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Polymerization of bromoundecylacrylate and alkylation methylimidazole

Shuziao Li

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Polymerization of Bromoundecylacrylate and Alkylating Methylimidazole

by

Shuxiao Li

Thesis

Submitted to the School of Engineering Technology
Eastern Michigan University
in partial fulfillment of the requirements

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MASTER OF SCIENCE
in
Polymer and Coatings Technology

Thesis Committee:
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Abstract

Polymerized ionic liquids (PIL) generally are solids, but a few examples have been reported that also exhibit liquidity in the neighborhood of room temperature called liquid polymerized ionic liquids (LPIL). The development of a platform suitable for exploring LPIL properties based on the monomer 11-bromoundecylacrylate (AcC\textsubscript{11}Br) was reported. Poly(AcC\textsubscript{11}Br) is itself a liquid polymer and can be easily used to alkylate 1-methylimidazole to produce poly(AcC\textsubscript{11}C\textsubscript{1}ImBr-co-AcC\textsubscript{11}Br). Various reaction conditions were explored to examine how extensively 1-methylimidazole can be attached to this polymer, and the extent of alkylation is determined quantitatively by silver ion potentiometry. These polymers retain liquidity at and below 70\% alkylation with 1-methylimidazole. Many examples produced in the past ten years suggest that the fully alkylated moiety does not melt or exhibit liquidity. The connection between 1-methylimidazolium alkylation and LPIL behavior was established.
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1. Introduction

An ionic liquid (IL) is an organic salt that melts below 100 °C. Ionic liquids not only have potential to increase chemical reactivity and lead to more efficient processes, but are also non-flammable and less toxic than conventional solvents due to their low vapor pressure.\(^1\) The first IL (ethyl-ammonium nitrate) was reported by Paul Walden in 1914, who at that time did not realize that ILs would become a major scientific topic of research and application after more than one hundred years.\(^1\) In the past two decades, researchers paid more and more attention to ILs in chemistry, materials science, chemical engineering, and environmental science.

Over the past few years, ILs have already been used in polymer synthesis as solvents or polymerization media in various processes such as free radical polymerization, atom transfer radical polymerization (ATRP), reversible addition-fragmentation transfer (RAFT), and also ionic polymerization. Besides the traditional polymerizations, ILs also can be used as the components of the polymeric matrixes for electrochemical polymerization, such as polymer gels, because of its excellent ionic conductivity.\(^2\)

Polymerized ionic liquids (PILs), which are composed by polymeric backbone and ionic liquid (IL) as repeating units, has integrated the attractive properties of monomer ILs. In the past five years, PILs are rapidly growing and varies PILs have been synthesized by introducing different anionic or cationic ILs into polymer backbones such as imidazolium, pyridinium, and pyrroldidonium. Most of PILs are single-ion conductors. However, there is an exception of PIL synthesized from polymerizable IL which has both cations and anions reported by Gu et al.\(^3\)

There are many attractive properties of PILs, among which ionic conductivity is one of the most important ones. Some factors may affect the ionic conductivity in PILs. One factor is glass transition temperature (Tg). PILs possess lower Tg than conventional linear polymers
because of the weak electrostatic ion pair interactions which result in higher ionic conductivity. Thus, the modification of Tg is important and it can be made by ion exchange process. The effect of four different ions, BF$_4^-$, TFSI$^-$, Tf$, \text{and PF}_6^-$, with imidazolium-based PIL (poly(1-[2-(methacryloyloxy)ethyl]-3-butylimidazolium) (poly(MEBIm)) backbone was studied by Ye et al. The thermal analysis proved that poly(MEBIm-TFSI) had the lowest glass transition temperature with the highest ionic conductivity compared with other anions. Meanwhile, the component of polymer backbone also affects the Tg of PILs. In general, the more flexible polymer backbone is, the lower Tg PILs with the higher ionic conductivity have. Qian et al. mentioned that the ionic conductivities increase considerably with the extension of the spacer in the side chains of both polycations and polyanions. The effect of molecular weight of PIL was also mentioned in the same paper. Fan et al. approved that ionic conductivity decreases with molecular weight increases until $10^5$ Da.

The tunable solvents solubility is another amazing property of PILs, which can be achieved by ion exchange. Marcilla et al. studied the solubility of Poly(ViEtImX)(poly(1-Vinyl-3-ethyl-imidazolium X)) and Poly(ViBuImX) polycations in six different solvents, as shown in Table 1-1, which present that the anion structures could affect the solubility of PILs.

Besides ionic conductivity and aqueous solubility, the thermal stability is another considerable factor of PILs during application. Depend on different applications, PILs could have wide range of glass transition temperature and decomposition temperature. Weber et al. studied the thermal properties of poly(4-vinylbenzyl alkylimidazolium X) (PVBn(alkyl)ImX, alkyl = –CH$_3$ (Me), –C$_4$H$_9$ (Bu), and –C$_6$H$_{13}$ (Hex), X = Cl$^-$, BF$_4^-$, PF$_6^-$, TFSI$^-$) as shown in Table 1-2.
Table 1-1. Solubility of poly(ViEtImX) and poly(ViBuImX) polycations in different solvents. Reproduced from Qian et al., Chem. Soc. Rev. 2017, 46 (4), 1124-1159.

<table>
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<th>H₂O</th>
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<th>ViEtIm⁺ Tl₂N⁻</th>
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<td>PF₆⁻</td>
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<td>+</td>
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<tr>
<td>CF₃SO₃⁻</td>
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<td>+</td>
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<tr>
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<tr>
<td>(CF₃C₂F₂SO₂)₂N⁻</td>
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<td>+</td>
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Different anions result in varies glass transition temperatures and decomposition temperatures. PVBN(alkyl)ImCl shows the relatively poor thermal stability and the narrow range of thermal decomposition temperatures of all homopolymers.

There are many applications of PILs in various of cases such as energy and environmental applications, analytical chemistry, materials science, biotechnology, catalysts or surface science among others. The most important application of PILs is used as electrolytes in electrochemical devices. The electrolytes which contain ILs can be used to improve the performance, speed, long-term stability and cyclability of electrochromic devices. The PIL-based polymer electrolytes present high ionic conductivities, wider electrochemical windows, high thermal stabilities, non-flammability and good compatibility and can be used for various electrochemical device such as in electrolytes for fuel cells, dye sensitized solar cells, batteries, super capacitors, electrochromic devices, transistors and so on. For example, Si et al. synthesized the phosphoric acid-doped crosslinked proton-conducting membranes with high
anhydrous proton conductivity and good chemical stability in phosphoric acid by in-situ crosslinking of styrene, acrylonitrile and vinylimidazole, with the following step of the sulfonation of pendant imidazole groups with butanesultone, and then doping with phosphoric acid.\textsuperscript{10} The resultant electrolyte membranes were flexible and exhibited high thermal stability and high-proton conductivity up to 160 °C and 10\textsuperscript{-2} S cm\textsuperscript{-1}, respectively. Gregorio et al. synthesized four different imidazole-based ionically conductive polymers and implemented in iodine/iodide based liquid electrolytes to formulate novel quasi-solid electrolytes for dye solar cells.\textsuperscript{11} This dye solar cell maintained its cell stability after 500 days of storage with the maximum power conversion efficiency of 5.73\%, which was superior to 85\% of the corresponding liquid electrolytes.


<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g) (°C)\textsuperscript{a}</th>
<th>(T_{\text{decomp}}) (°C)\textsuperscript{b}</th>
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<tr>
<td>PVBNMelmCl</td>
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<td>222, 320, 393</td>
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<tr>
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<tr>
<td>PVBNHexlmCl</td>
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<td>233, 405</td>
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<tr>
<td>PVBNHexImPF\textsubscript{6}</td>
<td>87</td>
<td>295, 385</td>
</tr>
<tr>
<td>PVBNHexImBF\textsubscript{4}</td>
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<td>291, 395</td>
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<tr>
<td>PVBNHexlmTFSI</td>
<td>9</td>
<td>345</td>
</tr>
</tbody>
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\textsuperscript{a} Determined from the average values observed on second and third heating by DSC.

\textsuperscript{b} Temperature at which 5\% weight loss is observed as determined by TGA for each observed decomposition event.
Stimuli-responsive PILs, which respond to chemical, physical or biochemical stimuli, have been studied for their potential applications in smart materials. For instance, the thermo-responsive PILs can be precipitated from a soluble state at a critical temperature. Tang et al. prepared a temperature-responsive composite membrane by covalently grafting a PIL functionalized temperature-responsive copolymer onto the brominated poly(2,6-dimethyl-1,4-phenylene oxide) supporting membrane. The size of membrane changed dramatically with the temperature changing. The pH-responsive PIL membranes, which was reported by Chen et al., can be synthesized through photo-crosslinking of imidazolium type IL monomers with acrylic acid, N-isopropylacrylamide, and acrylonitrile. The shape of the PIL membranes can be deformed by changing the PH value of aqueous solutions or gas atmospheres (NH₃/HCl). Such property of this PIL gives the potential applications in soft actuator, advanced sensors and functional materials. Also, there are many other researchers who report the stimuli-responsive PILs with photo-responsibility, solvent-responsibility and other properties, which enlarge the opportunity of PILs in smart materials.

Recently, carbon-rich ionic liquids are becoming a new family of carbon precursors because of their attractive features such as cation-anion combinations, low volatilities, and high thermal stabilities, which not only simplify the carbonization process but also give rise to carbons with more attractive properties compared to conventional polymer precursors. PILs can be also employed as catalytic supports, catalyst, and pre-catalyst. The multifunctional hybrid materials which combine polymers, having flexibility, process ability, and mechanical durability, with the electrical and catalytic properties, can be prepared by embedding metal nanoparticles into PILs. Moghaddam et al. coated the supported gold (III) on poly(ionic liquid) on magnetic poly(imidazole/imidazolium) nanoparticles for the synthesis of propargylamides. The reaction
became highly active, stable, and high loading by adding this catalyst which could be easily recovered and reused for 10 times. PILs were also used as adsorbents in many applications. For example, ILs have a potential application field in CO\textsubscript{2} capture and separation because of its reversible solubility of CO\textsubscript{2}. And it was found that PILs were even better with higher CO\textsubscript{2} capture efficiency. Photoresists, corrosion inhibitors, dispersants, stabilizers and many other application fields are also explored by many researchers recently.

There are two fundamental ways to generate PILs: one is direct polymerization of IL monomers, while another one is the chemical modification of existing polymers. Both two ways can be achieved by many different techniques, such as conventional polymerization, living radical polymerization including atom transfer radical polymerization and reversible addition-fragmentation chain transfer polymerization, step-growth polymerization, and so on. Conventional free radical polymerization includes emulsion polymerization, suspension polymerization, dispersion polymerization, ring opening polymerization, and others. For example, one approach to synthesize PILs was explored by Ohno et al., which consisted in synthesizing a variety of IL monomers by anion exchange reaction of a cationic 1-vinyl-3-alkyl imidazolium halide type monomer with different counter-anions. After that, the PILs were directly polymerized by different IL monomers.

Yu et al. reported the preparation and polymerization of microemulsions which contain IL polar cores dispersed in a polymerizable oil. In this paper, styrene was the polymerizable oil while [Bmim][BF\textsubscript{4}] was the IL with the appeal of 1-(2-methyl acryloyloxyundecyl)-3-methylimidazolium bromide (MAUM-Br) (shown in Figure 1-1) as surfactant. The resultant [Bmim][BF\textsubscript{4}]/polystyrene composite membranes yielded free-standing, flexible, and transparent polymer electrolytes with high conductivity at both room temperature and elevated temperature.
Another example of PILs synthesis was reported by Weng et al. who polymerized a series of novel PILs contained imidazolium, poly(2,5-bis{[6-(1-butyl-3-imidazolium)hexyl]oxy carbonyl}styrene salts) (denoted as P1-X, X=Br$^-$, BF$_4^-$, PF$_6^-$, and TFSI$^-$) by radical polymerization (shown in Figure 1-2).$^{20}$ The thermal stability and Tg of PILs heavily depended on their counter-anions.

![Figure 1-2. Chemical structures of PILs with different counter-anions P1-X$^-$](image)

Tang et al. synthesized two ionic liquid monomers, 1-(4-vinylbenzyl)-3-butyl imidazolium tetrafluoroborate (VBIT) and 1-(4-vinylbenzyl)-3-butyl imidazolium hexafluorophosphate (VBIH), through the quaternization of N-butylimidazole with 4-vinylbenzylchloride and a subsequent anion exchange reaction with sodium tetrafluoroborate or potassium hexafluorophosphate (see Figure 1-3). Then the copper-mediated atom transfer radical polymerization was used to polymerize VBIT and VBIH.$^{21}$ The TGA, DSC, and XRD results
showed that PVBiT was a thermally stable polymer with a Tg of 84 °C. The different catalysts, initiators and solvents had strong effects on the polymerization process.


Yan and Texter reported the synthesis of surfactant ILs, which are the polymerizable ionic liquid, that consist of an imidazolium cation polar group and a hydrophobic tail which are showed in Figure 1-4. The 1-dodecyl-3-methylimidazolium bromide (left on Figure 1-4) was synthesized by 1-bromododecane with 1-methylimidazole, while the 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide (right on Figure 1-4) was synthesized by 11-bromoundecanol and acryloyl chloride in tetrahydrofuran at first, in the presence of triethylamine, to get the
intermediate bromoalkane acrylate; then the 1-methylimidazole was attached to the bromoalkane and result in the polymerizable ionic liquid.

Dustin England also reported the synthesis and characterization of the ionic liquid, 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide (IL-Br), which obtained by the same reactant and process with Yan and Texter. He provided the synthesis and purification details that the intermediate 11-bromoundecylacrylate was first reacted under nitrogen atmosphere for 2 days at room temperature with 20% excess of both acryloyl chloride and triethylamine loaded, and then purified the product in solution by washing with 2% sodium bicarbonate DI water solution, and then passed through a gravity column filled by 0.75 inches of neutral alumina. The 11-bromoundecylacrylate was finally dried by rotary evaporation at 45 °C. The IL-Br was then synthesized by pure 11-bromoundecylacrylate with 20% excess of 1-methylimidazole, with the presence of 0.01% 2,6-di-tert-utyl-4-mrthylphenol as inhibitor, at 40 °C for 48 hours under nitrogen atmosphere. The polymerizable ionic liquid IL-Br was a waxy, tan solid before washing by neutral alumina with the average melting points of 40 ± 6 °C and became a powdery, white solid after passing the neutral alumina column and solvent evaporation, with higher melting point of 48 ± 4 °C. He also reported the thermal stability of IL-Br by TGA, which has the initial 5% weight loss between 25–100 °C of water, presents the hygroscopic nature ionic liquid, while the decomposition of IL-Br is about 200 °C.\(^\text{23}\)

![Figure 1-4. Two structures of ionic surfactants.](image-url)
To study the stability of IL-Br/PMMA copolymers, Dustin et al. synthesized the polyIL-Br by bulk polymerization and solution polymerization and characterized the thermal decomposition and physical transition properties of poly IL-Br. The TGA curves show that the first weight loss area of poly IL-Br is between 40 °C to 280 °C, while the second decomposition area is between 280 °C to 340 °C, and the last decomposition area is between 340 °C to 500 °C. Compared to polyIL-Br synthesized by bulk polymerization and solution polymerization, the same decomposition curve indicates that there is no effect on the synthesis environment. There are two glass transition temperatures of polyIL-Br present on DSC curve at -26.7 °C and 48.2 °C.

Nykaza et al. synthesized homopolymer poly(BrUMA) by first making monomer BrUMA (11-bromoundecyl methacrylate). As shown in Figure 1-5, BrUMA was synthesized by methacryloyl chloride and 11-bromo-1-undecanol with the mixture of triethylamine and dichloromethane under nitrogen at room temperature for 18 hours. A clear liquid of BrUMA was obtained which had the yield of 51%.

Figure 1-5. Synthesis of BrUMA (11-bromoundecyl methacrylate) monomer. Reproduced from Nykaza et al., Polymer 2014, 55 (16), 3360-3369.
The homopolymer poly(BrUMA) was polymerized by BrUMA through conventional free-radical polymerization with AIBN as thermal initiator, which was then functionalized by 1-butylimidazole to make PIL homopolymer, poly(MUBIm-Br), with the yield of 63.2%, as shown in Figure 1-6.

However, instead of methacrylate, acrylate has never been used for synthesis of PIL. The work of this paper is mainly focused on the polymerization of bromoundecylacrylate with various ratios and its alkylation under different conditions with 1-methylimidazole. Here the monomer bromoundecylacrylate was synthesized by 11-bromoundecanol and acryloyl chloride, which is the same process Dustin England for synthesizing the intermediate of IL-Br. Different from his further procedure, the 11-bromoundecylacrylate was first polymerized by conventional free radical polymerization to generate the homopolymers, and then alkylated with excess amount of 1-methylimidazole to get the polymerized ionic liquid. The free radical polymerizations at different concentration in different solvents were generated and the thermal properties of these homopolymers were investigated by TGA and DSC, while the molecular weight analysis was performed by GPC, along with the structure analysis by FTIR. Then the alkylation of homopolymers by different ratios of 1-methylimidazole were prepared and the extent of alkylation was determined quantitatively by silver ion potentiometry, along with TGA and DSC analysis.
The homopolymers polymerized by 11-bromoundecylacrylate were supposed to be a viscous liquid. However, during the synthesis of homopolymers, the gels were obtained unexpectedly which were non-soluble or slightly soluble in thirteen regular solvents. Crosslink density, \( v \), is defined as the crosslinked points per unit volume in mol/cm\(^3\), which presents the crosslink contents of the crosslinked polymers. It can be measured by solvent swelling method, stress-strain method, differential scanning calorimetry method, atomic force microscopy method, and intrinsic viscosity method.\(^{25}\) Since the gels are able to swell in toluene, xylene and NMP, the Flory-Huggins equation was used to identify the crosslink density. The gels should swell in the good solvent as much as possible to get the network equilibrium. The weight of swollen gel and its dry weight should be measured and the volume fraction of gel in swollen state is calculated and used in the Flory-Huggins equation to get the crosslink density. The polymer-solvent interaction parameter \( \chi \) has been found to increase with polymer concentration and decrease with temperature with a dependence that is approximately linear with, but in general not proportional.
to $1/T$ and also generally insensitive to the molecular weight of the polymer, except for systems with low molecular weight polymers.\textsuperscript{26}

This paper is organized in the following order: Chapter 2 will discuss the materials and methods of the synthesis. Then, the synthesis and characterization of 11-bromoundecylacrylate will be described in Chapter 3, following with the synthesis and characterization of poly(AcC\textsubscript{11}Br) gel in Chapter 4, and the normal poly(AcC\textsubscript{11}Br) in Chapter 5. The synthesis and characterization of poly[(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x}] will be discussed next in Chapter 6. And the result will finally be concluded in Chapter 7.
2. Experimental Materials and Methods

This chapter reports sources of materials, synthesis methods, and characterization techniques used in the experimental and analysis studies associated with this thesis work.

2.1. Materials

Acryloyl chloride (96%), 11-bromoundecanol (98%), triethylamine (99.5%), 1-methylimidazole (99%), and 2,6-di-tert-butyl-4-methylphenol (minimum 99% GC, powder), 2,2'-azobisisobutyronitrile (AIBN, 98%) were obtained from Sigma Aldrich and used as received.

Neutral aluminum oxide (activated, Brockmann I, standard grade, ~ 150 mesh, 58 Å) and magnesium sulfate (anhydrous, reagent grade, ≥ 97%) were used during the synthesis of 11-bromoundecylacrylate, and both were obtained from Sigma Aldrich.

Tetrahydrofuran (THF, anhydrous, ≥ 99.9%, inhibitor free), N,N-dimethylformamide (DMF, 99%), methylene chloride (stabilized, HPLC grade), toluene (anhydrous, 99.8%), xylenes (ACS reagent, ≥ 98.5 xylenes + ethylbenzene basis), N-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%), and dodecane (ReagentPlus®, ≥99%) were obtained from Sigma Aldrich. Chloroform-d (CDCl₃, 99.8 atom % D) was purchased from Across Organics. Deionized (DI) water was used and was obtained using Evoqua filtration (Evoqua Water Technologies, Holland, MI).

2.2. Synthetic Methods

2.2.1. Synthesis of 11-bromoundecylacrylate

11-Bromoundecylacrylate (AcC₁₁Br) was prepared by an addition of acryloyl chloride to 11-bromoundecanol in the presence of triethylamine in THF. The reaction atmosphere was
purged with nitrogen, and the reaction was stirred at room temperature for two days in a sealed
two-neck round-bottom flask. This monomer was purified after reaction by first drying with
magnesium sulfate. It then was diluted with methylene chloride and passed down a gravity
column filled with neutral aluminum oxide. The solvent was removed by rotary evaporation at
60 °C for half an hour followed with vacuum drying up to 50 °C for 3 hours. See Chapter 3 for
more details.

2.2.2. Synthesis of acrylate gels

Acrylate gels were obtained unexpectedly when synthesizing poly(AcC_{11}Br). These gels
were generated in polymerization that were 50% (by weight) monomer, 11-
bromoundecylacrylate in dodecane, DMF, and methylene chloride with addition of 0.5% and 1%
(by weight of monomer) thermal initiator, AIBN. These polymerizations were done in sealed
culture tubes, which were purged by nitrogen and reacted at 70 °C for 2 days. These gels were
“purified” in a vacuum oven up to 120 °C after reaction to remove solvent. See Chapter 4 for
more details.

2.2.3. Synthesis of poly(AcC_{11}Br)

Poly(AcC_{11}Br) was polymerized by using 5% (w/w) monomer, 11-
bromoundecylacrylate, in THF, with addition of 0.1%, 0.5%, or 1% (by weight relative to
monomer) AIBN as thermal initiator. These polymerizations were done in sealed culture tubes,
which were purged with nitrogen and heated at 70 °C for two days. The resulting homopolymers
were “purified” by removing solvent in a vacuum oven by heating up to 120 °C after reaction.
See Chapter 5 for more details.
2.2.4. Synthesis of poly(AcC₁₁Br)₁₋ₓ(AcC₁₁C₁ImBr)ₓ

Alkylation of methyl imidazole by poly(AcC₁₁Br) was a primary objective of this research. Poly[(AcC₁₁Br)₁₋ₓ(AcC₁₁C₁ImBr)ₓ] was synthesized by reacting the homopolymer poly(AcC₁₁Br) with 1-methylimidazole in tetrahydrofuran under a nitrogen atmosphere at 60 °C for two days. Unreacted 1-methylimidazole and THF were removed after reaction and in a vacuum oven at about 120 °C. See Chapter 6 for more details.

2.3. Characterization Methods

2.3.1. Thermogravimetric analysis (TGA)

TGA analysis was used to determine the purity and thermal decomposition temperatures of AcC₁₁Br monomers, resulting acrylate gels, poly(AcC₁₁Br) homopolymers, and alkylated polymers comprising poly(AcC₁₁C₁ImBr). TGA was done using TA Instruments (New Castle, DE) model TGA Q500, where samples were placed in aluminum DSC pans that were placed in a platinum TGA suspension pans. These aluminum DSC pans were used to minimize fouling the platinum suspension pans in the open part of the Q500 electrobalance. Typical analyses subjected samples to a 10 °C/min increasing temperature ramp that an upper limit of 580 °C under nitrogen as purge gas.

2.3.2. Differential scanning calorimetry (DSC)

DSC analysis was used to determine melting points and glass transition temperatures of AcC₁₁Br monomer, acrylate gels, poly(AcC₁₁Br) homopolymers, and 1-methylimidazole alkylated with homopolymer, poly[(AcC₁₁Br)₁₋ₓ(AcC₁₁C₁ImBr)ₓ]. Analysis was done using a TA Instruments model Q2000. Typically, samples were placed in Tzero aluminum pans, which were sealed by Tzero standard aluminum lids. Typical experimental heating and cooling cycles were
involved heat/cool/heat cycles at given scan rates. Samples typically were heated from room temperature to a desired highest hold temperature and held isothermally for about 5 min. Then a sample were cooled to a desired lower hold temperature and held there isothermally for 5 min before being subjected to a second heating ramp to a desired maximum temperature. All reported transitions were analyzed from the second heating in such cycling.

2.3.3. Proton nuclear magnetic resonance (\(^1\)H NMR)

\(^1\)H NMR analysis was used to determine structural spectrums of 11-bromoundecylacrylate monomer and of the homopolymer, polyAcC\(_{11}\)Br. The analysis was performed using a JEOL 400 MHz NMR. CDCl\(_3\) was first dried using anhydrous K\(_2\)CO\(_3\), and then the samples were prepared by dissolving 10-20 mg of sample in 2 ml CDCl\(_3\) in 5 mm O.D. NMR tubes.

2.3.4. Gel permeation chromatography (GPC)

GPC analysis was used to determine the molecular weight distributions of homopolymer, polyAcC\(_{11}\)Br, batches. The analysis was done using a Malvern Viscotek GPC/SEC system equipped with THF Styragel columns. THF was used as the mobile phase at a flow rate of 1.0 mL/min. Polystyrene (PS) standards with molecular weights ranging from 2.97 to 591 kDa were used for calibration. Samples were prepared by dissolving 3–5 mg of sample in 10 ml THF.

2.3.5. Fourier-transform infrared spectroscopy (FTIR)

FTIR analysis was used to determine infrared spectra in absorption or transmission modes of monomer, AcC\(_{11}\)Br, homopolymer, poly(AcC\(_{11}\)Br), and poly[(AcC\(_{11}\)Br)\(_x\)(AcC\(_{11}\)ClImBr)\(_y\)], and to verify the structures of each products. This analysis was done by using a Bruker Tensor 27 FTIR & OPUS Data Collection Program. Samples in THF
solution were placed dropwise onto a face of a KBr plate. A second KBr plate was sandwiched onto this first drop in order to spread the drop into a thin layer.

2.3.6. Potentiometric titration

$\text{Ag}^+$ potentiometry was used to identify the $\text{Br}^-$ content of $\text{poly}[(\text{AcC}_{11}\text{Br})_x, (\text{AcC}_{11}\text{C}_1\text{ImBr})_x]$ so that the extent of 1-methylimidazole alkylation by the homopolymeric undecylbromide pendant groups could be quantified. Samples (80 mg to 300 mg) of each product were diluted in 60 ml DI water/methanol (50/50 by weight) and titrated with nominally 0.1 $M$ AgNO$_3$ solution in water. AgNO$_3$ solutions were calibrated using KCl solutions. A reference Ag/AgCl electrode and an indicator Ag/Ag$_2$S electrode (Orion) were used to measure titration potentials. A Fisher Scientific Accumet 910 pH/mV meter was used with these electrodes to obtain solution potentials relative to the reference electrode potentials.
3. Synthesis and Characterization of 11-Bromoundecylacrylate

3.1. Synthesis of 11-bromoundecylacrylate

11-Bromoundecylacrylate is the monomer need to make poly(AcC\textsubscript{11}Br), its homopolymer. To synthesis it, 11-bromoundecanol (50 mmol, 12.06 g) was dissolved in 50 ml THF at room temperature in a two-neck round-bottom flask. This flask, with a magnetic stirring bar, was then placed in an ice bath on a magnetic stirrer. A nitrogen stream was used to purge the reaction solution using a needle through a septum in one neck of the flask. After that, triethylamine (60 mmol, 6.08 g) was dissolved in 50 ml THF in a 100 ml beaker and then slowly poured into the stirred solution through the other neck of the flask. Next, acryloyl chloride (60 mmol, 4.9 ml) was added to the stirring mixed solution drop by drop over 15 min using an addition funnel. The addition funnel was then removed, and the neck sealed. The ice bath was then removed, and the flask was put on to the magnetic stirrer directly. Subsequently, the nitrogen needle was removed. Then, the reaction flask was sealed under nitrogen atmosphere and stirred for 48 hours at room temperature. The synthetic scheme for preparing bromoundecylacrylate is shown in Figure 3-1.

![Figure 3-1. Synthetic scheme for preparing bromoundecylacrylate.](attachment:image.png)

After 48 hours, there were two phases evident in the flask. White solids were precipitated on the bottom. A clear solution with light-yellow color also remained. This precipitate was
removed by vacuum filtration, and the clear yellow filtrate was then collected and washed with 1/3 its volume of aqueous 2% (w/w) NaHCO₃ twice in a 250 mL separatory funnel. This washing step was repeated three times by England²³ but was reduced to twice here to decrease the amount of product lost and increase the yield. The extracted solution was separated after standing over night. The bottom extracted yellow phase was then collected and dried with anhydrous magnesium sulfate overnight. Afterwards, this dried product, diluted with 50 mL methylene chloride, was passed through a gravity column 0.5” in diameter and 0.5” high, which was filled by neutral alumina for further purification. The methylene chloride was removed by rotary evaporation at 60 °C for 30 min in the next step. Then the product was further dried in a vacuum oven at room temperature for 3 hours then at 50 °C for another 3 hours. The final product was a transparent liquid and yellow in color (shown in Figure 3-2). The yield of this reaction was about 50%. Compared to Nykaza’s monomer, bromoundecylmethacrylate, the same yield was obtained since he reported it as 51%.²⁴ The monomer product was stored in vials in a freezer; these vials were covered with aluminum foil. A free radical stabilizer (scavenger), 2,6-di-tert-butyl-4-methylphenol, was added at 0.01% by weight.

Figure 3-2. Appearance of 11-bromoundecylacrylate at room temperature. The vial is about 1.5 cm in diameter.
3.2. Characterization

3.2.1. FTIR analysis of 11-bromoundecylacrylate

To identify the structure of 11-bromoundecylacrylate, an FTIR spectrum is shown in Figure 3-3. A band at 1629.64 cm\(^{-1}\) indicates the peak of C=C. 1726.07 cm\(^{-1}\) is the stretching vibration of >C=O. 1459.92 cm\(^{-1}\) is typical of the bending vibration of -CH\(_2\)-. 1278.64 cm\(^{-1}\) and 1193.78 cm\(^{-1}\) are assigned to the asymmetric stretching vibration of -C-O-C-. 1060.71 cm\(^{-1}\) is the corresponding symmetric stretching vibration. As a result, this transmittance spectrum indicates that the hydroxyl group of 11-bromoundecanol was severed and connected onto the carbon of the carbonyl group on the acryloyl chloride to yield a discarded HCl side-product.

![Figure 3-3. IR spectrum of 11-bromoundecylacrylate (AcC\(_{11}\)Br).](image)

3.2.2. TGA analysis of 11-bromoundecylacrylate

The thermal stability of 11-bromoundecylacrylate was investigated by TGA and is shown in Figure 3-4. These samples were heated from room temperature to 580 °C at a rate of
10 °C/min with nitrogen as a purged gas. As seen in Figure 3-4, decomposition of 11-bromoundecylacrylate begins at approximately 150 °C, and there is no significant residue above 560 °C. There were two distinct regions of decomposition seen in the TGA analysis of 11-bromoundecylacrylate. The first decomposition starts at approximately 150 °C, while the second decomposition extends from 330 °C to 550 °C. To understand these different regions of 11-bromoundecylacrylate’s decomposition, three of the raw materials used for synthesis were investigated as well, 11-bromoundecanol, triethylamine and acryloyl chloride. From the overlaid decomposition curves of these three materials with that for 11-bromoundecylacrylate, the second decomposition area of 11-bromoundecylacrylate is not caused by triethylamine since triethylamine evaporates below 100 °C (triethylamine boils at 89 °C), and the acryloyl chloride also evaporates.

Figure 3-4. TGA analysis of 11-bromoundecylacrylate. The starting materials 11-bromoundecanol, triethylamine and acryloyl chloride are also included.
3.3.3. DSC analysis of 11-bromoundecylacrylate

11-Bromoundecylacrylate is a liquid at room temperature. It becomes solid when stored in a refrigerator’s freezer compartment and melts back to liquid at ambient conditions. The melting and crystallization points were checked by DSC for each batch of monomer. Each DSC examination used heating-cooling-heating cycles. An endothermic peak on heating indicates a melting process, which is around 0 °C, while an exothermic peak on cooling represents a freezing process at about -25 °C (see Figure 3-5). A glass transition temperature for 11-bromoundecylacrylate was found at about -81 °C, which can be estimated from the second heating in the DSC data of Figure 3-6. Each batch of monomer, 11-bromoundecylacrylate, was characterized by DSC, and the average melting point $T_m$ is -3 °C ± 4 °C. The average of melting and freezing points is -16 °C ± 5 °C. The data of Figure 3-6 were obtained from a DSC scan from -150 °C to 110 °C at of 10 °C/min. This transition was obscured for a while because we typically only cool to about -90 °C to -85 °C, and such glass transition are usually obscured because of anomalies encountered during reversing heating and cooling processes. Generally, the melting and freezing points are the same. However, the difference of these two points maybe caused by the high scan rate. Such difference can be reduced or eliminated by reducing the scanning rate to 5 °C/min, 2 °C/min or 1 °C/min.
Figure 3-5. DSC analysis of 11-bromoundecylacrylate. The scan was run from -80 °C to 150 °C at speed of 10 °C/min.

Figure 3-6. Glass transition of 11-bromoundecylacrylate.

3.3.4. NMR analysis of 11-bromoundecylacrylate (AcC\textsubscript{11}Br)

The structure of 11-bromoundecylacrylate was confirmed by \textsuperscript{1}H NMR. An NMR sample was prepared by dissolving 10-20 mg of AcC\textsubscript{11}Br in 2 mL CDCl\textsubscript{3}. The corresponding spectrum
is illustrated in Figure 3-7. By using $^1$H NMR (400 MHz, CDCl$_3$, $\delta$), the following spectral features were resolved: 1.30 (m, 18H, -CH$_2$(CH$_2$)$_9$CH$_2$Br), 1.65(m, 2H, OCH$_2$CH$_2$(CH$_2$)$_7$), 1.85(m, 2H, -(CH$_2$)$_7$CH$_2$CH$_2$Br), 3.40(t, 2H, -CH$_2$CH$_2$Br), 4.10(t, 2H, COO-CH$_2$CH$_2$-), 5.80(1H, CH$_2$=CH-), 6.10(1H, CH$_2$=CH-), 6.40(1H, CH$_2$=CH-). The noise around 3.70 indicates -CH$_2$OH, which leads to some residue of unreacted starting material 11-bromoundecanol in samples, while the peak at 4.10 proves successful ester group formation.

Figure 3-7. NMR analysis of 11-bromoundecylacrylate.
4. Synthesis and characterization of acrylate gel

The poly(AcC\textsubscript{11}Br) which is going to be synthesized next should be a viscous liquid. Nevertheless, an acrylate gel was obtained unexpectedly during the synthesis of the poly(AcC\textsubscript{11}Br). It was respectively synthesized in methylene chloride and dimethylformamide by adding high loading level of monomer 11-bromoundecylacrylate. This gel has similar properties with the poly(AcC\textsubscript{11}Br) except that it cannot be dissolved in most of the familiar solvent.

4.1. Synthesis of polyacrylate gel

First, 0.0148 g (1\%) of AIBN was dissolved in 1.5013 g (50\%) methylene chloride in 1 cm diameter culture tube. Then 1.4705 g (50\%) of monomer 11-bromoundecylacrylate was added. The mixture solution was then purged by nitrogen gas and bubbled for 5 minutes. The culture tube was placed in oil bath at 60 °C and reacted for 28 hours. The tube was shaken by hand 3 times during the reaction.

After reaction, there was a transparent light-yellow color formed gel in the culture tube with a few free solvents left in the tube observed when sloping. The gel could not be dissolved when shaking the tube by hand. It was put into vacuum oven and dried at room temperature for 3 hours and then dried at 65 °C, 120 °C and 150 °C for 3 hours, 3 hours, and overnight, respectively.

The same as the reaction in methylene chloride, dimethylformamide was used as the solvent in the ratio of 1:1 to monomer, with the load of 1\% AIBN. The reaction was done at 65 °C for 28 hours. After reaction, a turbid solution with light-yellow color was obtained. After one week leaving in the hood with cap sealed, the solution separated into two phases. The top phase was clear, and the bottom phase was turbid. The turbid solution could get to clear slowly
with the increasing temperature until 150 °C in the first time trying. However, it was not repeatable: the solution could not get to clear up to 150 °C at the second time. The gel was put into vacuum oven and dried at room temperature for 3 hours. Then, it was further dried at 65 °C, 120 °C and 150 °C for 3 hours, 3 hours and overnight, respectively.

Both the synthesis of gel in methylene chloride and in dimethylformamide were repeated at the same quantity and condition. The repeated synthesis of gel in methylene chloride remained same result. However, the repeated synthesis in dimethylformamide present a transparent gel after reaction, which is similar to the one in methylene chloride of the first synthesis described above in DMF. The gels were showing light transparent yellow color but turned to a non-transparent brownish yellow one after drying. The color became darker and darker each time when the gel was heated to above 100 °C. By cutting the pieces of the gel carefully, the crosscut area shows the same color as its surface. The appearance of gels made in DMF and methylene chloride are shown in Figure 4-1.
4.2. Characterization

4.2.1. TGA analysis of polyacrylate gel

The thermal stability of acrylate gel synthesized in both methylene chloride and
dimethylformamide was investigated by TGA. The samples were heated from room temperature
to 580 °C at a rate of 10 °C/min. The decomposition temperature of gels has significantly
increased compared to the one of monomers after polymerization. Figure 4-2 is showing that
there are first stage weight losses of gels starting from 150 °C to 320 °C, while the gel made in methylene chloride has a weight loss of about 10% and the other one made in DMF has about 20%. Because the boiling point of methylene chloride is 39.6 °C while the boiling point of DMF is 153 °C, such difference makes the gel made in DMF have 10% more weight loss than the one made in methylene chloride. The 10% of weight loss might be caused by unreacted monomer, 11-bromoundecylacrylate, whose decomposition temperature is about 160 °C to 320 °C.

The second weight loss area starts from 320 °C and ends about 400 °C. This 30% to 40% weight loss is the period of acrylate polymers thermal degradation. In this area, the breakages of carbonyl groups COO- and C-O occur and results in the main chain scission, while the C-H bonds break before 310 °C but they don’t produce any weight loss.27

The final weight loss period is between 400 °C and 520 °C. Since the degradation occurred among carbonyl groups COO- and C-O in the previous stage, the carbon-carbon backbones are left in this final stage. Compared to Figure 4-3, the thermal degradation of PE and PP under nitrogen atmosphere happens between 400 °C–500 °C,25 which matches with the third stage of gels decomposition.
Figure 4-2. TGA of gels reacted in both methylene chloride and DMF. The thermal decomposition of monomer 11-bromoundecylacrylate is also included.

4.2.2. **DSC analysis of polyacrylate gel**

The physical transitions of the acrylate gel made in both methylene chloride and DMF were determined by DSC of each batch. Both DSCs ran from -90 °C to 150 °C at a speed of 10 °C/min. Figure 4-4 shows the overlay of the two DSC analysis. The curve of gel made in methylene chloride has two peaks. One of them is endotherm peak starts at about -50 °C and ends at about -10 °C with an energy of 15.66 J/g, and another one is exotherm peak starts at about -55 °C and ends at about -10 °C with an energy of 15.09 J/g. Similar as the one of the gel made in DMF, the DSC curve of the gel made in methylene chloride also shows an endotherm peak and an exotherm peak around at the same temperature.

Both curves are similar as the DSC curve of poly(AcC11Br) (see Figure 5-3), which indicates that the gel has similar physical transitions to the poly(AcC11Br). Since the product has already been a gel at room temperature, the endotherm peak and exotherm peak of the gel cannot be considered as its melting and freezing points in a usual sense. One possibility is that the gel may have a low crosslinking density so that the polymer backbone may maintain part of the physical properties compared to the one of poly(AcC11Br). Thus, the exotherm peak of the gel at -44.4 °C may be caused by partial crystallization of the polymer chain.
4.2.3. Solubility of acrylate gel

To understand the solubility properties of gels, thirteen solvents were used for testing. 9–22mg of gel pieces were put into various solvents separately, with an approximately ratio of 1:100, in the sealed culture tubes. The culture tubes were placed in shaker overnight and then were left at ambient environment for a week. NVM (non-volatile matter) test was done after that to identify the solubility of gel in each solvent. 1.2 ± 0.1 g of the clear solution from each culture tubes was transferred into the aluminum dishes (approximately 60 mm in diameter, 15 mm in depth, 2 g or less in mass, disposable). The aluminum dishes were heated in the oven at 140 °C for two hours next. Then the dishes were cooled to the room temperature and weighed. Three samples from each culture tube were tested at the same time, and the average result was noted. The calculation of NVM is shown below:

\[ NVM = \frac{D - A}{S - A} \times 100 \]
Where: NVM — the non-volatile content in percentage

A — the weight of aluminum dish in grams

S — the weight of aluminum dish with sample solution before heating in grams

D — the weight of aluminum dish with dried sample after heating in grams

The NVM results are showed in Table 4-1 along with the weight of gel pieces soaked by certain weight of solvent for solubility test. The results are in an arrange between 0.00% and 0.10%. The gel could be slightly soluble in chloroform with NVM of 0.10%. The diethyl ether, hexane, 2-octanol, and dodecane could not dissolve the gel at all. The gel was practically insoluble or insoluble in the rest of the solvents, including NMP, xylene, acetone, THF, butanol, methanol, benzene, and cyclohexane.
Table 4-1. Solubility of acrylate gels

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Wt. of gel pieces (mg)</th>
<th>Wt. of solvent (g)</th>
<th>NVM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>13.7</td>
<td>1.37</td>
<td>0.03</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>18.1</td>
<td>1.81</td>
<td>0.00</td>
</tr>
<tr>
<td>Xylene</td>
<td>21.9</td>
<td>2.20</td>
<td>0.05</td>
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<td>Chloroform</td>
<td>13.1</td>
<td>1.37</td>
<td>0.10</td>
</tr>
<tr>
<td>Acetone</td>
<td>16.7</td>
<td>1.69</td>
<td>0.02</td>
</tr>
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<td>THF</td>
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<td>2.28</td>
<td>0.08</td>
</tr>
<tr>
<td>Hexane</td>
<td>20.3</td>
<td>2.03</td>
<td>0.00</td>
</tr>
<tr>
<td>Butanol</td>
<td>23.7</td>
<td>2.08</td>
<td>0.02</td>
</tr>
<tr>
<td>Methanol</td>
<td>13.5</td>
<td>1.85</td>
<td>0.01</td>
</tr>
<tr>
<td>2-Octanol</td>
<td>9.9</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Benzene</td>
<td>14.5</td>
<td>1.45</td>
<td>0.03</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>13.5</td>
<td>1.36</td>
<td>0.02</td>
</tr>
<tr>
<td>Dodecane</td>
<td>23.0</td>
<td>2.5</td>
<td>0.00</td>
</tr>
</tbody>
</table>
4.2.4. Swelling of acrylate gel

Swelling test was done in order to identify if the crosslinking reaction has happened when forming the gel. Since the gel was tested not to be swelling in water, the density of the gel was first measured by putting it into a 10 ml beaker filled by DI water and collected the overflowing water to measure its volume. Next, a piece of gel around 50 mg was put in a culture tube and swelled in 2 ml of solvent. The sealed culture tube was kept at ambient environment for a week. The Figure 4-5 shows the appearance of the gel before swelling and in swollen state.

![Swelling test of gel](image)

Figure 4-5. Swelling test of gel. Left: the initial gel just put into solvent. Right: the gel after swelling for a week.

Afterward, the swollen gel was taken out from the solvent and let the swollen solvent evaporate at ambient temperature. The weight of it versus time was recorded. Three kind of different solvents were investigated including toluene, xylene, and NMP.

Table 4-2 describes the swelling test acrylate gel (50.9 mg, made in methylene chloride) in xylene. Time exposed means the time that the swollen gel piece was exposed at ambient temperature right after taking it out of solvent. The weight of gel means the weight of exposed swollen gel each time recorded; weight percentage compared to original gel means the weight percentage of exposed swollen gel for each time recorded compared to the piece of gel before swelling (50.9 mg). The weight percentage of swollen gel at equilibrium (zero time exposed is
the weight of gel right after taking it out of solvent) in xylene is 891%, while this weight percentage is 1004% in toluene (see Appendix Table A-1), and this weight percentage in NMP is 889%. The same test was repeated, and similar results were obtained. Consequently, these results are the most significant evidence of these gels being crosslinked.

This test was repeated for the gel made in DMF, and Table 4-3 below shows the swelling results of acrylate gel, which was made in DMF in the same solvents: xylene, NMP, and toluene. The results indicate that the acrylate gel made in DMF has smaller swelling than the gel made in methylene chloride, which means it has a higher crosslink density when formed in DMF. The crosslink density of both gels, made in DMF and methylene chloride, will be calculated and compared in the next section.
Table 4-2. Swelling of acylate gel in xylene.

<table>
<thead>
<tr>
<th>Time exposed (hour)</th>
<th>Wt. of gel pieces (mg)</th>
<th>Wt. percent compared to original gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>453.8</td>
<td>891.55%</td>
</tr>
<tr>
<td>1</td>
<td>413.4</td>
<td>812.18%</td>
</tr>
<tr>
<td>2</td>
<td>368.1</td>
<td>723.18%</td>
</tr>
<tr>
<td>3.5</td>
<td>241.5</td>
<td>474.46%</td>
</tr>
<tr>
<td>4.5</td>
<td>175.2</td>
<td>344.20%</td>
</tr>
<tr>
<td>6</td>
<td>103.3</td>
<td>202.95%</td>
</tr>
<tr>
<td>7.5</td>
<td>54.3</td>
<td>106.68%</td>
</tr>
<tr>
<td>After Vacuum Drying</td>
<td>50.5</td>
<td>99.21%</td>
</tr>
</tbody>
</table>

Table 4-3. Swelling of acylate gel made in DMF.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wt. of original gel pieces (mg)</th>
<th>Wt. of swollen gel pieces (mg)</th>
<th>Wt. percent compared to original gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>46.4</td>
<td>255.2</td>
<td>550%</td>
</tr>
<tr>
<td>NMP</td>
<td>43.3</td>
<td>222.9</td>
<td>515%</td>
</tr>
<tr>
<td>Toluene</td>
<td>48.6</td>
<td>236.7</td>
<td>487%</td>
</tr>
</tbody>
</table>
4.2.5. Crosslinking density

The swelling test has proved that crosslinking reaction has occurred when forming the gel. Therefore, the measurement of crosslinking density is important for further understanding the crosslinking reaction mechanism. The Flory-Huggins theory was used to find out the crosslinking density of the gel based on its swelling properties in xylene. Its equation defines the crosslinking density by introducing a polymer-solvent interaction parameter $\chi$ as follows:

$$ v = -\frac{1}{V_s} \cdot \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_r^{1/3} - \frac{V_r}{2}} $$

Where: $v$ — Crosslink density in mol per unit volume (mol/cm$^3$)

$V_r$ — Volume fraction of rubber in equilibrium swollen

$V_s$ — Mole volume of used solvent at room temperature in cm$^3$/mol

$\chi$ — Flory-Huggins polymer-solvent interaction parameter

The interaction parameter ($\chi$) is suggested to be 0.4 for the linear polyacrylate-xylene. Simultaneously, it is supposed to be larger in gels than in the corresponding linear polymers, which indicates that $\chi_{gel} > \chi$.\textsuperscript{28} As a result, the calculated result ($v$) might be lower than the practical crosslink density of the gel.

During the swelling test of gel (made in methylene chloride) in xylene, 80.9 mg (0.075 ml, $V_g$) of gel was swelled in 2 ml xylene for two weeks to get equilibrium, and the weight of swollen gel was 719.4 mg ($m_{gs}$, 889.24% compared to its size before swollen). Hence, the weight of swollen solvent ($m_{xylene}$) is the difference of the weight of gel after swelling ($m_{gs}$) and the weight of dry gel ($m_{gel}$):

$$ m_{xylene} = m_{gs} - m_{gel} = 719.4mg - 80.9mg = 638.5mg = 0.6385g $$
With the density of xylene to be 0.86 g/cm³ (ρ_{xylene}), the volume fraction of rubber in equilibrium swollen (V_r) can then be calculated by the following:

\[
V_r = \frac{V_g}{V_g + \frac{m_{xylene}}{\rho_{xylene}}} = \frac{0.075}{0.075 + 0.6385/0.86} = 0.09175
\]

The mole volume of used solvent at room temperature can also be calculated with the molar mass of xylene to be 106.16 g/mol (M_{xylene}) as follows:

\[
V_s = \frac{m_{xylene}/\rho_{xylene}}{m_{xylene}/M_{xylene}} = \frac{638.5/0.86}{638.5/106.16} = 123.44\text{cm}^3/\text{mol}
\]

The crosslink density (ν) can then be calculated by substitute all the results including V_r, V_s, and χ into the Flory-Huggins formula as follows:

\[
ν = -\frac{1}{V_s} \cdot \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_r^{1/3} - V_r/2}
\]

\[
= -\frac{1}{123.44} \times \frac{\ln(1 - 0.09175) + 0.09175 + 0.4 \times 0.09175^2}{0.09175^{1/3} - 0.09175/2}
\]

\[
= 2.24 \times 10^{-5}\text{mol/cm}^3
\]

The same test and calculations were also investigated in toluene. 100.3 mg (0.092 ml) of gel (made in methylene chloride) was swelled in 2.5 ml toluene for two weeks to get equilibrium, and the weight of swollen gel is 1007.4 mg. The χ was selected to be 0.07 for linear poly(n-butyl acrylate)-Toluene. With the density of toluene as 0.87 g/cm³ and the molar mass of toluene as 92.14 g/mol, the result is shown as follows:

\[
m_{\text{toluene}} = m_{gs} - m_{gel} = 1007.4\text{mg} - 100.3\text{mg} = 907.1\text{mg} = 0.9071\text{g}
\]

\[
V_r = \frac{V_g}{V_g + \frac{m_{\text{toluene}}}{\rho_{\text{toluene}}}} = \frac{0.092}{0.092 + 0.9071/0.87} = 0.081
\]
\[ V_s = \frac{m_{\text{toluene}}/\rho_{\text{toluene}}}{m_{\text{toluene}}/M_{\text{toluene}}} = \frac{907.1/0.87}{907.1/92.14} = 106.27 \text{cm}^3/\text{mol} \]

\[ V = -\frac{1}{V_s} \cdot \frac{ln(1 - V_r) + V_r + \chi V_r^2}{V_r^{1/3} - V_r/2} \]

\[ = -\frac{1}{106.27} \times \frac{ln(1 - 0.081) + 0.081 + 0.07 \times 0.081^2}{0.081^{1/3} - 0.081/2} \]

\[ = 7.22 \times 10^{-5} \text{mol/cm}^3 \]

To compare the crosslink density between the gels made in methylene chloride and DMF, the calculations were also done for the gel made in DMF. From the swelling data in last section, the crosslink density of the 46.4 mg (0.043 ml) gel (made in DMF) swelled in xylene can be calculated as follows:

\[ m_{\text{xylene}} = m_{gs} - m_{gel} = 222.9mg - 46.4mg = 176.5mg = 0.1765g \]

\[ V_r = \frac{V_g}{\frac{m_{\text{xylene}}}{\rho_{\text{xylene}}}} = \frac{0.0425}{0.0425 + 0.1765/0.86} = 0.205 \]

\[ V_s = \frac{m_{\text{xylene}}/\rho_{\text{xylene}}}{m_{\text{xylene}}/M_{\text{xylene}}} = \frac{638.5/0.86}{638.5/106.16} = 123.44 \text{cm}^3/\text{mol} \]

\[ V = -\frac{1}{V_s} \cdot \frac{ln(1 - V_r) + V_r + \chi V_r^2}{V_r^{1/3} - V_r/2} \]

\[ = -\frac{1}{123.44} \times \frac{ln(1 - 0.172) + 0.172 + 0.4 \times 0.172^2}{0.172^{1/3} - 0.172/2} \]

\[ = 8.46 \times 10^{-5} \text{mol/cm}^3 \]

And the crosslink density of the 48.6 mg (0.045 ml) gel (made in DMF) swelled in toluene can be calculated as follows:

\[ m_{\text{toluene}} = m_{gs} - m_{gel} = 236.7mg - 48.6mg = 188.1mg = 0.1881g \]

\[ V_r = \frac{V_g}{\frac{m_{\text{toluene}}}{\rho_{\text{toluene}}}} = \frac{0.045}{0.045 + 0.1881/0.867} = 0.170 \]
\[
V_s = \frac{m_{\text{toluene}}/\rho_{\text{toluene}}}{m_{\text{toluene}}/M_{\text{toluene}}} = \frac{907.1/0.87}{907.1/92.14} = 106.27 \text{cm}^3/\text{mol}
\]

\[
v = -\frac{1}{V_s} \cdot \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_r^{1/3} - V_r/2}
\]

\[
= -\frac{1}{106.27} \times \frac{\ln(1 - 0.170) + 0.170 + 0.4 \times 0.170^2}{0.170^{1/3} - 0.170/2}
\]

\[
= 2.87 \times 10^{-4} \text{mol/cm}^3
\]

As the calculation shows, the crosslink density of the gel (made in methylene chloride) in xylene (2.24 \times 10^{-5} \text{ mol/cm}^3) is smaller than the one of the gel (made in DMF) in xylene (8.46 \times 10^{-5} \text{ mol/cm}^3). Similar to the gels in toluene, the result of the gel made in methylene chloride (7.22 \times 10^{-5} \text{ mol/cm}^3) is smaller than the one made in DMF (2.87 \times 10^{-4} \text{ mol/cm}^3). Consequently, it is clear to see that the crosslink density of gel made in DMF is larger than the one made in methylene chloride.

4.2.6. Other experiments

The color of the gel was becoming darker and darker after annealing. At the meantime, the two sections above have approved that the crosslink reaction existed during the gel formation. As a result, one of the hypotheses is shown as Figure 4-6 that the Br-C bond on end of the side chain is broken and generate Br\(\cdot\), which composes Br\(\_\)2 with other free Br\(\cdot\) in the system. Another hypothesis is shown as Figure 4-7 that the Br- is E1 eliminated with the H- at the adjacent carbon, which composes HBr and double bonds, makes the crosslink reaction happened.
Figure 4-6. Crosslink reaction hypothesis 1 of gel formation which composes Br₂.

Figure 4-7. Crosslink reaction hypothesis 2 of gel formation which composes HBr.

To verify these hypotheses, a piece of gel (54 mg) was ground in 1 ml DI water in mortar by pestle. Subsequently, the trituated gel was filtered out and the filtrate was collected. The filtrate shows a light-yellow color as Figure 4-8 shows, while the color of trituated gel is lighter than the gel before grinding. It has a pH between 6 and 7 which shows a very low acid concentration. The gel has also been ground in chloroform and toluene. Only very light-yellow color was shown in chloroform filtrate, while no obvious color was presented in toluene filtrate.
Both the bromine and hydrobromic acid in water can show a light-yellow color. However, although the 80% of bromine in water will be converted to hydrobromic acid and hypobromous acid, there is still a few bromines which can be dissolved in water and shows an orange-yellow color. To further detect if there is bromine existing in the extracted filtrate, potassium iodide DI water solution (15 mg KI in 1 g DI water) was added into the filtrate but there was no visible color change. A drop of starch was then added into the extracted filtrate, and it turned to a turbid white dispersion which indicates that there was no bromine but only hydrobromic acid in the filtrate. Furthermore, the rate of elimination reaction is in proportion to its reactant, and gel formation only happened at a high ratio of the monomer 11-bromoundecylacrylate. Also, to check if the solvent can affect the gel formation, a 100% of monomer without any solvent or AIBN was heated at 65 °C for 28 hours as well, and the gel was still formed.

Potentiometric titration was also done to identify the amount of Br- in extracted filtrate. Another 100.9 mg of gel was ground in 2 ml DI water and the extracted filtrate was collected. Then the filtrate was diluted by DI water to 20 ml and titrated by 0.099 mol/L AgNO₃ DI water
solution. The 50 μl finnpipette, Ag+/S- and reference electrodes were used for titration. The titration process and curve are shown in Figure 4-9 and Figure 4-10.

Sodium bromide, 5.6 mg, was diluted with 20 ml DI water and titrated by 0.099 mol/L AgNO₃ water solution. The molar mass of sodium bromide is 102.89 g/mol, so that 5.6 mg NaBr is equal to 0.0544 mmol. The theoretical end point of the titration should be at 545.45 μl, which is close to the endpoint in the titration curve (about 570 μl).

Then 540 μl was picked as the endpoint of the extracted filtrate curve. Therefore, the Br⁻ in the extracted filtrate was:

\[ 540\mu l \times 0.099\text{mol/L} = 0.0486\text{mmol} \]

The molar mass of monomer 11-bromoundecylacrylate is 304.9 g/mol, so the molar of 100.9 mg gel was:

\[ 100.9\text{mg} / 304.9\text{g/mol} = 0.332\text{mmol} \]

Therefore, 100.9 mg (0.332 mmol) of gel has 0.0486 mmol of Br⁻ in the extracted filtrate, which is about 0.146 by molar.
Figure 4-9. Potentiometric titration process of extracted filtrate.

Figure 4-10. Potentiometric titration curve of extracted filtrate. The titration of NaBr for calibration is also included.
5. Synthesis and characterization of poly(AcC$_{11}$Br)

Poly(AcC$_{11}$Br) is the homopolymer which is polymerized from monomer 11-bromoundecylacrylate and can be used to further synthesize the poly(AcC$_{11}$C$_1$ImBr) with 1-methylimidazole. By reducing the ratio of monomer 11-bromoundecylacrylate to solvent, which introduced THF in this chapter, gel formation was avoided and liquid poly(AcC$_{11}$Br) was successfully synthesized.

5.1. Synthesis of poly(AcC$_{11}$Br)

The poly(AcC$_{11}$Br) was synthesized in THF at 5% (by weight) monomer with 0.1%, 0.5% and 1% (by weight) AIBN. First, 1.0mg, 5.0mg and 10.0mg (0.1%, 0.5% and 1%, respectively) of AIBN were dissolved in 20.00 g THF, respectively, in three culture tubes which was 1 cm diameter. Then 1.00 g of monomer 11-bromoundecylacrylate was added to each culture tubes. The mixture solutions were then purged by nitrogen gas and bubbled for 5 minutes. The culture tubes were placed in oil bath at 70 °C and reacted for 24 hours. The tube was shaken by hand 3 times during the reaction in order to make monomer well polymerized.

After reaction, the uniform, light-yellow solutions were formed in the culture tubes. The solutions were then transferred from culture tubes to petri dishes which left in the hood for a week to let the solvent evaporate and were further transferred to vacuum oven for drying. The products were dried in vacuum oven at room temperature overnight, and then at 80 °C, and 150 °C for 3 hours at each temperature. The yellow liquids were obtained from each batch after drying. The reaction scheme is shown in Figure 5-1.
5.2. Characterization

5.2.1. TGA analysis of poly(AcC₁₁Br)

The thermal stability of poly(AcC₁₁Br) synthesized in THF was investigated by TGA. The samples were heated from room temperature to 580 °C at a rate of 10 °C/min. Figure 5-2 is shown the thermal degradation properties of the homopolymers made in different percentage of AIBN, along with the TGA curve of gel, which is only showing the one made in DMF, since the gel made in two different solvents has very similar thermal degradation properties. Comparing three TGA curves of poly(AcC₁₁Br) to each other, the AIBN loading level doesn’t affect the thermal decomposition properties of poly(AcC₁₁Br), which is also evidence that the same polymer structure was obtained by each synthesis process. Similar to the TGA of acrylate gels, the first 10% weight loss area is between 100 °C to 300 °C, which is caused by the unreacted monomer since the solvent THF (boiling point is 66 °C) evaporate before 100 °C; while the second weight loss area, 300 °C to 420 °C, is the polymer main chain scission caused by the breakages of carbonyl groups, COO- and C-O groups. The third weight loss period, 420 °C to 520 °C, presents the carbon-carbon backbone degradation. Therefore the thermal degradation temperature of poly(AcC₁₁Br) starts around 300 °C and ends about 520 °C. The 1%–4% residues are also presenting on each homopolymer decomposition curves. However, compared to the thermal decomposition curve of the monomer 11-bromoundecylacrylate, the residue is not caused by the unreacted monomer. The thermal degradation temperature of homopolymers are
significantly increased, while the degree of polymerization does not affect the thermal degradation properties of homopolymers.

Figure 5-2. TGA graph of poly(AcC_{11}Br) made by different AIBN loading levels. The TGA curves of gel and monomer are also included.

5.2.2. DSC analysis of poly(AcC_{11}Br)

The physical transitions of poly(AcC_{11}Br) was determined by DSC of each batch. The test was started from room temperature and run from 150°C to -90°C in a process of heating/cooling/heating by using nitrogen as purging gas. Some of the tests were run from -150°C to 130°C, in order to identify the Tg of homopolymers. Figure 5-3 and Figure 5-4 are shown the endothermal and exothermal peaks of homopolymers made in different AIBN loading level. Comparing this three DSC curves to each other, different AIBN loading levels don’t affect the physical transition properties of poly(AcC_{11}Br), which is also an evidence to prove that each synthesis process obtained the same polymer structure. The melting point which
indicated by the endothermal peak on heating is around -41°C with energy of 14 J/g, while the exothermal peak on cooling presents the crystallization point around -48°C with 13 J/g. The glass transition temperature of poly(AcC11Br) is around -80°C, which is shown in Figure 5-5 from the DSC ran from -150°C to 130°C on heating. Compared to the thermal properties of monomer 11-bromoundecylacrylate, both of the melting point and crystallization point decrease about 20 °C while the glass transition maintain the same temperature. Compared the DSC curves of poly(AcC11Br) to gels, the melting point and crystallization point are both 5 °C lower, while the endothermal and exothermal energies are slightly lower than the gels.

![DSC graph](image)

Figure 5-3. Endothermal peaks of poly(AcC11Br) made by different AIBN loading levels.
5.2.3. NMR studies of poly(AcC\textsubscript{11}Br)

The structure of poly(AcC\textsubscript{11}Br) was confirmed by \textsuperscript{1}H NMR as the same as 11-bromoundecylacrylate. 10–20 mg of sample was dissolved in 2ml CDCl\textsubscript{3} and used as prepared. As shown in Figure 5-6, by using \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \textit{δ}), the following spectral features
were resolved: 1.30 (m, 18H, -CH₂(CH₂)₉CH₂Br), 1.65(m, 2H, OCH₂CH₂(CH₂)₇), 1.85(m, 2H, -(CH₂)₇CH₂CH₂Br), 3.40(t, 2H, -CH₂CH₂Br), 4.10(t, 2H, COO-CH₂CH₂-). The disappear of the peaks at 5.80(1H, CH₂=CH-), 6.10(1H, CH₂=CH-), 6.40(1H, CH₂=CH-) compared to monomer 11-bromoundecylacrylate indicates that the acrylate groups have been successfully reacted. The noises around 3.70 indicates -CH₂-OH, which means the starting material 11-bromoundecanol left in monomer also exists in the homopolymer. The peak located at 2.1 indicates the acetone left in the NMR tubes after cleaning, which does not have effect on the structure analysis.

Figure 5-6. NMR results poly(AcC₁₁Br).
5.2.4. FTIR analysis of \(\text{poly(AcC}_{11}\text{Br})\)

To identify the structure of \(\text{poly(AcC}_{11}\text{Br})\), the FTIR spectrum result is shown in Figure 5-7. 1732.57 \(\text{cm}^{-1}\) is the stretching vibration of \(>\text{C}=\text{O}\). 1456.80 \(\text{cm}^{-1}\) is the bend vibration of \(-\text{CH}_2\). 1278.64 \(\text{cm}^{-1}\) and 1167.91 \(\text{cm}^{-1}\) are the asymmetric stretching vibration of \(-\text{C}-\text{O}-\text{C}\). 1068.40 \(\text{cm}^{-1}\) is the symmetric stretching vibration. Compared to the IR spectrum of monomer 11-bromoundecylacrylate, the peak at 1629.64 \(\text{cm}^{-1}\), which points to the \(\text{C}=\text{C}\) of acrylate, does not exist anymore. This indicates the monomer was fully reacted and the homopolymer was successfully generated.

![FTIR Spectrum](image)

Figure 5-7. The FTIR spectrum of \(\text{poly(AcC}_{11}\text{Br})\), along with the spectrum of monomer.

5.2.5. MW studies of \(\text{poly(AcC}_{11}\text{Br})\)

The MW distribution of \(\text{poly(AcC}_{11}\text{Br})\) synthesized by different AIBN loading was determined by GPC. Samples for testing were prepared by dissolving 3–5mg of sample in 10ml THF. The GPC results are shown below. It shows that the MW increases with the AIBN content increases. More experiments are required to be done to analyze the data.
Table 5-1. MW distribution of poly(AcC₁₁Br) by GPC.

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Mn</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% AIBN, 5% monomer</td>
<td>998</td>
<td>1233</td>
</tr>
<tr>
<td>0.5% AIBN, 5% monomer</td>
<td>1637</td>
<td>2446</td>
</tr>
<tr>
<td>1% AIBN, 5% monomer</td>
<td>2563</td>
<td>4157</td>
</tr>
</tbody>
</table>
6. Synthesis and characterization of poly(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x}

6.1. Synthesis of poly(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x}

The poly(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x} was synthesized by adding 1-methylimidazole into poly(AcC\textsubscript{11}Br) dissolved in THF. For three different batches poly(AcC\textsubscript{11}Br) synthesized in different AIBN loading level (0.1%, 0.5%, 1.0%), each batch was further reacted with 10% and 50% molar excess 1-methylimidazole, respectively. To compare the extent of reaction, the reaction No. 7 listed in Table 6-1 which reacted with 40% of 1-methylimidazole has been synthesized as well. The details of each reactions are shown in Table 6-1.

Table 6-1. Poly(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x} synthesis parameters.

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>AIBN loading level for poly(AcC\textsubscript{11}Br) synthesis</th>
<th>mmol of monomer loading</th>
<th>mmol of 1-methylimidazole loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1%</td>
<td>1.20 mmol</td>
<td>1.32 mmol (10% excess)</td>
</tr>
<tr>
<td>2</td>
<td>0.1%</td>
<td>1.20 mmol</td>
<td>1.80 mmol (50% excess)</td>
</tr>
<tr>
<td>3</td>
<td>0.5%</td>
<td>1.56 mmol</td>
<td>1.72 mmol (10% excess)</td>
</tr>
<tr>
<td>4</td>
<td>0.5%</td>
<td>1.56 mmol</td>
<td>2.34 mmol (50% excess)</td>
</tr>
<tr>
<td>5</td>
<td>1.0%</td>
<td>1.25 mmol</td>
<td>1.37 mmol (10% excess)</td>
</tr>
<tr>
<td>6</td>
<td>1.0%</td>
<td>1.25 mmol</td>
<td>1.87 mmol (50% excess)</td>
</tr>
<tr>
<td>7</td>
<td>0.5%</td>
<td>0.82 mmol</td>
<td>0.36 mmol (40%)</td>
</tr>
</tbody>
</table>
The 1-methylimidazole was added by droppers into poly(AcC_{11}Br) solutions in the culture tubes and then the nitrogen was purged and bubbled for 5 min. The sealed tubes were immersed in oil bath at 60 °C and reacted for 48 hours.

After reactions, the batches with 10% molar excess and 40% 1-methylimidazole (reaction No.1, No.3, No.5, No.7 in Table 6-1) result in a uniform, light-yellow solution, while there were yellow, liquid polymer phases observed which were separated from THF and stayed on the bottom for the batches with 50% molar excess 1-methylimidazole (reaction No.2, No.4 and No.6 in Table 6-1). The separated THF phases were clear with very light-yellow color. The tubes were shaken by hand and the turbid, light-yellow dispersions were obtained. The two phases could be re-separated after leaving overnight. Then the THF phases were carefully removed by syringes and needles, and the bottom polymer phases were extracted and washed by THF two times.

Each batch was dried in the hood for a day for solvent evaporation and further dried in vacuum oven at room temperature, 50 °C, 80 °C, and 150 °C for 3 hours at each stage. The red-brown tacky liquids with very high viscosity were obtained after drying. The average yield is 70%, which was about 63% of making poly(MUBIm-Br) reported by Nykaza. The reaction scheme is shown in Figure 6-1.
6.2. Characterization

6.2.1. TGA analysis of poly(AcC<sub>11</sub>Br)<sub>1-x</sub>(AcC<sub>11</sub>C<sub>1</sub>ImBr)<sub>x</sub>

The thermal stabilities of poly(AcC<sub>11</sub>Br)<sub>1-x</sub>(AcC<sub>11</sub>C<sub>1</sub>ImBr)<sub>x</sub> synthesized in THF by different molecular weight of poly(AcC<sub>11</sub>Br) and different 1-methylimidazole loading levels were investigated by TGA. The samples were heated from room temperature to 580 °C at a rate of 10 °C/min. As seen in Figure 6-2 from No.1 to No.6, each TGA curve has three main decomposition areas. The first weight loss area, about 3% to 10% by weight, is between 40 °C to 280 °C, while the second decomposition area is between 280 °C to 380 °C, and the last decomposition area is between 400 °C to 540 °C. Each TGA curve leaves some residue between 3% to 8% by weight. Due to the hygroscopic properties of ionic liquid, the initial weight loss before 100 °C is attributed to the moisture present. Compared to the thermal decomposition curves of 1-methylimidazole, which was posted by Dustin England, the excess 1-methylimidazole during the synthesis may also be responsible for the first weight loss area since it decomposes between 40 °C to 175 °C. Compared to the thermal decomposition curves of
poly(AcC\textsubscript{11}Br) in Figure 5-2, the first weight loss may also be affected by the residual monomer from the homopolymers, which have the first weight loss areas between 100 °C to 300 °C. The second weight loss area, from 280 °C to 380 °C, should be the polymer main chain scission caused by the breakages of carbonyl groups, COO- and C-O groups, the same decomposing area with poly(AcC\textsubscript{11}Br).

The similar decomposition feature in the last weight loss area also exists in Dustin’s ionic liquid, IL-Br. To explore the possibility for the causes, he synthesized 1-hexyl-3-methylimidazolium bromide by 1-methylimidazole and 1-bromohexane in methylene chloride. Comparing the starting materials of making IL-Br with 1-hexyl-3-methylimidazolium, the undecylacrylate group was replaced by a non-polymerizable hexyl chain, so that the last weight loss area may be caused by the quaternized imidazolium group, while the residue is seen for the remainder of the heating profile.\textsuperscript{23} He also reported the thermal gravity analysis of poly IL-Br, which can be considered as poly(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x}, where x equal to 1. The first and second weight loss areas were also occurring between 40 °C to 280 °C and 280 °C to 340 °C. Comparing the last weight loss area of poly IL-Br to poly(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x}, the poly IL-Br had about 13% weight loss, which was higher than poly(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x}. Since the last decomposition area is highly caused by the quaternized imidazolium group as discussed before, it is reasonable that poly IL-Br, x equal to 1, contains more quaternized imidazolium group, since the x of poly(AcC\textsubscript{11}Br)\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x} is less than 1 which will be proved in the next sections in this chapter. The reaction No.7, which is alkylated by 40% of 1-methylimidazolide, shows a little bit different decomposition area from the others. The main decomposition area of No.7 is from 220 °C to 360 °C, which remains the decomposition properties of unreacted homopolymer, poly(AcC\textsubscript{11}Br).
6.2.2. DSC analysis of poly(AcC\textsubscript{11}Br\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x}

The physical transitions of poly(AcC\textsubscript{11}Br\textsubscript{1-x}(AcC\textsubscript{11}C\textsubscript{1}ImBr)\textsubscript{x} was determined by DSC of each batch. The tests were started from room temperature and running from 150°C to -90°C in a process of heating/cooling/heating by using nitrogen as purging gas. Reactions No. 1 and No. 3 have similar endothermal peaks around -6.72 °C and 0.58 °C with exothermal peaks around -13.77 °C and -16.90 °C respectively (see Figure 6-3 and Figure A-7), while the other reactions, including No. 2, No. 4, No. 5, and No. 6 present very wide exothermal and endothermal area (see Figure 6-4 and Figures A-8, A-9, and A-10). However, the two glass transitions at about -24 °C and 29 °C were observed, which Dustin England has reported at about -27 °C and 48 °C of the polyILBr.\textsuperscript{23} The DSC curve of reaction No.7 has two melting points around -10 °C and -38 °C, and two freezing points around -13 °C and -50 °C, which shows the evidence of the unreacted
homopolymer existence when the alkylation was completed at 40% 1-methylimidazole loading level.

Figure 6-3. DSC of reaction No. 3 listed in Table 6-1.

Figure 6-4. DSC of reaction No. 6 listed in Table 6-1.
6.2.3. Potentiometric titration

Potentiometric titration by Ag⁺ was used to identify the Br⁻ content of alkylated poly(AcC₁₁Br) so as to indicate the reaction content and the x value of poly(AcC₁₁Br)₁₋ₓ(AcC₁₁C₁ImBr)ₓ. Samples (size between 80 mg and 300 mg) of each product were diluted by 60 ml DI water/methanol (50/50 by weight) and titrated by 0.099 M AgNO₃ solution, which was calibrated by KCl solution first. A reference electrode and an indicator Ag⁺/S⁻ electrode were used to measure the potential and the values were carried out by Fisher Scientific Accumet 910 pH mV Meter.

The titration was prepared as follows: 8.5 g AgNO₃ was first added in a 500 ml volumetric flask. DI water was carefully added to the flask until the fluid reaches the standard line. The AgNO₃ solution was calibrated by 0.02 mol/L KCl DI water/methanol (50/50 by weight) and showed a concentration of 0.099 M (C_{AgNO₃}).

107.4 mg of the sample from reaction No. 1 listed in Table 6-1 was then put into a 100 ml beaker with 60 ml DI water/methanol (50/50 by weight), and the mixture was stirred by a small spatula until all samples dissolved. A light-yellow uniform solution obtained. Two electrons, a reference and an indicator electron which were connected to the pH/mV meter, were put into the sample solution. The heads of electrons were ensured to be fully immersed into the sample solution without touching the wall or the bottom of the beaker. A burette of 50 ml is used for titration. The burette was first rinsed by 0.099 M AgNO₃ DI water solution, and then filled by the same AgNO₃ DI water solution until the liquid level reached to 0. The AgNO₃ DI water solution was added carefully drop by drop into sample solution from the burette which was placed on a stand. During the titration, the potentials of each drop including the initial one was recorded from meter after shaking the beaker by hand carefully until the numbers were stable. The volume of
AgNO₃ DI water solution after each addition was recorded by reading the scale from the burette. The number was input into Excel at the same time for each reading. A graph was plotted and updated at the same time. The final graph was plotted in Figure 6-5.

![Graph: Silver titration curve of reaction No. 1.](image)

Figure 6-5. Silver titration curve of reaction No. 1.

As the result of titration shows, the end point of titration is around 2.1 ml ($V_{AgNO_3}$). Since 1 mole of Ag⁺ can precipitate 1 mole of Br⁻, the mole of Br⁻ ($n_{Br}$) is

$$n_{Br} = V_{AgNO_3} \cdot C_{AgNO_3} = 2.10 ml \times 0.099 M = 0.23760 mmol$$

Assume that the AcC₁₁C₁ImBr has a ratio of $x$ in the polymer, the structure of the polymer is poly[(AcC₁₁C₁ImBr)$_x$-(AcC₁₁Br)$_{1-x}$], in which the molar mass of AcC₁₁C₁ImBr is 387
g/mol ($M_{AcC_{11}ImBr}$) and the molar mass of AcC$_{11}$Br is 304.9 g/mol ($M_{AcC_{11}Br}$) so that the molar mass of the polymer is:

$$F_w = M_{AcC_{11}ImBr}x + M_{AcC_{11}Br}(1 - x) = 387x + 304.9(1 - x) g/mol$$

With 107.4 mg ($m_{poly}$) of sample polymer used for the titration, the mole of polymer ($n_{poly}$) can be calculate as:

$$n_{poly} = \frac{m_{poly}}{F_w} = \frac{107.4 mg}{387x+304.9(1-x)g/mol}$$

Finally, the equation with the ratio of AcC$_{11}$C$_1$ImBr in polymer can be calculated as

$$n_{poly}x = n_{Br}$$

where the ratio of AcC$_{11}$C$_1$ImBr $x$ is

$$x = \frac{n_{Br}}{n_{poly}} = \frac{n_{Br}F_w}{m_{poly}} = \frac{(M_{AcC_{11}ImBr}x + M_{AcC_{11}Br}(1 - x))(V_{AgNO_3} \cdot C_{AgNO_3})}{m_{poly}}$$

Thus,

$$x = 0.7071$$

The $x$ value of each reaction was calculated separately by the same method shown above.

The titrations have also been repeated for each reaction. As a result, the $x$ value of poly(AcC$_{11}$Br)$_{1-x}$(AcC$_{11}$C$_1$ImBr)$_x$ which synthesized under different stoichiometry ratios are shown in Table 6-2.
Table 6-2. Mole fraction alkylation, x, in poly(AcC\(_{11}\)Br)\(_{1-x}(\text{AcC}\(_{11}\)C\(_1\text{ImBr})_x\).

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>AIBN loading level for poly(AcC(_{11})Br) synthesis</th>
<th>mmol of 1-methylimidazole loading</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1%</td>
<td>10% excess</td>
<td>0.7071</td>
</tr>
<tr>
<td>2</td>
<td>0.1%</td>
<td>50% excess</td>
<td>0.7281</td>
</tr>
<tr>
<td>3</td>
<td>0.5%</td>
<td>10% excess</td>
<td>0.7013</td>
</tr>
<tr>
<td>4</td>
<td>0.5%</td>
<td>50% excess</td>
<td>0.7598</td>
</tr>
<tr>
<td>5</td>
<td>1.0%</td>
<td>10% excess</td>
<td>0.6838</td>
</tr>
<tr>
<td>6</td>
<td>1.0%</td>
<td>50% excess</td>
<td>0.7316</td>
</tr>
<tr>
<td>7</td>
<td>0.5%</td>
<td>40%</td>
<td>0.2671</td>
</tr>
</tbody>
</table>

It can be seen that the x value in poly(AcC\(_{11}\)Br)\(_{1-x}(\text{AcC}\(_{11}\)C\(_1\text{ImBr})_x\), which synthesized by 50% excess of 1-methylimidazole loaded has the average about 0.73, and it is higher than the one of poly(AcC\(_{11}\)Br)\(_{1-x}(\text{AcC}\(_{11}\)C\(_1\text{ImBr})_x\), which synthesized by 10% excess of 1-methylimidazole loaded. This difference indicates the alkylation with 1-methylimidazole is slightly higher in the synthesis of 50% excess of 1-methylimidazole. The 40% 1-methylimidazole loading also has the similar conversion content, which about 70% of 1-methylimidazole has been alkylated, compared to the total amount. Also, there is no obvious difference of the alkylation content between the homopolymers which were made by different levels of AIBN during the synthesis.
In the other word, the molecular weight of homopolymer has no effect on the alkylation reactions.
7. Conclusions

The monomer 11-bromoundecylacrylate (AcC\textsubscript{11}Br) was synthesized by 11-bromoundecanol and acryloyl chloride in the presence of triethylamine and further purified. The average yield of making monomers is 50%. The monomer has been much more extensively characterized than in previous reports. NMR provides a good basis for further interpretations of homopolymer structures. The average melting point $T'_m$ is -3 °C ± 4 °C, while the average freezing point $T'_f$ is -28 °C ± 8 °C, which were identified by DSC. The glass transition temperature is around -81 °C, which can also be concluded from DSC.

The homopolymer poly(AcC\textsubscript{11}Br) was initially polymerized by monomer AcC\textsubscript{11}Br at a high monomer (50%) and AIBN (1%) level, but a gel was formed unexpectedly which could not be dissolved in any solvent. De facto crosslinking reaction was proven by swelling measurements. The crosslink density of gel was estimated by Flory-Huggins theory. These results show that the crosslink density of the gel made in methylene chloride, which is $4.73 \times 10^{-5}$ mol/cm\textsuperscript{3} in average, is a little bit lower than the gel made in DMF, which has crosslink density of $1.86 \times 10^{-4}$ mol/cm\textsuperscript{3} in average. By grinding the gel in DI water, the Br\textsuperscript{-} content was quantitively identified by potentiometric titration and the molar content of Br\textsuperscript{-} in the extracted filtrate was 14.6% of total bromide. While crosslinking irrefutably occurred, a mechanism for such cross-linking is uncertain. It is tempting to say that the high initiator levels produced alkyl radicals that led to crosslinking, but we could not find a reasonable precedent in the literature.

The experiments have identified the high possibility of HBr existence. However, current experiments cannot prove the accuracy of hypothesis, so there are more possibilities and opportunities to bring out more hypothesis or prove the current ones.
By reducing the ratio of monomer to 5% under different AIBN ratio of 0.1%, 0.5% and 1% by weight, the liquid homopolymer poly(AcC_{11}Br) was successfully synthesized and isolated. And the glass transition temperature of homopolymer was about -80 °C. Melting and freezing peaks for the homopolymer at about -48 °C and -41 °C were identified very well in DSC measurements. The same melting and freezing peaks also were observed in DSC measurement of the gels, except these gels were room temperature solids.

The poly(AcC_{11}Br)_{1-x}(AcC_{11}C_{1}ImBr)_x was synthesized by adding 40%, 110% to 150% 1-methylimidazole relative to bromoundecyl pendant groups into poly(AcC_{11}Br) dissolved in THF. These PILs remain their liquidity when reacting with different ratios of 1-methylimidazole (40%, 110% and 150%). The average yield of each reaction was about 70%, while Nykaza has reported it about 63% of making poly(MUBIm-Br). The two glass transitions at about -24 °C and 29 °C were observed from the products which had 150% 1-methylimidazole level, while Dustin England has reported it at about -27 °C and 48 °C of the polyILBr. The silver ion titration quantitatively measured the Br^- content which identified the reaction content of alkylation under different stoichiometry ratio of poly(AcC_{11}Br) to 1-methylimidazole. This ratio remains about 70% at different conditions. Also, the molecular weight of poly(AcC_{11}Br) had no effect on the alkylation reaction content. This imidazolium bromide was very well characterized by silver ion potentiometric titration.

Designs for the acrylate-based polymers and copolymers that are liquid polymeric ionic liquids (LPIL) offer alternative approaches to producing macro-plasticizers. And limited use of such plasticizers is expected to provide increasing toughness without significant loss of modulus, which can be used to combat embrittlement imposed by incorporation of filler.
These bromoundecyl and imidazolium undecyl pendant groups provide interesting starting materials for advanced polymer materials. The bromoundecyl groups could be easily modified to become alkyl-azide groups. Such modifications may be a simple way to anchor such LPIL to solid surfaces. Also, it would be interesting to see if di-amino moieties, if not di-imidazolium groups, could be used to crosslink such polymers.
References


Appendix: Other tables and figures

Figure A-1. TGA curve of another 11-bromoundecylacrylate batch.

Figure A-2. DSC of 11-bromoundecylacrylate run between -150 °C to 120 °C.
Figure A-3. Another batch of 11-bromoundecylacrylate at room temperature.

Figure A-4. DSC of another 11-bromoundecylacrylate batch run between -150 °C to 120 °C.
Figure A-5. DSC of another 11-bromoundecylacrylate batch run between -90 °C to 150 °C.

Figure A-6. DSC curve of poly(AcC_{11}Br) made in THF with 0.5% AIBN. The scan was run from -150 °C to 130 °C.
Table A-1. Swelling of acylate gel in toluene.

<table>
<thead>
<tr>
<th>Time exposed</th>
<th>weight</th>
<th>Wt. percent (compare to original)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>1.0074g</td>
<td>1004.39%</td>
</tr>
<tr>
<td>1 min</td>
<td>1.0040g</td>
<td>1000.99%</td>
</tr>
<tr>
<td>2 min</td>
<td>1.0008g</td>
<td>997.81%</td>
</tr>
<tr>
<td>5 min</td>
<td>0.9981g</td>
<td>995.11%</td>
</tr>
<tr>
<td>25 min</td>
<td>0.9840g</td>
<td>981.06%</td>
</tr>
<tr>
<td>47 min</td>
<td>0.9697g</td>
<td>966.80%</td>
</tr>
<tr>
<td>69 min</td>
<td>0.9508g</td>
<td>947.96%</td>
</tr>
<tr>
<td>84 min</td>
<td>0.9309g</td>
<td>928.12%</td>
</tr>
<tr>
<td>118 min</td>
<td>0.9060g</td>
<td>903.29%</td>
</tr>
<tr>
<td>146 min</td>
<td>0.8860g</td>
<td>883.35%</td>
</tr>
<tr>
<td>177 min</td>
<td>0.8644g</td>
<td>861.81%</td>
</tr>
<tr>
<td>224 min</td>
<td>0.8399g</td>
<td>837.39%</td>
</tr>
<tr>
<td>After vacuum drying</td>
<td>100.1mg</td>
<td>99.80%</td>
</tr>
</tbody>
</table>
Figure A-7. DSC curve of reaction No. 1 listed in Table 6-1.

Figure A-8. DSC curve of reaction No. 2 listed in Table 6-1.
Figure A-9. DSC curve of reaction No. 4 listed in Table 6-1.

Figure A-10. DSC curve of reaction No. 5 listed in Table 6-1.