Synthesis and characterization of methacrylamidopropyltrimethylammonium chloride and N-substituted acrylamide ionomers

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Abstract. Quaternary ammonium ionomers of Methacrylamidopropyltrimethyl ammonium chloride with N-substituted acrylamides were prepared at 55±1°C using azobiscyanvaleric acid (ACVA) initiator. The monomers and ionomers were characterized by 1H- and 13C-NMR spectroscopy and the copolymer composition was calculated from elemental analysis data. The reduced viscosity of ionomers in methanol behaves as non-polyelectrolytes at lower mole percentage and as polyelectrolyte at higher mole percentage. The molecular weights of ionomers were found to be high and the polydispersity index values indicate termination mainly by disproportionation. The glass transition temperature (\(T_g\)) of ionomers were greater than those of the corresponding homopolymers, attributed to a reduction in segmental mobility. The initial decomposition temperature (IDT) showed that the stability of ionomers increases with increasing mole percentage of ionic content.

Keywords: rheology, ionomers, gel permeation chromatography (GPC), thermal properties

1. Introduction

A variety of ion-containing polymers have been developed in the recent past. These polymers are extensively used in paper manufacturing, textile finishes, oil production, plastics, coatings, biomedical applications etc. Cationic quaternary polyelectrolytes have manifold applications. They are used as primary coagulants, flocculants, oil conditioners, hair sprays, shampoo additives, grease thickeners etc. The use of polyelectrolytes based on acrylamide is of increasing interest in the fields of ore separation and waste treatment. The term ionomer is used to denote polymers which contain 0–15% ionic groups and those polymers with higher ionic group contents are classified as polyelectrolytes [1].

The N-substituted acrylamides are used to prepare thermosensitive polymers like poly(N-isopropylacrylamide) and copolymers of N-alkylacrylamide and styrene [2]. Thermosensitive polymers have great potential in applications as drug delivery system [3] human gene vector [4] and biocatalysts [5]. The neutral and strongly basic polyelectrolyte hydrogels are prepared from Methacrylamidopropylitrimethylammonium chloride and N-isopropylacrylamide respectively [6]. A survey of the open literature indicates that much work has been done on the physical properties of ionomers. The preparation and characterization of various quaternary salts from reaction of methyl iodide with dimethylaminoethyl methacrylate, diethy laminoethyl methacrylate, N-(3-dimethylaminopropyl) acrylamide or N-(3-dimethylaminopropyl) methacryl-
amide, has been reported by Lee et al. [7]. McCormick and Blackmon [8] studied the copolymers of acrylamide with 2-acrylamido-2-methylpropanedimethylammonium chloride. The molecular weights of copolymers were significantly lower than the molecular weight of the polyacrylamide. Lower degree of polymerization are likely due to increased cross-termination rates in the copolymerisation. Recently, Pazhanisamy et al. [9] have reported the synthesis and characterization of ionomers of Methacrylamidopropyl-N,N’-dimethyl-N-hexadecylammonium iodide (MPDMAC16) or Methacrylamidopropyl-N,N’-dimethyl-N-octadecylammonium iodide (MPDMAC18 ) with N-substituted acrylamides. The reduced viscosity of ionomers showed non-polyelectrolyte behavior and shear rate dependency of viscosity of ionomers showed viscoplastic behavior. The present study described in this article deals with the preparation, spectral characterization, thermal behavior and solution properties of Methacrylamidopropyltrimethylammonium chloride (MPTMAC) and N-substituted acrylamides ionomers.

2. Experimental

2.1. Materials

Methacrylamidopropyltrimethylammonium chloride (MPTMAC) used as a commercial sample (Aldrich Co) is available as an aqueous solution (50% by weight). It was diluted with an equal amount of distilled water and decolourised with activated carbon prior to use. The initiator 4,4’-azobis (4-cyanovaleric acid), (ACVA) was recrystallized from chloroform. Methanol was refluxed along with quick lime (CaO) for 5 h and distilled for use. Benzene was dried overnight using anhydrous CaCl2 and distilled before use. The monomers N-tert-amylacrylamide (AA), N-tert-butylacrylamide (BA) and N-cyclohexylacrylamide (CA) were prepared by a procedure described in literature [10].

2.2. Copolymerization

A solution containing 2.5 g (0.18 mole) of AA, 1.25 g (0.0057 mole) of MPTMAC and 0.1 g (0.0071 mole) of ACVA in 50 ml of 3:1 methanol/water medium was placed in a polymerization tube. The solution was flushed with oxygen free dry nitrogen gas for about 30 min and polymerization tube was closed by means of rubber tubings with pinch cock. The tube was then placed in a thermostated water bath at 55±1°C. After 12 h the reaction solution obtained was poured into ice-cold water and the copolymer (ionomer) precipitated by adding 0.1 M NaCl solution. The precipitated polymer was washed with benzene to remove the unreacted monomer and dried for 24 h at 60°C under vacuum (93.4% yield). The monomer feed was varied in order to prepare copolymers having different mol% of MPTMAC, as shown in Table 1. The other ionomers of MPTMAC-BA and MPTMAC-CA were also prepared similarly. In each system, ionomers of different mol% of MPTMAC were prepared by varying the feed composition (Table 1).

2.3. Instrumentation

The 1H-NMR and 13C-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer (JEOL, Tokyo, Japan) operating at 100 MHz and 400 MHz respectively in CDCl3 or DMSO(–d6). Elemental analysis of the copolymers were analysed using Heraeus-CHN–O rapid elemental analyzer. The Ubbelohde suspended level viscometer (Schott Medica GmbH Wertheim/
Main, Germany) was used to measure the viscosities of copolymers in methanol at 30±0.5°C. Brookfield viscometer (Brookfield Instruments Middleboro, MA) was used to study the effect of shear rate on viscosity of copolymers using a concentration of 1 g per 100 ml in DMF solvent at 30±1°C. The molecular weight analysis was performed using a gel permeation chromatograph (Waters Associates Milford, MA) equipped with a 410 model RI detector. The solvent DMF was stabilized with 0.01% LiBr with a flow rate of 1 ml/min and the columns used were Styragel. Number-average molecular weight (\(M_n\)) and Weight-average molecular weight (\(M_w\)) were calibrated with polystyrene standards. A Perkin-Elmer DSC-7 Differential scanning calorimeter was used to study the thermal behavior of ionomers at a heating rate of 20°C/min under nitrogen atmosphere. Thermogravimetric analysis was carried out using TGA-7 at a heating rate of 20°C/min under nitrogen atmosphere.

3. Results and discussion

Free radical copolymerization of hydrophilic cationic monomer MPTMAC with N-substituted acrylamides was carried out in aqueous methanol using ACVA as initiator. Since MPTMAC monomer was in the form of an aqueous solution (50%) and the N-tertiary alkyl acrylamides are insoluble in water, methanol/water (3:1) medium was used for copolymerization. The schematic representation of ionomer is shown in Figure 1. The copolymerization was carried out by varying the monomer feed composition to get different mol% of cationic monomer in copolymer.

3.1. Characterization

The \(^{13}\text{C}-\text{NMR}\) spectral values of N-tert-butyrlacrylamide is as follows:

\(^{13}\text{C}-\text{NMR}\) (CDCl\(_3\), \(\delta\) (ppm)):

- \(\delta\) 164.9 (CH\(_2\)=CH–CO–NH…);
- \(\delta\) 132.15 (CH\(_2\)=CH–CO–NH…);
- \(\delta\) 124.71 (CH\(_2\)=CH–CO–NH…);
- \(\delta\) 50.86 (–CO–NH–C(CH\(_3\))\(_3\));
- \(\delta\) 28.39 (–CO–NH–C(CH\(_3\))\(_3\)).

The \(^1\text{H}-\text{NMR}\) and \(^{13}\text{C}-\text{NMR}\) spectral values of MPTMAC is as follows:

\(^1\text{H}-\text{NMR}\) (CDCl\(_3\), \(\delta\) (ppm)) at 3.1 \(\delta\) (–N(CH\(_3\))\(_3\)); 5.6–5.8 \(\delta\) (CH\(_2\)=CH–); 8.2 (–NH);
3.4–3.5 \(\delta\) (NH–CH\(_2\)–CH\(_2\)–CH\(_2\)–N\(^+\)–); and 1.6 \(\delta\) (CH\(_2\)=C(CH\(_3\))\(_3\)).

\(^{13}\text{C}-\text{NMR}\) (CDCl\(_3\), \(\delta\) (ppm)):

- \(\delta\) 18.30 (CH\(_2\)=C(CH\(_3\))–);
- \(\delta\) 22.87 (–NH–CH\(_2\)–CH\(_2\)=CH\(_2\)–N\(^+\)–(CH\(_3\))\(_3\));
- \(\delta\) 36.58 (–NH–CH\(_2\)–CH\(_2\)=CH\(_2\)–N\(^+\)–(CH\(_3\))\(_3\));
- \(\delta\) 64.31 (–NH–CH\(_2\)–CH\(_2\)–CH\(_2\)=CH\(_2\)–N\(^+\)–(CH\(_3\))\(_3\));
- \(\delta\) 121.76 (CH\(_2\)=C(CH\(_3\))–CO–NH–);
- \(\delta\) 138.89 (CH\(_2\)=C(CH\(_3\))–CO–NH–);
- \(\delta\) 170.96 (CH\(_2\)=C(CH\(_3\))–CO–NH–);

The \(^{13}\text{C}-\text{NMR}\) spectrum of MPTMAC-BA ionomer is shown in Figure 2. The \(^{13}\text{C}-\text{NMR}\) spectrum of MPTMAC-BA ionomer shows the disappearance of vinyl carbon peaks at 121.76 and 138.89 ppm of MPTMAC monomer. The spectrum shows the presence of a peak at 52.1 ppm, due to N–CH\(_3\) group of MPTMAC unit. The peak at 28.37 ppm is due to tert-butyl group of N-tert-butyrlacrylamide (BA) unit. The carbonyl carbon peaks appears at 163.53 and 174.54 ppm are due to the BA and MPTMAC units respectively. The peak values confirm the occurrence of copolymerization.
3.2. Determination of mol percentage of MPTMAC

The mol% of cationic monomer, MPTMAC in the MPTMAC-AA copolymers were calculated from elemental analysis data using C/N ratio [8]. Copolymers MPTMAC with N-tert-amylacrylamide (AA) have the following weight percentages of carbon and nitrogen represented by

\[
\%
C = 96.08 \text{[AA]} + 120.1 \text{[MPTMAC]}
\]

\[
\%
N = 14.01 \text{[AA]} + 28.02 \text{[MPTMAC]}
\]

The mol% of MPTMAC in the copolymer is obtained from the Equation (1):

\[
\text{Mol}\% \text{ of MPTMAC in copolymer} = \frac{7 \times (\% C) - 48 \times (\% N)}{12 \times (\% N) - 7 \times (\% C)} \times 100
\]  

Similarly for the other ionomers the corresponding equations were derived and the mol% was calculated. The calculated mol% of MPTMAC are given in Table 1. The calculated mol% of MPTMAC in the copolymers indicate the formation of ionomers. In the case of MPTMAC-AA, the content of ionic charge (mol% of MPTMAC) in copolymer is higher than in feed, when the feed mol% is at 4 and 10. But, the mol% of MPTMAC in copolymer is lower than in feed, when the feed mol% is 32. The influence of MPTMAC decreases with increasing the feed mol%. Whereas, in the case of MPTMAC-CA, the influence of MPTMAC increases with increasing the feed mol%. The increasing and decreasing trends of MPTMAC in copolymer depend on the nature of the comonomers.

3.3. Viscosity study

From Table 1 it is clear that the reduced viscosity of ionomers increases with increasing mol% of MPTMAC and it is due to molecular weight of ionomers. The reduced viscosity \( \eta_r/C \) versus concentration C plots of MPTMAC-BA copolymers in methanol are shown in Figure 3. The plots corresponding to mol% of MPTMAC equal to 5.51 and 8.99 do not show an increase of reduced viscosity with the decreasing of concentration, whereas the plot corresponding to 25.46 mol% of MPTMAC shows a steep raise of reduced viscosity with decreasing concentration. So the copolymers with the mol% of 5.51 and 8.99 of MPTMAC possess a behavior close to that of non-polyelectrolyte [11, 12]. The decrease of reduced viscosity for 5.51 mol% of MPTMAC in MPTMAC-BA ionomer at low polymer concentration is due to intramolecular associations at low polymer concentrations. Therefore ‘polyelectrolyte behavior’ was not observed for this ionomer because of ion-pair interactions [9]. Whereas the copolymer with higher mol% 25.46 of MPTMAC behaves as a polyelectrolyte. This is due to the coil expansion of ionomer chains at extreme dilution [13]. The ionic repulsion of the pendant quaternary ammonium cations

Figure 2. \(^{13}\text{C-NMR spectrum of MPTMAC-BA ionomer (8.99 mol%)}\)
attached to the polymer backbone resulting from the dissociation of gegenions like Cl\textsuperscript{-} or I\textsuperscript{-}-leads to polymer chain expansion. A similar trend has been observed by other workers in the case of sulphonated polystyrene ionomers [14] and quaternary polymers [11]. The reduced viscosity \( \eta_{sp}/C \) versus concentration \( C \) plots of MPTMAC-AA copolymer in methanol are shown in Figure 4. Copolymers having different mol\% of MPTMAC content viz., 10.70, 13.15 and 22.65 (Table 1) have been studied. In all these cases the reduced viscosity increases remarkably with decreasing polymer concentration thereby exhibiting polyelectrolyte behavior. The concentration dependency of the reduced viscosity in polar solvents appear to be related to the molecular weight of the polymers. In the case of MPTMAC-CA copolymers (1.31 and 5.96 mol\%) the reduced viscosity increases with decrease in polymer concentration up to a concentration of 0.3 g-dl\textsuperscript{-1}, after which it decreases with decreasing concentration (Figure 5). At lower polymer concentration the mutual attraction between positive and negative charges may cause bending of the polymeric chains and decrease the reduced viscosity. But for copolymer having mol\% of MPTMAC equal to 21.42 the reduced viscosity increases with decreasing concentration and hence it behaves as a polyelectrolyte. These ionomers behave as poly-

Figure 3. Reduced viscosity plots of MPTMAC-BA ionomer

Figure 4. Reduced viscosity plots of MPTMAC-AA ionomer

Figure 5. Reduced viscosity plots of MPTMAC-CA ionomer
electrolyte at higher mol% of ionic content and behave as non-polyelectrolyte at lower mol% of ionic content [9].

3.4. Rheological studies

Viscosity behavior at varying shear rate was studied using a Brookfield viscometer (Brookfield instruments. Middleboro, MA) for MPTMAC-BA (8.99 mol%) and poly BA in DMF at 30°C. The plot of viscosity [cps] versus shear rate [rpm] for ionomer and the homopolymer are shown in Figure 6. The change in the viscosity dependency on shear rate was found to be less in the ionomer than that of homopolymer. The viscoplastic nature of the ionomer less pronounced than that of homopolymer. The sizable content of MPTMAC groups in the ionomer, which produced intramolecular interactions there by reducing that entanglements [15].

3.5. GPC Analysis

The analysis was carried out in the presence of 0.01% Li Br in DMF at 30°C. The molecular weight distribution of hydrophilic ionomers are given in Table 2. The molecular weights are found to be high ($M_w = 3.95 \cdot 10^5$). The polydispersity index of these ionomers MPTMAC-N-substituted acrylamides range from 1.57 to 2.17 (Table 2) and these value indicates that the termination mainly by disproportionation [16]. The higher molecular weight of ionomers are due to higher degree of polymerization. The steric hindrance caused by the pendant ionic group is less compared with long alkyl moiety [9]. Moreover, the molecular weight of ionomers increases in the order of MPTMAC-CA <MPTMAC-AA<MPTMAC-BA may be due to the influence of N-alkyl substituent of acrylamides (bulkiness of N-alkyl group).

3.6. Thermal analysis

3.6.1. Glass transition temperature

The glass transition temperature ($T_g$) is the temperature at which the amorphous domain of a polymer takes on the characteristic properties of glassy state. The $T_g$ depends on the morphology of the polymer and the $T_g$ values are presented in Table 3. From the table it is clear that the $T_g$ of poly(N-tert-buty lacrylamide) homopolymer is 64.8°C and that of the corresponding ionomer is 79.4°C. The increase in $T_g$ may be attributed to a reduction in segmental mobility due to the electrostatic attraction between the pendent ionic group of the polymer chain and the counterions. The ionomers of N-tert-amylacrylamide and N-cyclohexylacrylamide with MPTMAC have higher $T_g$ values compared to the corresponding homopolymers of N-substituted acrylamides.

3.6.2. Thermogravimetric analysis

The TGA data for the ionomers of MPTMAC with N-substituted acrylamides are given in Table 3.

### Table 2. GPC analysis of MPTMAC-N-substituted acrylamide Ionomers

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>Mol% of MPTMAC in copolymer</th>
<th>$M_w \cdot 10^{-5}$</th>
<th>$M_n \cdot 10^{-5}$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPTMAC-BA</td>
<td>08.99</td>
<td>3.95</td>
<td>1.90</td>
<td>2.08</td>
</tr>
<tr>
<td>MPTMAC-AA</td>
<td>13.15</td>
<td>1.52</td>
<td>0.97</td>
<td>1.57</td>
</tr>
<tr>
<td>MPTMAC-CA</td>
<td>05.96</td>
<td>1.51</td>
<td>0.70</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Figure 6. Plots of viscosity vs shear rate of MPTMAC-BA (●) and poly BA (○)

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typical TGA curves for MPTMAC-AA ionomers are shown in Figure 7. All the ionomers exhibit double stage decomposition. MPTMAC-AA shows an increase in initial decomposition temperature (IDT), with increase in mol% of MPTMAC. Hence the stability of the ionomers increases with the increasing mol% of ionic content. The initial weight loss (8.8%) is observed for these ionomers due to the moisture absorption. For 13.15 mol% ionomer, the weight loss in the stage 1 is about 6.1% corresponding to $T_1 = 265.6^\circ C$ and the weight loss in the stage 2 is about 78.4% corresponding $T_2 = 445.5^\circ C$. The weight loss occurring in the stage 1 may be due to dequaternization at N$^+$ site of MPTMAC unit. The maximum weight loss occurring in stage 2 may be due to scission in amide linkage of both monomeric units of ionomer. For 22.65 mol% ionomer the $T_1 = 349.4^\circ C$ and $T_2 = 444.6^\circ C$. The decomposition temperature in the stage 1 ($T_1$) increases with increase of mol% of MPTMAC. A similar trends have been observed in the other ionomer systems.

4. Conclusions
Quaternary ammonium ionomers were prepared by copolymerization of MPTMAC with N-substituted acrylamides at 55±1°C. The monomers and ionomers were characterized by $^1$H- and $^{13}$C-NMR spectroscopy and the mole percentage of cationic monomer in copolymer was calculated from elemental analysis using C/N ratio. The reduced viscosity of ionomers in methanol showed non-polyelectrolyte behavior at lower mole percentage and behaves as polyelectrolytes at higher mole percentage. This is due to coil expansion of ionomer chains at extreme dilution. Shear rate dependency of viscosity of ionomers showed viscoplastic behavior. The molecular weights of ionomers are found to be high due to higher degree of polymerization. Polydispersity index values of ionomers indicate that the termination occurred mainly by disproportionation. The $T_g$ values of ionomers are higher than those of the corresponding homopolymers and the increase in $T_g$ attributed to reduction in segmental mobility. In TGA, all the ionomers showed double stage decomposition. The IDT shows that the stability of ionomers increases with increasing mole percentage of ionic content.

References