Synthesis and Characterization of Quaternary Ammonium Ionomers

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ABSTRACT: The cationic monomers, $MPDMAC_{16}$ and $MPDMAC_{18}$, were obtained by quaternization of methacryl-amidopropyl–N,N'-dimethylamine with n-alkyl iodides (1-iodohexadecane and 1-iodooctadecane) in ethyl acetate. Hydrophobic ionomers of $MPDMAC_{16}$ and $MPDMAC_{18}$ with N-substituted acrylamides were prepared at $60 \pm 0.1°C$ in DMF using AIBN initiator. The cationic monomers and ionomers were characterized by ^1H- and ^{13}C-NMR spectroscopy. The copolymer composition was evaluated from elemental analysis data using carbon/nitrogen (C/N) ratio. The mo-lecular weight distributions of ionomers were obtained from GPC analysis. Both the dilute solution and concentrated solution properties of ionomers were studied by viscometry at 30°C. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1100–1105, 2005

Key words: ionomers; gel permeation chromatography (GPC); viscosity; polyelectrolytes; molecular weight distribution

INTRODUCTION

Ion-containing polymers are referred to as "polyelectrolytes" when they have sufficient ionic charge to be soluble[1] or as " ionomers" when the ionic group concentration is low.[2] A survey of the open literature indicates that much work has been done on the physical properties of ionomers.[3–6] However, there has been comparatively much less work on their solution behavior. Salamone et al.[7,8] reported on the quaternary salts of 1-vinylimidazole and found that the long side-chain polyions, which are hydrophobic, appeared to form polysoaps and remained in the aqueous solution. Nagai et al.[9] studied the polymerization of quaternary alkyl salts of dimethylaminoethyl methacrylate with different alkyl chain lengths. The reduced viscosity, in dimethylformamide (DMF) and methanol, of poly(lauryl bromide salt) prepared in water increased with dilution but that for the polymer obtained in benzene exhibited an inverse concentration dependency. The present study described in this article deals with the synthesis, characterization, and solution properties of hydrophobic ionomers.

EXPERIMENTAL

Materials

Methacrylamidopropyl-N,N'-dimethylamine (MPDMA) was distilled twice at reduced pressure (bp 125°C at 5 mmHg). The initiator, azobisisobutyronitrile (AIBN) was recrystallized from chloroform.

Ethyl acetate was refluxed overnight in the presence of CaH_2 and distilled at 77°C and stored over molecular sieves (4 Å). Methanol was refluxed with CaO for 5 h and distilled for use.

Preparation of N-substituted acrylamides

The monomers N-*tert*-amylacrylamide (AA), N-*tert*-butylacrylamide (BA), and N-cyclohexylacrylamide (CA) were prepared by a procedure described by Plaut and Ritter.[10]

Preparation of hydrophobic cationic monomers

Methacrylamidopropyl-N,N'-dimethyl-N-hexadecylammonium iodide ($MPDMAC_{16}$)

About 0.026 mol of MPDMA in 50 mL ethyl acetate was added dropwise to a solution (0.028 mol) of 1-iodohexadecane with stirring at room temperature. The solution was then heated in a water bath at 60°C with stirring for 30 h. After being allowed to stand for 1 h at room temperature, the solution was cooled to 0°C, at which temperature the solid separated. The crude product was filtered and recrystallized from dry ethyl

TABLE I
Copolymerization of AA with Cationic Monomers MPDMAC$_{16}$ and MPDMAC$_{18}$

Ionomer	Mol % in feed	C%	H%	N%	Mol % in copolymer	η_{red} (dL g^{-1}) at 0.4 gd L^{-1}
	04.0	62.52	10.21	9.32	1.88	0.11
MPDMAC$_{16}$–AA	10.0	61.13	10.02	9.29	3.47	0.07
	04.0	60.58	10.52	8.78	0.46	—
MPDMAC$_{18}$–AA	10.0	60.25	10.40	8.41	3.07	—

acetate. The resulting crystalline compound melted at 62. 0–63.0°C.

^{13}C-NMR (CDCl$_3$), δ (ppm): δ 169.22 [CH$_2$=C(CH$_3$)—*CO*—NH–]

δ 139.13 [CH$_2$=C(CH$_3$)—CO—NH–]; δ 121.15 [*CH$_2$*=C(CH$_3$)—CO—NH–]

δ 64.91 [CH$_2$=C(CH$_3$)—CO—NH—CH$_2$—CH$_2$—*CH$_2$*—N$^+$—(CH$_3$)$_2$—CH$_2$–]

δ 62.90 [CH$_2$=C(CH$_3$)—CO—NH—CH$_2$—CH$_2$—CH$_2$—N$^+$—(CH$_3$)$_2$—*CH$_2$*–]

δ 51.61 [CH$_2$=C(CH$_3$)—CO—NH—CH$_2$—CH$_2$—CH$_2$—N$^+$—(*CH$_3$*)$_2$—CH$_2$–]

δ 36.48 [CH$_2$=C(CH$_3$)—CO—NH—*CH$_2$*—CH$_2$—CH$_2$—N$^+$—(CH$_3$)$_2$—CH$_2$–]

δ 31.98 [–N$^+$—(CH$_3$)$_2$—CH$_2$—CH$_2$—(*CH$_2$*)$_{11}$—CH$_2$—CH$_2$—CH$_3$]

δ 29.56 [–N$^+$—(CH$_3$)$_2$—CH$_2$—CH$_2$—(*CH$_2$*)$_{11}$—CH$_2$—CH$_2$—CH$_3$]

δ 26.32 [CH$_2$=C(CH$_3$)—CO—NH—CH$_2$—*CH$_2$*—CH$_2$—N$^+$—(CH$_3$)$_2$–]

δ 23.23 [CH$_2$=C(CH$_3$)—CO—NH—(CH$_2$)$_3$—N$^+$(CH$_3$)$_2$—CH$_2$—*CH$_2$*—(CH$_2$)$_{11}$–]

δ 22.74 [–N$^+$—(CH$_3$)$_2$—(CH$_2$)$_{14}$—*CH$_2$*—CH$_3$]

δ 19.27 [CH$_2$=C(*CH$_3$*)—CO—NH–]

δ 14.18 [–N$^+$—(CH$_3$)$_2$—(CH$_2$)$_{14}$—CH$_2$—*CH$_3$*]

^{1}H-NMR (CDCl$_3$), δ (ppm): δ 5.3–5.9 [*CH$_2$*=C(CH$_3$)—CO—NH–]

δ 2.0 [CH$_2$=C(*CH$_3$*)—CO—NH–]
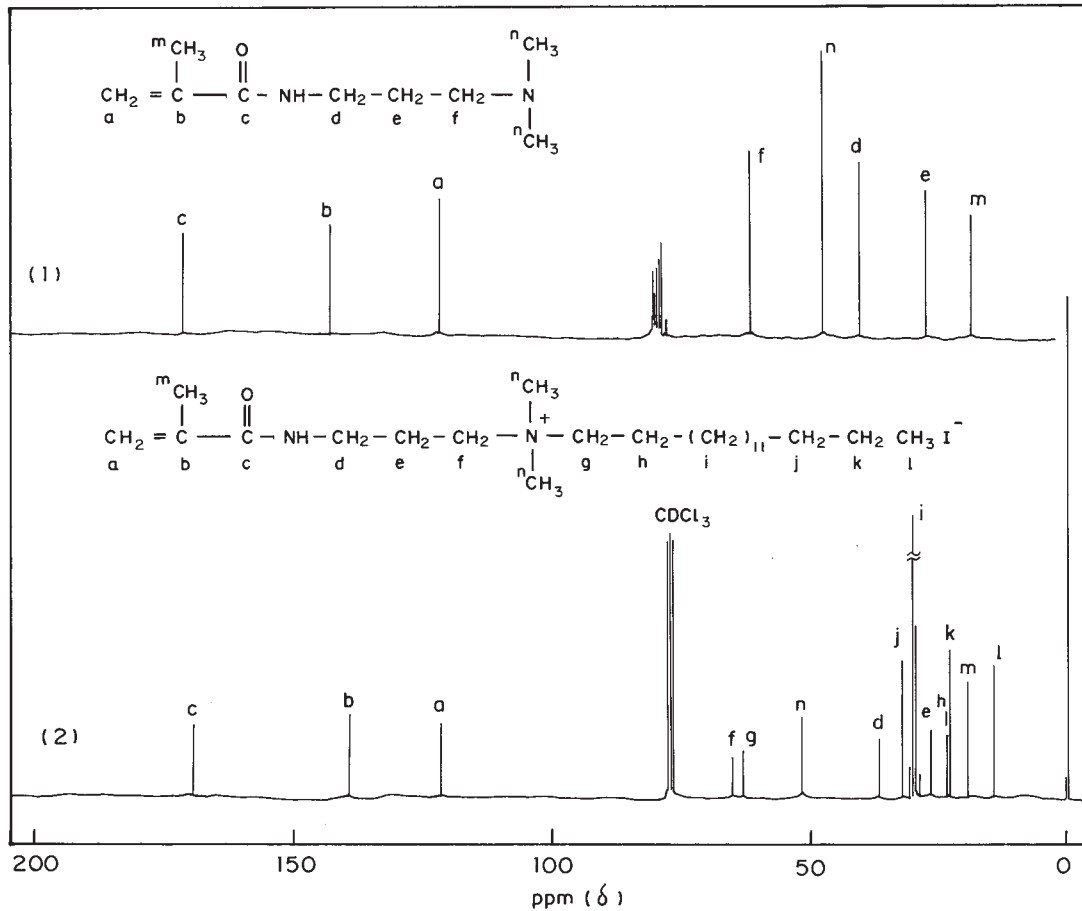
Figure 1 ^{13}C-NMR spectra of (1) MPDMA and (2) MPDMAC$_{16}$.

δ 7.4 [CH_2=$C(CH_3)$—CO—$\underline{NH}$–]
δ 3.1 [–CO—NH—$\underline{CH_2}$—CH_2—CH_2—$N^+(CH_3)_2$–]
δ 2.2 [–CO—NH—CH_2—$\underline{CH_2}$—CH_2—$N^+(CH_3)_2$–]
δ 3.7 [–CO—NH—CH_2—CH_2—$\underline{CH_2}$—$N^+(CH_3)_2$–]
δ 3.24 [–CO—NH—CH_2—CH_2—CH_2—$N^+(\underline{CH_3})_2$–]
δ 3.5 [–$N^+(CH_3)_2$—$\underline{CH_2}$—$(CH_2)_{13}$—CH_2—CH_3]
δ 1.2–1.4 [–$N^+(CH_3)_2$—CH_2—$(\underline{CH_2})_{13}$—CH_2—CH_3]
δ 1.8 [–$N^+(CH_3)_2$—CH_2—$(CH_2)_{13}$—$\underline{CH_2}$—CH_3]
δ 0.85 [–$N^+(CH_3)_2$—CH_2—$(CH_2)_{13}$—CH_2—$\underline{CH_3}$]
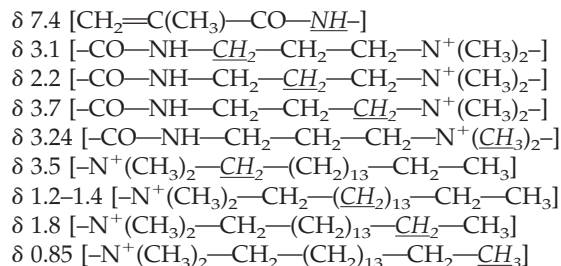
Methacrylamidopropyl-*N*,*N'*-dimethyl-*N*-octadecylammonium iodide (MPDMAC$_{18}$)

The monomer MPDMAC$_{18}$ was prepared similarly to MPDMAC$_{16}$ by the reaction of MPDMA with 1-iodooctadecane at 65°C. The crude product was recrystallized from ethyl acetate to give crystals melting at 68.0–70.0°C.

Hydrophobic ionomers

**Copolymerization of MPDMAC$_{16}$ with N-substituted acrylamide**

In a polymerization tube 50 mL of DMF solution, consisting of 2.0 g (0.013 mol) of CA, 0.27 g (0.0005 mol) of MPDMAC$_{16}$, and 100 mg of AIBN, was prepared. The solution was flushed with oxygen-free dry nitrogen gas for 30 min and the polymerization tube was closed by means of rubber tubing with a pinch cock. The tube was then placed in a thermostatic water bath maintained at 60°C. The reaction was allowed to proceed for 16 h, after which the copolymer was precipitated from solution by adding 0.1*M* NaI. The precipitated polymer was washed with benzene to remove the unreacted monomer and the polymer was dried for 24 h at 60°C under vacuum. The other ionomers of MPDMAC$_{16}$ with BA and CA were also similarly prepared. In each system, ionomers of different mol % of MPDMAC$_{16}$ were prepared by varying the feed composition (Table I).

Copolymerization of MPDMAC$_{18}$ with N-substituted acrylamides

The ionomers of MPDMAC$_{18}$ with N-substituted acrylamides (AA, BA, and CA) with different mol % were prepared by the above-described procedure in DMF solvent 60°C.

Instrumentation

The ^{1}H-NMR spectra of copolymers were recorded on a GSX-400 spectrometer (JEOL, Tokyo, Japan), operating at 400 MHz in CDCl$_3$ or DMSO-d_6. The ^{13}C-NMR spectra of copolymers were recorded on the same instrument operating at 100 MHz. The FTIR spectra of
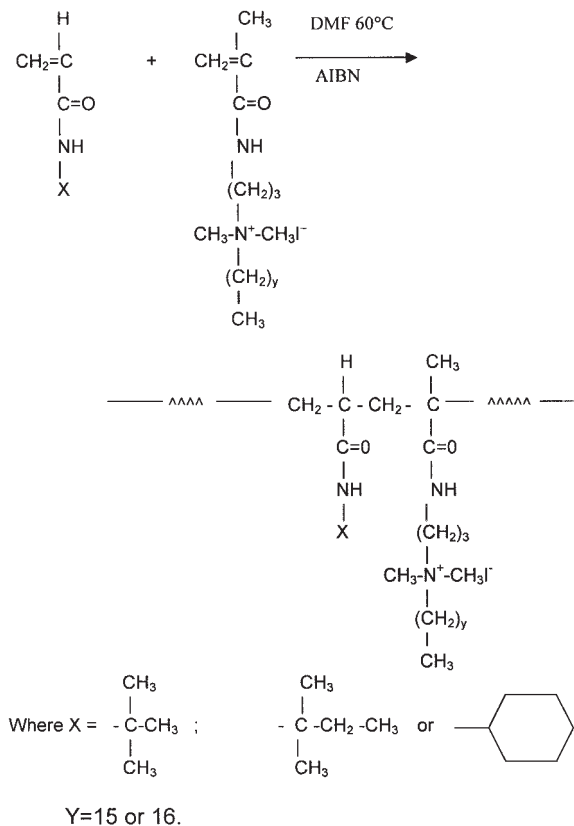
Scheme 1

monomers were recorded on an IFS 66 FTIR spectrometer (Bruker Instruments, Darmstadt, Germany) using KBr pellets. Elemental analysis of copolymers was carried out on a CHN-O Rapid Element Analyzer (Heraeus, Hanau, Germany). The molecular weight analysis was performed using a gel permeation chromatograph (Waters Associates, Milford, MA), equipped with a 410 model RI detector. The solvent used was DMF stabilized with 0.01% LiBr at a flow rate of 1 mL/min. The columns used were μ-Styragel of 10^3, 10^4, 10^5, and 10^6 Å pore size. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were calibrated with standard polystyrenes.

RESULTS AND DISCUSSION

Hydrophobic ionomers

The hydrophobic cationic monomers MPDMAC$_{16}$ and MPDMAC$_{18}$ were prepared by quaternization of MPDMA with 1-iodohexadecane and 1-iodooctadecane, respectively, in ethyl acetate. The ^{13}C-NMR spectra of MPDMA and MPDMAC$_{16}$ are shown in Figure 1. The assignments of all resonances are depicted in the same figure. The quaternized ammonium ion shows a deshielding effect on its methyl groups and shifted the
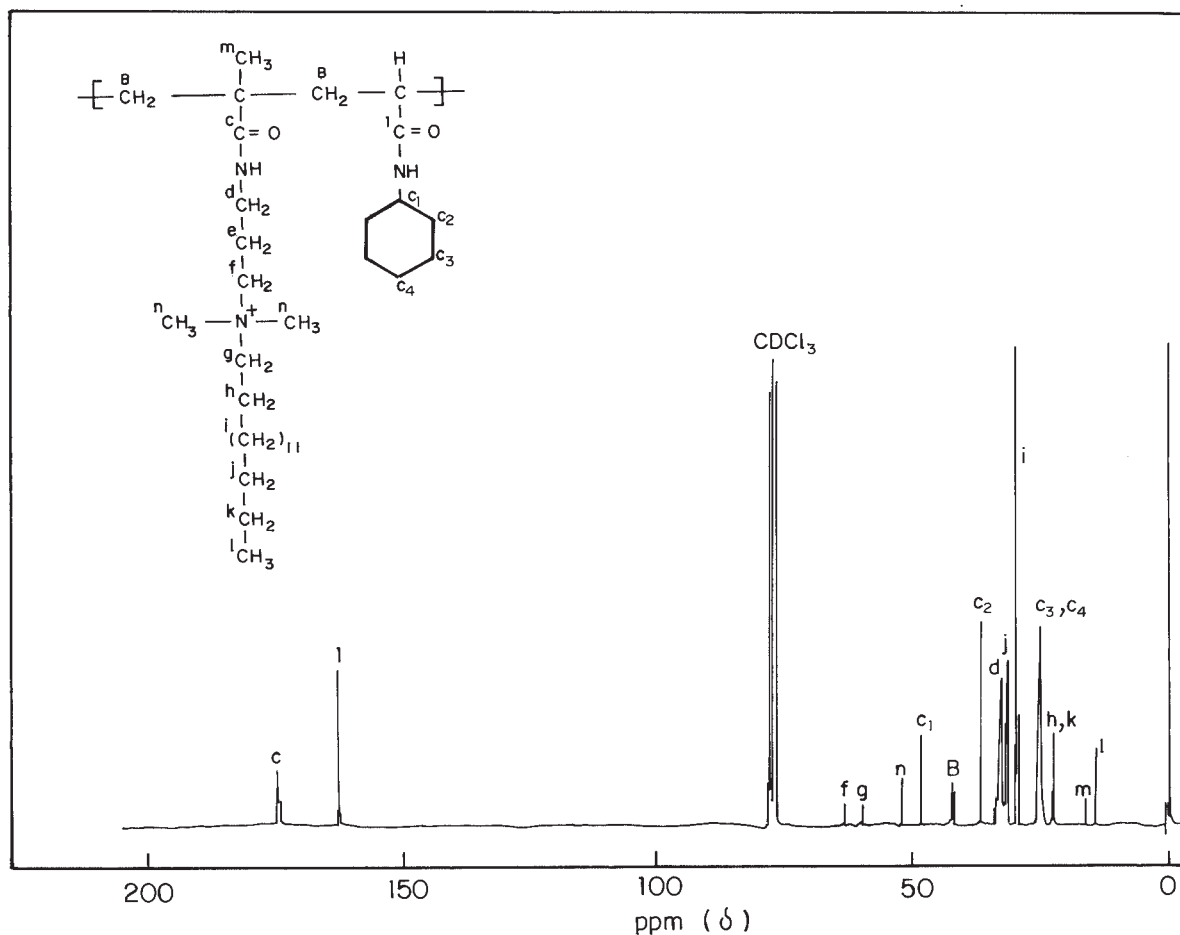
Figure 2 ^{13}C-NMR spectrum of MPDMAC$_{16}$–CA ionomer.

peak (δ 44.10 ppm) assigned to the methyl groups adjacent to nitrogen of MPDMA to downfield (δ 51.61 ppm). The same deshielding effect is also found for MPDMAC$_{18}$.

In the FTIR spectrum of MPDMAC$_{16}$, the strong peaks at 2920 and 2850 cm^{-1} correspond to the C—H stretching of methylenes in the long alkyl group: NH, 3360 cm^{-1}; C=O, 1660 cm^{-1}; C=C, 1612 cm^{-1}; methylene rock, 721 cm^{-1}.

The hydrophobic ionomers were prepared by free-radical copolymerization of hydrophobic cationic monomers MPDMAC$_{16}$ and MPDMAC$_{18}$ with N-substituted acrylamides in DMF using AIBN as initiator as shown in the schematic representation of the ionomer preparation.

The copolymerization was conducted with two different feed compositions: 4 and 10 mol % of cationic monomer in DMF solvent.

The ^{13}C-NMR spectrum of MPDMAC$_{16}$–CA ionomer is shown in Figure 2. The ^{13}C-NMR spectrum of the ionomer shows the disappearance of vinylic carbon peaks at δ 121.25 and 139.15 ppm of MPDMAC$_{16}$. The strong peak at δ 29.26–29.75 ppm is attributed to the long

alkyl chain of MPDMAC$_{16}$ unit and the peaks at δ 25.56, 36.55, and 48.57 ppm are assigned to cyclohexyl carbons C$_3$, C$_4$, and C$_2$ and C$_1$, respectively. The peak values confirm the occurrence of copolymerization.

Determination of mol percentage of MPDMAC$_{16}$

The mol % values of MPDMAC$_{16}$ in the copolymer were calculated from elemental analysis data using the C/N ratio.[11] Copolymers of MPDMAC$_{16}$ with N-tert-amylacrylamide (AA) have the following weight percentages of carbon and nitrogen represented by

%C = 96.08 [AA] + 300.25 [MPDMAC$_{16}$]

%N = 14.01 [AA] + 28.02 [MPDMAC$_{16}$]

The mol % of MPDMAC$_{16}$ in the copolymer is obtained from the following equation:

$$\text{mol \% of MPDMAC}_{16} = \frac{7(\%C) - 48(\%N)}{102(\%N) - 7(\%C)} \times 100$$

Similarly for other ionomers the corresponding equations were derived and the mol % calculated. The

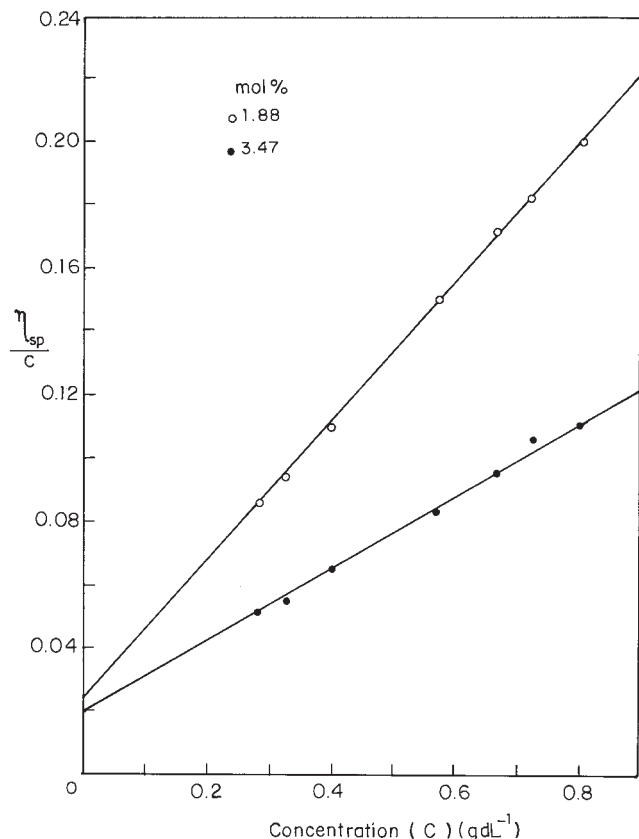**Figure 3** Reduced viscosity plots of MPDMAC$_{16}$–AA iono-mer.

calculated mol % of MPDMAC$_{16}$ in the copolymers indicates the formation of ionomers.

Viscosity study

The viscosity measurements for the MPDMAC$_{16}$–AA ionomer with 1.88 and 3.47 mol % MPDMAC$_{16}$ were done in methanol using a Ubbelohde viscometer (Schott Medica GmbH, Wertheim/Main, Germany). The plots of $\eta_{sp/c}$ versus concentration C are given in Figure 3. The reduced viscosity increased with in-creasing concentration. The decrease of reduced vis-cosity is greater (at low polymer concentrations) for 1.88 mol % MPDMAC$_{16}$ containing ionomer com-pared to 3.47 mol %. This behavior can be explained by the intramolecular associations at low polymer concentrations. Therefore "polyelectrolyte behavior " was not observed for these ionomers because of ion-pair interactions. Such a variation in reduced viscosity with the concentration may be related to the low mo-lecular weight of the ionomer.

Viscosity behavior at varying shear rates was stud-ied using a Brookfield viscometer (Brookfield Instru-ments, Middleboro, MA) for MPDMAC$_{16}$–BA iono-mer in DMF. The plot of viscosity (cps) versus shear

rate (rpm) for the ionomer is shown in Figure 4. Shear rate dependency of viscosity for the homopolymer poly–BA was also studied. The change in the viscosity dependency on shear rate was found to be less in the ionomer than that in the homopolymer. The viscoplas-tic nature of the ionomer is less pronounced than that of the homopolymer: the sizable content of hydropho-bic groups in the ionomer, which produced an abun-dance of intramolecular interactions thereby reducing the entanglements, may be the cause for it.[12] The MPDMAC$_{18}$–BA ionomer (Fig. 4) showed a similar behavior.

GPC analysis

The molecular weight distributions of hydrophobic ionomers were relatively low ($M_w = 0.9$–3.0×10^4). A typical molecular weight distribution curve of the MP-DMAC$_{18}$–BA ionomer system is shown in Figure 5. The polydispersity index of these ionomers, MPD-MAC$_{18}$–N-substituted acrylamides, range from 1.9 to 2.2 (Table II). The value suggests a strong tendency for termination mainly by disproportionation.[13] The low molecular weights of hydrophobic ionomers may be attributed to the solvent effect exerted by DMF. Alter-natively, the steric hindrance caused by the long alkyl
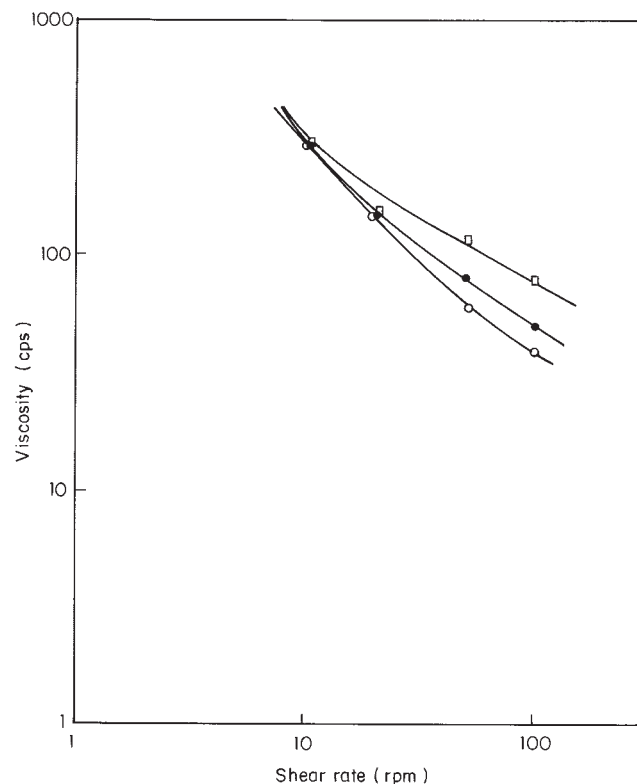

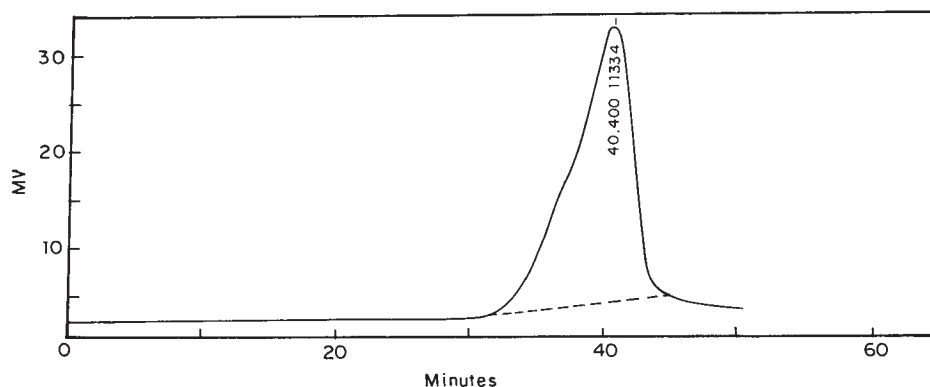**Figure 4** Plots of viscosity versus shear rate of MPD-MAC$_{16}$–BA ionomer (□), MPDMAC$_{18}$–BA ionomer (●), and poly–BA (○).

Figure 5 Molecular weight distribution curve of MPDMAC$_{18}$–BA ionomer.

TABLE II
GPC Analysis of Hydrophobic Ionomers

Ionomer	Mol % of MPDMAC$_{18}$ in feed	Mol % of MPDMAC$_{18}$ in copolymer	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
MPDMAC$_{18}$–BA	10	—	3.01	1.37	2.19
MPDMAC$_{18}$–AA	10	3.07	1.64	0.85	1.91
MPDMAC$_{18}$–CA	10	—	1.51	0.80	1.88

moiety may reduce the degree of polymerization, thereby lowering the molecular weight of the polymer.

CONCLUSIONS

Hydrophobic ionomers were prepared by copolymerization of MPDMAC$_{16}$ or MPDMAC$_{18}$ with N-substituted acrylamides at 60°C. Characterization of monomers and ionomers was performed with ^{1}H- and ^{13}C-NMR spectroscopy and the mole percentage of cationic monomer in the copolymer was calculated from elemental analysis using C/N ratio. The reduced viscosity of hydrophobic ionomers showed nonpolyelectrolyte behavior. The decrease of viscosity with decreasing concentration is explained by the ion-pair interactions. Shear rate dependency of viscosity of ionomers showed viscoplastic behavior. GPC analysis showed low molecular weight for hydrophobic ionomers. The lowering of molecular weight in hydrophobic ionomers was attributed to the solvent effect exerted by DMF and the steric hindrance caused by the long alkyl moiety. Polydispersity index values of ionomers suggest a tendency for termination mainly by disproportionation.

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