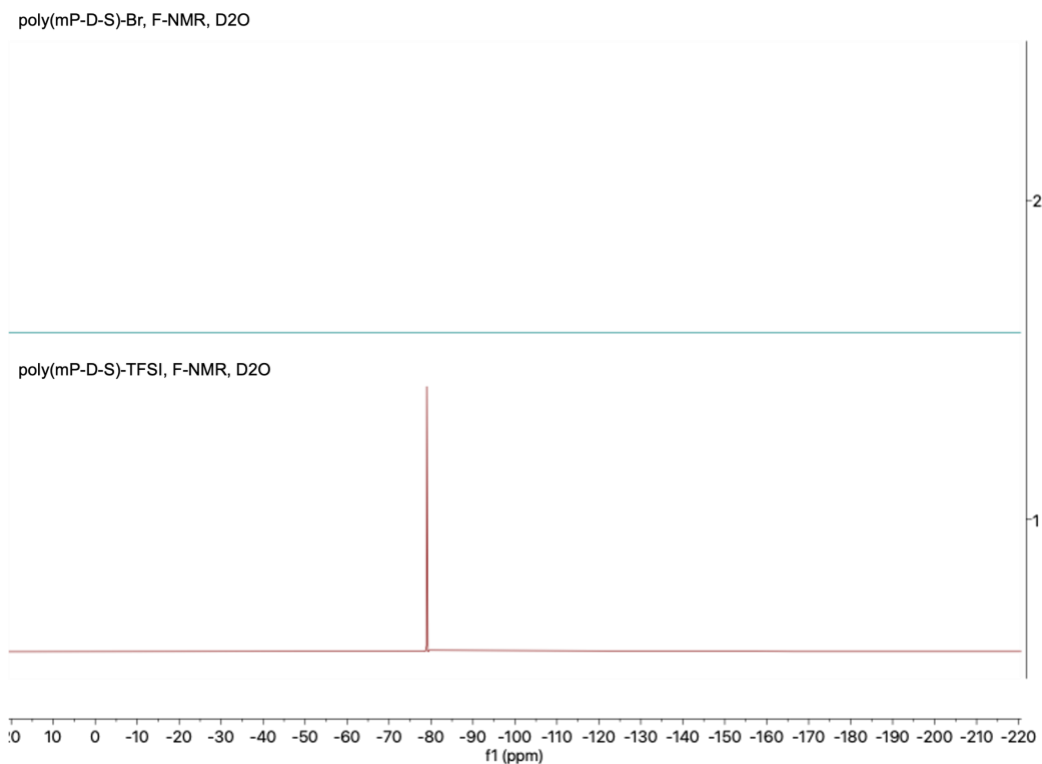


Figure S4. ^{19}F -NMR before and after counterion exchange of poly(mP-D-S)-TFSI (alkylated 25%)

Table S1. PIL synthesis deployed molar equivalents.

ID	BlocBuilder	Deployed Molar Eq.		
		Styrene	DMAEMA	mPEGMA
poly(mP-D-S)	1	6	100	100

Table S2. PIL synthesis summary. FS, FDMAEMA, and FmPEGMA represent the frequency of monomer in the polymer. ^1H -NMR was used to determine monomer conversion and composition in the polymer.

ID	F _S	F _{DMAEMA}	F _{mPEGMA}	Conversion (%)	Yield (%)
poly(mP-D-S)	0.04	0.46	0.50	54	38

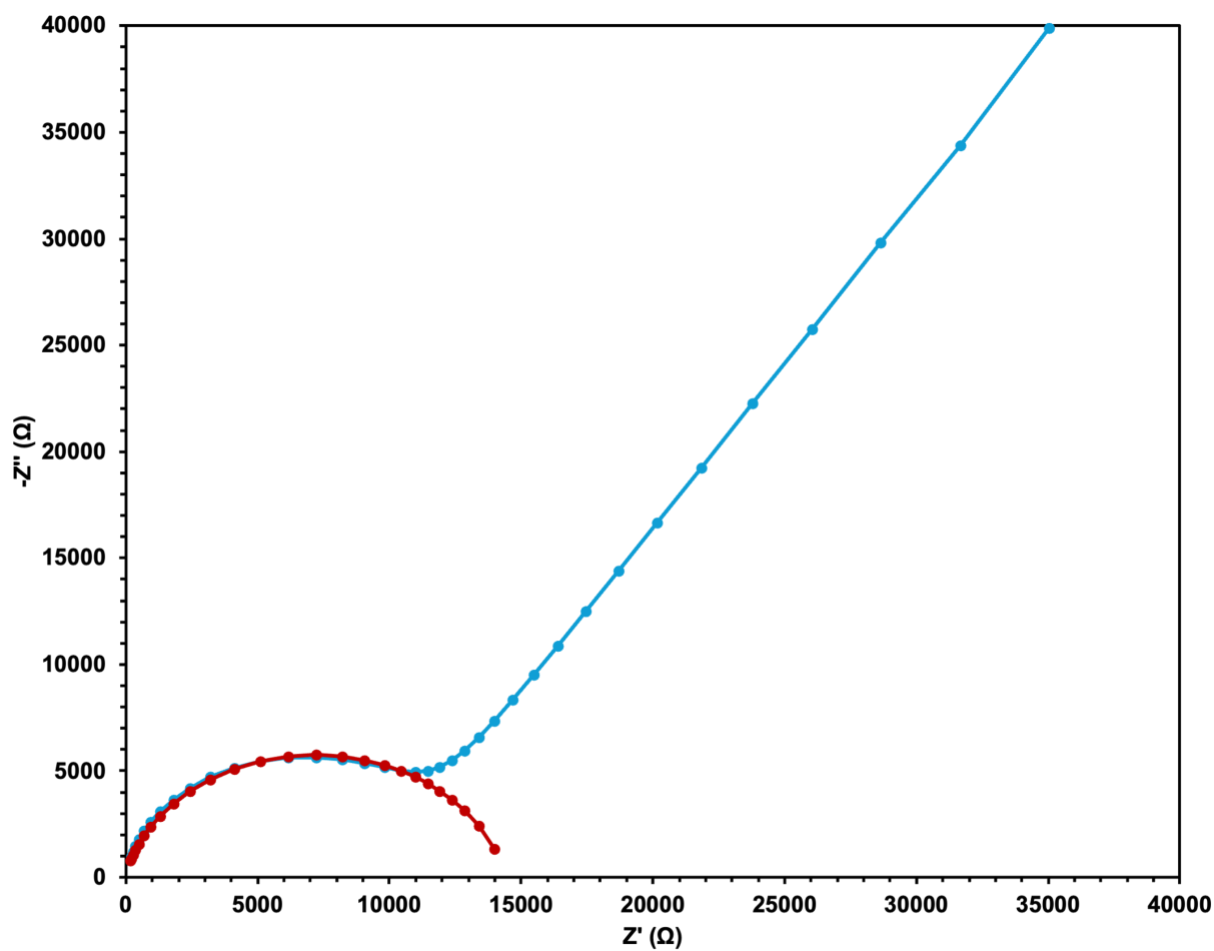


Figure S5. Representative Nyquist plot from MIM capacitor. Ionic conductivity was determined by performing a circular fit from the semi-circle portion seen in red.

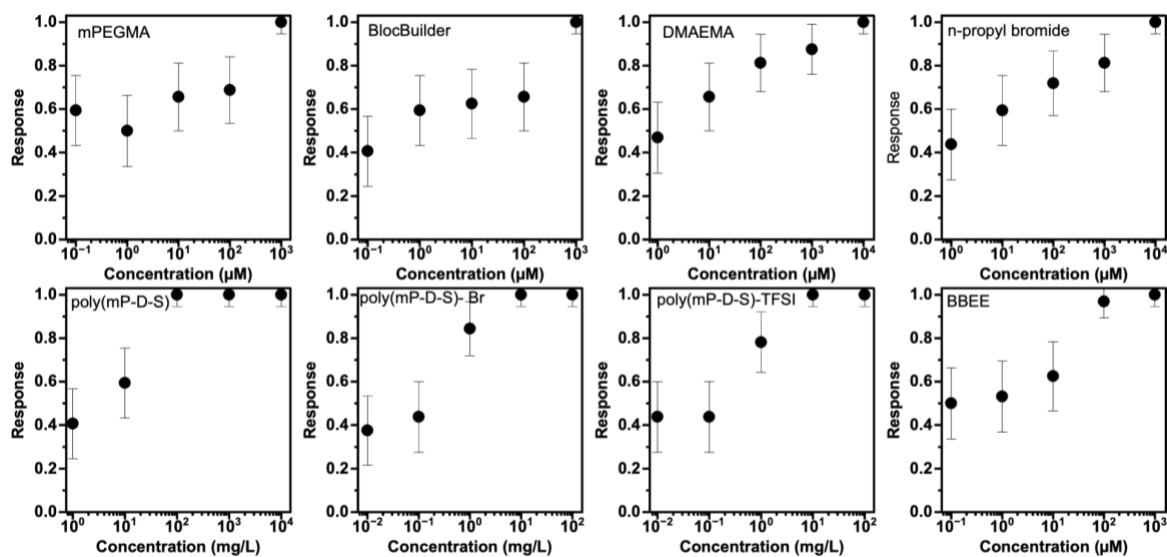


Fig S6. ZFET results of reactants, alkylating agent, crosslinking agent, and polymers. Effect concentration response curve of each sample where the X-axis is the concentration and Y-axis is the response meaning how many embryos exhibited malformations, n=32 for each data point.

Table S3. MIM capacitor profilometry and film information summary, roughness is the R_q , and n represents number of working devices.

Film ID	Thickness (nm)	Roughness (nm)	n
poly(mP-D-S)-TFSI 25%	806 ± 198	25 ± 7	17
poly(mP-D-S)-TFSI 50%	655 ± 27	24 ± 13	16
poly(mP-D-S)-TFSI 75%	631 ± 16	17 ± 7	10
poly(mP-D-S)-TFSI 85%	690 ± 36	29 ± 16	18
poly(mP-D-S)-TFSI 95%	639 ± 30	27 ± 7	14

Table S4. MIM capacitor EIS results summary

Film ID	EDL onset (Hz)	κ at 0.05 Hz	C_i at 0.05 Hz ($\mu\text{F}/\text{cm}^2$)	Ionic Conductivity (S/cm)
poly(mP-D-S)-TFSI 25%	19942	17002 ± 6784	18.54 ± 6.88	3.3×10^{-7}
poly(mP-D-S)-TFSI 50%	25106	9693 ± 4510	13.10 ± 6.08	4.7×10^{-7}
poly(mP-D-S)-TFSI 75%	50098	13928 ± 4304	19.54 ± 6.01	7.6×10^{-7}
poly(mP-D-S)-TFSI 85%	12581	19250 ± 4129	24.67 ± 5.27	3.9×10^{-7}
poly(mP-D-S)-TFSI 95%	39793	12329 ± 3154	17.07 ± 4.44	6.5×10^{-7}

Table S5. Zebrafish Embryo Hatching during exposure at 120 hpf

Compound	Concentration (mg/L)	Unhatched (%)
poly(mP-D-S)	0	15.63
	1	6.25
	10	12.5
	100	15.63
	1000	100
	10000	100
poly(mP-D-S)-Br	0	21.88
	0.01	15.63
	0.1	15.63
	1	28.13
	10	34.38
	100	100
poly(mP-D-S)-TFSI	0	15.63
	0.01	15.63
	0.1	15.63
	1	25
	10	34.38
	100	46.88

Compound	Concentration (μM)	Unhatched (%)
BBEE	0	31.25
	0.1	25
	1	28.13
	10	34.38
	100	50
	1000	100
mPEGMA	0	25
	0.1	21.88
	1	21.88
	10	28.13
	100	25
	1000	53.13
BlocBuilder	0	21.88
	0.1	9.38
	1	21.88
	10	18.75
	100	25
	1000	46.88
DMAEMA	0	18.75
	1	15.63
	10	15.63
	100	18.75
	1000	25
	10000	50
n-Propyl bromide	0	12.5
	1	18.75
	10	18.75
	100	21.88
	1000	37.5
	10000	100

3.10 References

- 1 World Health Organization, Electronic waste (e-waste), [https://www.who.int/news-room/fact-sheets/detail/electronic-waste-\(e-waste\)](https://www.who.int/news-room/fact-sheets/detail/electronic-waste-(e-waste)), (accessed February 27, 2026).
- 2 S. M. Parvez, F. Jahan, M.-N. Brune, J. F. Gorman, M. J. Rahman, D. Carpenter, Z. Islam, M. Rahman, N. Aich, L. D. Knibbs and P. D. Sly, *The Lancet Planetary Health*, 2021, **5**, 905–920.
- 3 L. Andeobu, S. Wibowo and S. Grandhi, *Sustainability*, 2023, **15**, 10405.
- 4 Z. Yang, D. Yue, Y. Yao, J. Li, Q. Chi, Q. Chen, D. Min and Y. Feng, *Polymers*, 2022, **14**, 1160.
- 5 H. Li, Y. Zhou, Y. Liu, L. Li, Y. Liu and Q. Wang, *Chem. Soc. Rev.*, 2021, **50**, 6369–6400.
- 6 T. Zhang, H. Sun, C. Yin, Y. H. Jung, S. Min, Y. Zhang, C. Zhang, Q. Chen, K. J. Lee and Q. Chi, *Progress in Materials Science*, 2023, **140**, 101207.
- 7 M. O'Rourke, N. Duffy, R. D. Marco and I. Potter, *Membranes*, 2011, **1**, 132–148.
- 8 H. Tang, X. Jiang, J. Wang and C. Zhao, *J. Mater. Chem. B*, 2026, **14**, 5820–5835.
- 9 M. Abdollahi, A. Baharian, M. Mohamadhoseini, M. Hassanpour, P. Makvandi, M. Habibizadeh, B. Jafari, R. Nouri, Z. Mohamadnia and N. Nikfarjam, *J. Mater. Chem. B*, 2024, **12**, 9478–9507.
- 10 S. Locatelli, L. I. Ronco, M. Prato, R. J. Minari and G. C. Luque, *J. Mater. Chem. B*, 2026, **14**, 1474–1493.
- 11 X. Ma, J. Yu, Y. Hu, J. Texter and F. Yan, *Ind. Chem. Mater.*, 2023, **1**, 39–59.
- 12 A. S. Shaplov, R. Marcilla and D. Mecerreyes, *Electrochimica Acta*, 2015, **175**, 18–34.
- 13 H. A. Elwan, R. Thimmappa, M. Mamlouk and K. Scott, *Journal of Power Sources*, 2021, **510**, 230371.
- 14 A. J. Peltekoff, V. E. Hiller, G. P. Lopinski, O. A. Melville and B. H. Lessard, *ACS Appl. Polym. Mater.*, 2019, **1**, 3210–3221.
- 15 L. Kastl, D. Sasse, V. Wulf, R. Hartmann, J. Mircheski, C. Ranke, S. Carregal-Romero, J. A. Martínez-López, R. Fernández-Chacón, W. J. Parak, H.-P. Elsasser and P. Rivera-Gil, *ACS Nano*, 2013, **7**, 6605–6618.
- 16 W. Zhao, Y. Chen, N. Hu, D. Long and Y. Cao, *Ecotoxicology and Environmental Safety*, 2024, **272**, 116023.
- 17 L. M. Schuijt, F.-J. Peng, S. J. P. van den Berg, M. M. L. Dingemans and P. J. Van den Brink, *Science of The Total Environment*, 2021, **795**, 148776.
- 18 National Research Council, *Toxicity Testing for Assessment of Environmental Agents: Interim Report*, The National Academies Press, Washington, DC, 2006.
- 19 L. Truong, M. T. Simonich and R. L. Tanguay, in *High-Throughput Screening Assays in Toxicology*, eds. H. Zhu and M. Xia, Springer, New York, NY, 2016, pp. 89–98.
- 20 F. Busquet, R. Strecker, J. M. Rawlings, S. E. Belanger, T. Braunbeck, G. J. Carr, P. Cenijn, P. Fochtman, A. Gourmelon, N. Hübler, A. Kleensang, M. Knöbel, C. Kussatz, J. Legler, A. Lillicrap, F. Martínez-Jerónimo, C. Polleichtner, H. Rzodeczko, E. Salinas, K. E. Schneider, S. Scholz, E.-J. van den Brandhof, L. T. M. van der Ven, S. Walter-Rohde, S. Weigt, H. Witters and M. Halder, *Regulatory Toxicology and Pharmacology*, 2014, **69**, 496–511.

- 21 OECD, *Test No. 236: Fish Embryo Acute Toxicity (FET) Test*, OECD Publishing, Paris, 2013.
- 22 Y. Shim, M. Shim and D. S. Kim, *Membranes*, 2022, **12**, 450.
- 23 T. C. Rhoades, J. C. Wistrom, R. Daniel Johnson and K. M. Miller, *Polymer*, 2016, **100**, 1–9.
- 24 M. Volkov, A. Machikhin, V. Bukova, D. Khokhlov, A. Burlakov and V. Krylov, *Sci Rep*, 2022, **12**, 20884.
- 25 H. Mirmajidi, H. Lee, N. Nipu, J. Thomas, Z. Gajdosechova, D. Kennedy, J. A. Mennigen and E. Hemmer, *J. Mater. Chem. B*, 2024, **13**, 160–176.
- 26 A. Nagaraj, S. Poda, V. V. Konduri, L. Gunti and N. K. Kalagatur, *J. Mater. Chem. B*, 2026, **14**, 4646–4666.
- 27 I. Passi, K. Sugantharam, C. Sumithaa, A. M. Kumar, M. Velusamy and M. Ganeshpandian, *J. Mater. Chem. B*, 2025, **13**, 7714–7727.
- 28 P. Gut, S. Reischauer, D. Y. R. Stainier and R. Arnaout, *Physiological Reviews*, 2017, **97**, 889–938.
- 29 S. Ali, D. L. Champagne, H. P. Spaink and M. K. Richardson, *Birth Defects Research Part C: Embryo Today: Reviews*, 2011, **93**, 115–133.
- 30 C. B. Kimmel, W. W. Ballard, S. R. Kimmel, B. Ullmann and T. F. Schilling, *Developmental Dynamics*, 1995, **203**, 253–310.
- 31 S. McKillop, L. E. Dickson, H. Cho, M. Ourabi, J. G. Manion, V.-A. DiPalo and B. H. Lessard, *J. Mater. Chem. C*, 2025, **13**, 20085–20093.
- 32 A. J. Peltekoff, S. Bixi, J. Niskanen and B. H. Lessard, *JACS Au*, 2021, **1**, 1044–1056.
- 33 M. A. Farzin, S. M. Naghib and N. Rabiee, *J. Mater. Chem. B*, 2025, **13**, 8653–8682.
- 34 N. Nipu, L. Wei, L. Hamilton, H. Lee, J. Thomas and J. A. Mennigen, *Commun Biol*, 2025, **8**, 120.
- 35 R. L. Tanguay, *Toxicol Sci*, 2025, **208**, 40–41.
- 36 B. M. Hedgpeth, A. D. Redman, R. A. Alyea, D. J. Letinski, M. J. Connelly, J. D. Butler, H. Zhou and M. A. Lampi, *Environmental Toxicology and Chemistry*, 2019, **38**, 1302–1312.
- 37 J. Duan, Y. Yu, H. Shi, L. Tian, C. Guo, P. Huang, X. Zhou, S. Peng and Z. Sun, *PLOS ONE*, 2013, **8**, e74606.
- 38 T. Hong, J. Park, G. Song and W. Lim, *Molecules and Cells*, 2024, **47**, 100090.
- 39 E. S. Committee, A. Hardy, D. Benford, T. Halldorsson, M. J. Jeger, K. H. Knutsen, S. More, A. Mortensen, H. Naegeli, H. Noteborn, C. Ockleford, A. Ricci, G. Rycken, V. Silano, R. Solecki, D. Turck, M. Aerts, L. Bodin, A. Davis, L. Edler, U. Gundert-Remy, S. Sand, W. Slob, B. Bottex, J. C. Abrahantes, D. C. Marques, G. Kass and J. R. Schlatter, *EFSA Journal*, 2017, **15**, 4658.
- 40 V.-A. DiPalo, L. E. Dickson, M. Cruz, H. Cho and B. H. Lessard, *ACS Appl. Polym. Mater.*, 2025, **7**, 14541–14549.
- 41 R. Abbasi, A. Mitchell, P. G. Jessop and M. F. Cunningham, *RSC Appl. Polym.*, 2024, **2**, 214–223.
- 42 H. R. Lamontagne and B. H. Lessard, *ACS Appl. Polym. Mater.*, 2020, **2**, 5327–5344.
- 43 B. H. Lessard, X. Savelyeva and M. Marić, *Polymer*, 2012, **53**, 5649–5656.

- 44 M. Maric, *Can. J. Chem. Eng.*, 2021, **99**, 832–852.
- 45 M. N. Tousignant, M. Ourabi, J. Niskanen, B. Mirka, W. J. Bodnaryk, A. Adronov and B. H. Lessard, *Flex. Print. Electron.*, 2022, **7**, 034004.
- 46 N. A. Rice, W. J. Bodnaryk, B. Mirka, O. A. Melville, A. Adronov and B. H. Lessard, *Advanced Electronic Materials*, 2019, **5**, 1800539.
- 47 S. Vavra, E. Ahlberg and A. Martinelli, *Phys. Chem. Chem. Phys.*, 2022, **24**, 24469–24479.
- 48 J. N. Neal, D. J. Wesolowski, D. Henderson and J. Wu, *Journal of Molecular Liquids*, 2018, **270**, 145–150.
- 49 J. R. Keith, N. J. Rebello, B. J. Cowen and V. Ganesan, *ACS Macro Lett.*, 2019, **8**, 387–392.
- 50 F. Yang, M. Zhao, D. Smith, P. Cebe, S. Lucisano, T. Allston and T. W. Smith, *Polymers*, 2022, **14**, 254.
- 51 Jukka Niskanen, Mathieu N. Tousignant, Alexander J. Peltekoff, and Benoît H. Lessard, *ACS Appl. Polym. Mater.*, 2022, **4**, 1559–1564.
- 52 V. C. Crucitti, H. Hajiali, A. A. Dundas, V. Jayawarna, D. Tomolillo, I. Francolini, C. Vuotto, M. Salmeron-Sanchez, M. J. Dalby, M. R. Alexander, R. D. Wildman, F. R. A. J. Rose and D. J. Irvine, *J. Mater. Chem. B*, 2025, **13**, 4657–4670.
- 53 K. Duis, T. Junker and A. Coors, *Environ Sci Eur*, 2021, **33**, 21.
- 54 D. Ghosh, A. Khan, S. Bag, A. I. Mallick and P. De, *J. Mater. Chem. B*, 2024, **12**, 11826–11840.
- 55 A. Aliabadi, M. Hasannia, M. Vakili-Azghandi, F. Araste, K. Abnous, S. M. Taghdisi, M. Ramezani and M. Alibolandi, *J. Mater. Chem. B*, 2023, **11**, 9325–9368.
- 56 *An Act respecting the interoperability of health information technology and to prohibit data blocking by health information technology vendors*, 2026.
- 57 B. Caron, M. Maresca, A. Leroux, M. Lemesle, J. L. Coussegat, L. Fontaine, E. A. Murphy, C. M. Bates, P. H. Nguyen, P. A. Kohl, O. Soppera, S. Canaan, I. Poncin, Y. Guillaneuf and C. Lefay, *J. Mater. Chem. B*, 2026, **14**, 6343–6354.
- 58 F. Alifui-Segbaya and R. George, *Inventions*, 2018, **3**, 52.
- 59 Z. Nejedlá, D. Poustka, R. Herma, M. Liegertová, M. Štofík, J. Smejkal, V. Šícha, P. Kaule and J. Malý, *RSC Advances*, 2021, **11**, 16252–16267.
- 60 A. G. Kramer, J. Vuthiganon and C. S. Lassiter, *Environ Toxicol Pharmacol*, 2016, **43**, 159–165.
- 61 Ebru Emekli Alturfan, Babak Altayib, Gizem Eğilmezer, İsmail Ünal, Ünsal Veli Üstündağ, and Rifat Gözneli, *Eur. J. Res. Dent.*, 2019, **3**, 25–28.
- 62 P. Manuel, M. Almeida, M. Martins and M. Oliveira, *Environmental Research*, 2022, **213**, 113584.
- 63 Organisation for Economic Co-operation and Development, *SIDS Initial Assessment Profile: 2-Dimethylaminoethyl Methacrylate (CAS No. 2867-47-2)*, OECD, Paris, 2002.
- 64 G. of J. Ministry of the Environment, *Results of Aquatic Toxicity Tests of Chemicals Conducted by Ministry of the Environment in Japan (–March 2018)*, Ministry of the Environment, Government of Japan, Tokyo, 2018.
- 65 J. S. Mackenzie and M. Jeggo, *Tropical Medicine and Infectious Disease*, 2019, **4**, 88.

- 66 H. Zhang, J. Jiang, H. Wang, Z. Zhou, Y. Xie, Q. Chen and T. Long, *Journal of Hazardous Materials*, 2025, **499**, 140246.

4. Conclusion and Future Works

4.1 Thesis conclusion

PIL-based dielectrics represent a promising class of materials for flexible and sustainable next-generation electronics.¹⁻³ Their electrical, mechanical, and toxicological properties can be tuned through rational polymer design, including the selection of monomers, side chains, counterions, and overall polymer architecture.^{4,5} This thesis demonstrates how the interplay between performance and toxicological effects can be modulated from the earliest stages of material design. As such, polymer design provides a critical framework for developing application-specific dielectric materials with balanced functionality, processability, and safety.

In Chapter 2, a novel PIL composed of mPEGMA, DMAEMA, and styrene was synthesized and evaluated as a crosslinkable dielectric material.⁶ The effects of monomer composition, percentage of alkylation, and amount of crosslinking were investigated to establish structure-property relationships governing dielectric performance. The optimal crosslinking condition was determined to be 0.1 molar equivalents of BBEE relative to DMAEMA, which was subsequently used for film deposition throughout the study. Monomer composition was found to influence EIS performance, although the effect was less pronounced than that of alkylation. Among the unalkylated PILs examined, the 70:30 mPEGMA:DMAEMA formulation exhibited the most favourable dielectric properties, with an EDL onset frequency of 794.33 Hz, a capacitance density of $7.57 \pm 1.39 \mu\text{F}/\text{cm}^2$ at 0.01 Hz, and an ionic conductivity of $2.68 \times 10^{-8} \text{ S}/\text{cm}$.⁶ In contrast, the degree of alkylation had a more substantial effect on dielectric performance. For the 50:50 mPEGMA:DMAEMA PIL, the optimal performance was achieved when 75% of the DMAEMA units were alkylated with an EDL onset frequency of 125 890 Hz, a capacitance density of $16.08 \pm 3.08 \mu\text{F}/\text{cm}^2$ at 0.01 Hz, and an ionic conductivity of $1.58 \times 10^{-5} \text{ S}/\text{cm}$.⁶ This demonstrated that ion concentration and polymer mobility are key factors in regard to capacitance, conductivity, and EDL formation. Overall, Chapter 2 established that the electrical properties of PIL-based dielectrics can be significantly tuned through polymer composition and post-polymerization modification.

In Chapter 3, the role of counterion selection was investigated as an additional design parameter for tuning both dielectric performance and toxicological response. EIS was used to evaluate PILs containing TFSI as the counterion, and the resulting performance was compared with the bromide-containing PILs examined in Chapter 2. The use of TFSI reduced the extent of which dielectric performance depended on alkylation, suggesting that counterion identity strongly influences ion transport and EDL formation.^{5,7} Furthermore, TFSI-containing PILs achieved improved dielectric performance at lower degrees of alkylation relative to the bromide analogues, demonstrating that counterion exchange provides an effective strategy for enhancing performance while reducing the

extent of chemical modification required. The toxicological effects of the unalkylated polymer, the 25% alkylated bromide-containing polymer, and the 25% alkylated TFSI-containing polymer were evaluated using the ZFET assay.^{8–12} Both counterions increased toxicity relative to the unalkylated polymer, as reflected by lower LC₅₀ and EC₅₀ values. These results indicate that a lower concentration of the alkylated PILs was required to induce lethal or sublethal effects in zebrafish embryos.^{11,13,14}

The findings from Chapters 2 and 3 demonstrate that counterion selection, percentage of alkylation, and monomer composition are interconnected design variables that influence both dielectric performance and biological response. This highlights the importance of integrating toxicological evaluation into the early stages of polymer development, particularly for electronic materials intended for flexible, wearable, or environmentally relevant applications.^{15,16}

4.2 Ongoing and Future Work

High-throughput screening is crucial for safe-by-design materials development, as it enables the rapid evaluation of material performance and environmental impact.^{11,14,17} The development of the ZFET assay has provided a high-throughput approach for toxicity assessment, providing results in less than one week compared with conventional toxicity testing methods that may require several months.^{8–10} In addition to high-throughput toxicity screening, a similar platform for rapid characterization of electrical performance would be highly beneficial. Currently, EIS measurements are performed manually, limiting sample throughput and increasing the time required to evaluate new materials.^{18,19} However, this process could be automated.

Previous work by Dallaire et al. demonstrated the value of automation for high-throughput characterization of OTFTs.²⁰ The automated testing platform was developed to address the time-intensive testing of manual probe station measurements, where each device required the user to position probes, run measurements, and record data which was a major bottleneck in the workflow. The Gen 1 autotester addressed this limitation by using automated switching, pogo-pin contacts, and LabVIEW control to sequentially test multiple devices on a chip with minimal user input. This “one-click-and-go” approach significantly reduced active laboratory time, as the Gen 1 autotester enabled six chips to be tested in 4–5 h with only 15–30 min of active user effort, compared to 7–8 h of continuous active engagement required with a conventional probe station, while also improving reproducibility. As a result, this allowed researchers to collect statistically meaningful device datasets while performing other tasks. By reducing the testing time, this allowed for an increase in data acquisition volume and productivity. Building on this existing infrastructure, we adapted the autotester for capacitor testing by modifying the shadow masks for dielectric-focused measurements to create similar capacitive areas as the current setup uses for EIS testing. This allowed capacitor devices to be tested in a

similarly automated manner, reducing the need for continuous manual operation, saving active time in the laboratory, and increasing testing throughput.

4.2.1 High-throughput EIS Testing

Preliminary work was conducted to adapt the existing OTFT autotester for capacitor-based EIS measurements. This required several modifications, including repurposing the OTFT autotester hardware, designing new shadow masks for top and bottom electrode deposition, developing a LabVIEW program capable of interfacing with the EIS measurement protocol and switchboard, and validating the resulting platform to ensure data reliability and repeatability.

New shadow masks were designed to produce capacitor areas comparable to those obtained using the existing manually tested devices. The redesigned masks were fabricated for 20 mm × 15 mm quartz substrates, allowing compatibility with the autotester pinboard. This new design accommodates 20 capacitor sites on a single substrate, doubling the number of sites relative to the preceding mask design (Figure 4.1). The corresponding capacitor site areas for the previous and redesigned templates are summarized in Table 4.1.

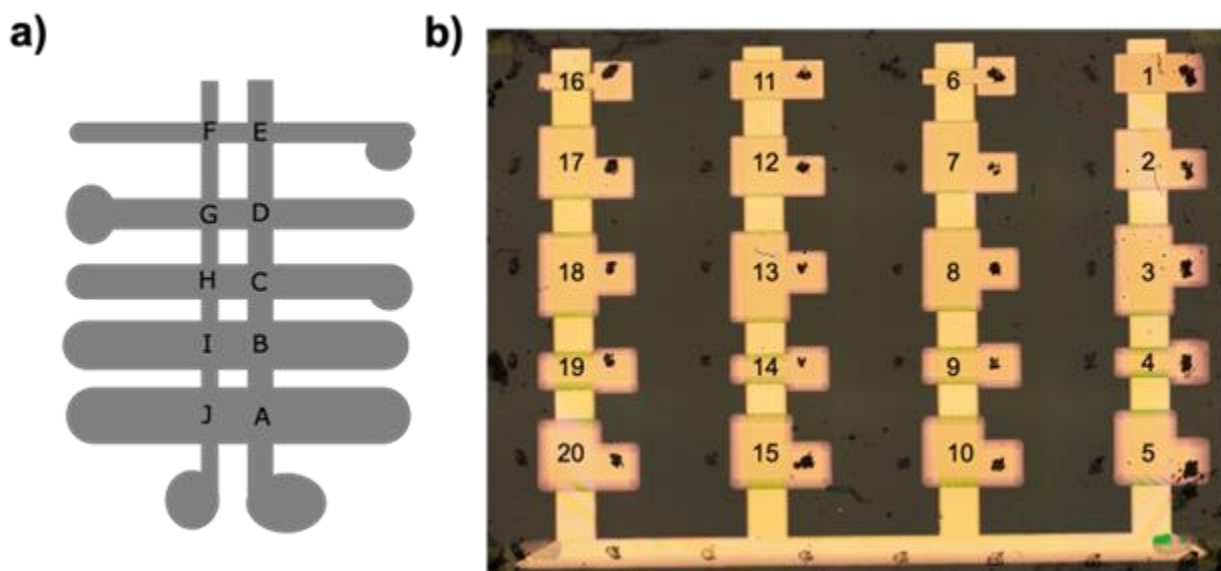


Figure 4.1 Shadow-mask templates used for capacitor fabrication: (a) previous template used for manual EIS testing and (b) redesigned template for high-throughput EIS testing.

Table 4.1 Capacitor site areas for the previous and redesigned shadow-mask templates.

Old Template		New Template			
Capacitor Site	Area (mm ²)	Capacitor Site	Area (mm ²)	Capacitor Site	Area (mm ²)
A	2.879±0.110	1	1.058±0.039	11	1.042±0.034
B	2.382 ±0.122	2	1.626±0.056	12	1.624±0.073
C	1.775±0.110	3	2.380±0.073	13	2.389±0.056
D	1.199±0.067	4	0.651±0.020	14	0.661±0.029
E	0.632±0.043	5	1.839±0.045	15	1.861±0.067
F	0.353±0.031	6	0.440±0.027	16	0.449±0.026
G	0.682±0.039	7	1.948±0.053	17	1.948±0.078
H	1.020±0.050	8	2.225±0.046	18	2.170±0.128
I	1.355±0.057	9	0.876±0.037	19	0.858±0.044
J	1.621±0.076	10	1.777±0.048	20	1.692±0.064

To enable electrode deposition using the existing physical vapour deposition setup, the new 20 mm × 15 mm quartz substrates needed to be compatible with the holder originally designed for 25 mm × 25 mm substrates. This was achieved through collaboration with the machine shop, where custom adapters were fabricated to hold the smaller quartz substrates securely within the existing deposition configuration.

Automation of the EIS measurements required the development of custom software that replicated the manual testing workflow which was achieved in collaboration with the electronics shop. The software consisted of two primary components: the EIS frequency response analyzer (FRA) protocol and the switchboard control protocol. The FRA protocol was designed to perform the same impedance measurement used during manual testing by sweeping the applied frequency.^{18,21} The switchboard protocol controlled the activation of individual capacitor sites according to the substrate layout (Figure 4.1.1a). During operation, the switchboard activates a selected capacitor site, after which the FRA protocol performs the EIS measurement and collects the corresponding data. Once the measurement is complete, the switchboard deactivates the tested site and activates the next site in the programmed sequence. This process is repeated until all selected capacitor sites have been measured.

Preliminary validation of the capacitor autotester was performed by comparing its response with that of the manual EIS setup. Validation was first conducted using inhouse

standard diagnostic measurements for troubleshooting of the manual EIS system. In the manual setup, a shorted device, in which the top and bottom electrodes are in direct contact due to the absence of a dielectric layer, typically produces a negative phase angle. In contrast, a no-contact condition, where the probes are not electrically connected to a capacitor, produces a noisy response with phase angle values ranging from approximately -150° to 150° .

The same diagnostic measurements were then performed using the capacitor autotester. A shorted device was fabricated by sequentially depositing the bottom and top electrodes without an intervening dielectric layer, thereby allowing direct contact between the electrodes. The no-contact condition was evaluated using a pristine substrate containing no electrodes or dielectric layer. The capacitor autotester produced responses consistent with those observed using the manual setup, indicating that the automated platform can correctly distinguish between shorted and no-contact conditions

Data accuracy was further evaluated by measuring the same PIL-based capacitor using both the automated and manual EIS setups and comparing the resulting dielectric properties. To minimize environmental and material stability effects, both measurements were performed within the same week under similar conditions. Using the capacitor autotester, the EDL onset frequency and maximum capacitance density were determined to be 39.811 Hz and 19.37 ± 0.65 nF/mm² at 0.01 Hz, respectively, n=17 (Figure 4.2). In comparison, the manual setup produced an EDL onset frequency of 19.953 Hz and a maximum capacitance density of 17.84 ± 0.33 nF/mm² at 0.01 Hz, n=17 (Figure 4.2). While the EDL onset frequency measured using the autotester was higher than that obtained from the manual setup, both values remain within the same order of magnitude. Similarly, the maximum capacitance densities measured using the two methods were reasonably comparable. This difference is considered acceptable at this preliminary stage, as small variations may arise from differences in electrical contacts, or wiring configuration differences between the autotester and probe set-up. Although additional validation is required across a broader range of dielectric materials and device geometries, these preliminary results demonstrate progress toward an automated EIS testing platform capable of evaluating the electrical properties of new dielectric materials. With further optimization, this capacitor autotester could enable high-throughput electrical screening and accelerate the development of safe-by-design PIL-based dielectrics.

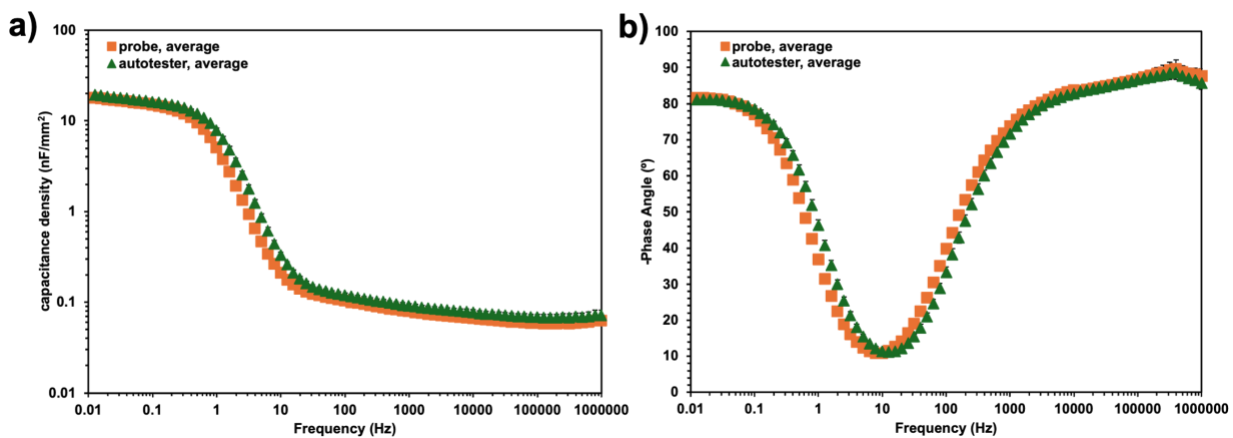


Figure 4.2 EIS results for the PIL-based capacitor used for validation of the automated testing platform (n=17): (a) phase angle as a function of frequency and (b) capacitance density as a function of frequency.

4.3 References

- 1 J. Yuan, D. Mecerreyes and M. Antonietti, *Prog. Polym. Sci.*, 2013, **38**, 1009–1036.
- 2 M. N. Tousignant, M. Ourabi, J. Niskanen, B. Mirka, W. J. Bodnaryk, A. Adronov and B. H. Lessard, *Flex. Print. Electron.*, 2022, **7**, 034004.
- 3 A. J. Peltekoff, S. Bixi, J. Niskanen and B. H. Lessard, *JACS Au*, 2021, **1**, 1044–1056.
- 4 O. Lebedeva, D. Kultin and L. Kustov, *Eur. Polym. J.*, 2024, **203**, 112657.
- 5 J. R. Keith, N. J. Rebello, B. J. Cowen and V. Ganesan, *ACS Macro Lett.*, 2019, **8**, 387–392.
- 6 S. McKillop, L. E. Dickson, H. Cho, M. Ourabi, J. G. Manion, V.-A. DiPalo and B. H. Lessard, *J. Mater. Chem. C*, 2025, **13**, 20085–20093.
- 7 D. S. Silvester, R. Jamil, S. Dobliger, Y. Zhang, R. Atkin and H. Li, *J. Phys. Chem. C*, 2021, **125**, 13707–13720.
- 8 OECD, *Test No. 236: Fish Embryo Acute Toxicity (FET) Test*, OECD Publishing, Paris, 2013.
- 9 T. Hong, J. Park, G. Song and W. Lim, *Mol. Cells*, 2024, **47**, 100090.
- 10 F. Busquet, R. Strecker, J. M. Rawlings, S. E. Belanger, T. Braunbeck, G. J. Carr, P. Ceniin, P. Fochtman, A. Gourmelon, N. Huebler, A. Kleensang, M. Knoebel, C. Kussatz, J. Legler, A. Lillicrap, F. Martinez-Jeronimo, C. Polleichtner, H. Rodeczko, E. Salinas, K. E. Schneider, S. Scholz, E.-J. van den Brandhof, L. T. M. van der Ven, S. Walter-Rohde, S. Weigt, H. Witters and M. Halder, *Regul. Toxicol. Pharmacol.*, 2014, **69**, 496–511.
- 11 R. L. Tanguay, *Toxicol. Sci.*, 2025, **208**, 40–41.
- 12 N. Nipu, L. Wei, L. Hamilton, H. Lee, J. Thomas and J. A. Mennigen, *Commun. Biol.*, 2025, **8**, 120.
- 13 B. M. Hedgpeth, A. D. Redman, R. A. Alyea, D. J. Letinski, M. J. Connelly, J. D. Butler, H. Zhou and M. A. Lampi, *Environ. Toxicol. Chem.*, 2019, **38**, 1302–1312.
- 14 L. Truong, M. T. Simonich and R. L. Tanguay, in *High-Throughput Screening Assays in Toxicology*, eds. H. Zhu and M. Xia, Springer, New York, NY, 2016, pp. 89–98.
- 15 L. Fang, Y. Zhou and Q. Huang, *Adv. Mater.*, 2025, 2502140.
- 16 I. Abdel Aziz and D. Mecerreyes, *Progress in Polymer Science*, 2025, **167**, 101994.
- 17 J. S. Ball, A. Tochwin, M. J. Winter, M. Trznadel, R. Currie, K. Wolton, J. M. French, M. J. Hetheridge and C. R. Tyler, *Reprod. Toxicol.*, 2025, **132**, 108837.
- 18 A. Lazanas and B. Prieto Simon, *Sensors*, 2025, **25**, 6260.
- 19 M. O'Rourke, N. Duffy, R. D. Marco and I. Potter, *Membranes*, 2011, **1**, 132–148.
- 20 N. Dallaire, N. T. Boileau, I. Myers, S. Bixi, M. Ourabi, E. Raluchukwu, R. Cranston, H. R. Lamontagne, B. King, B. Ronnasi, O. A. Melville, J. G. Manion and B. H. Lessard, DOI:10.1002/adma.202406105.
- 21 Metrohm, *Electrochemical Impedance Spectroscopy (EIS) Part 4 - Equivalent Circuit Models*, Application Note AN-EIS-004.