Polymerization of Ion-Pair Comonomers of Related Structures

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ABSTRACT

Two ion-pair comonomers of 2-methacryloyloxyethyltrimethyl-ammonium 2-methacryloyloxyethanesulfonate (METMA·MES) and 3-acrylamido-3-methylbutyltrimethylammonium 2-acrylamido-2-methylpropanesulfonate have been synthesized. The spontaneous and radical homocopolymerizations of these monomer pairs, wherein no nonpolymerizable counterions are present, have also been studied. Moreover, the intrinsic viscosity of the homocopolymer derived from METMA·MES was found to increase with increasing KCl concentration in aqueous solutions.

INTRODUCTION

During the past few years we have begun an investigation of the synthesis and polymerization behavior of a new class of ionic monomer system. This class of polymerizable compound is termed an ion-pair comonomer and is composed of a vinylic cation and a vinylic anion wherein no nonpolymerizable ions, such as inorganic cations and anions, are present [1-7].

Our initial investigation in this field began during our studies on the spontaneous polymerization of vinylpyridinium salts where the anionic moiety was a free radically polymerizable sulfonate. Of particular interest was the preparation of the ion-pair comonomer of 4-vinylpyridinium p-styrenesulfonate (I) and its spontaneous polymerization to an alternating ampholytic copolymer (II) [8].
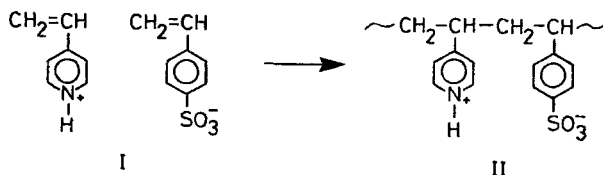
Because of the inherent difficulty in handling 4-vinylpyridinium salts due to their ease of spontaneous polymerization, it was decided to investigate the synthesis of ion-pair comonomers in which both components were relatively stable toward such behavior. In particular, while the 4-vinylpyridinium p-styrenesulfonate case contained monomers of opposite polarity (i.e., acceptor and donor, respectively), it was decided to utilize two monomers of similar polarities to prevent charge transfer homocopolymerization. The monomers chosen were a commercially available cation and a commercially available anion, and the resulting compound produced was 3-methacrylamidopropyl-trimethylammonium 2-acrylamido-2-methylpropanesulfonate (III). This monomer pair was relatively stable and could be synthesized by several pathways, and was easily polymerized by free radical initiation to yield IV.

In general, both ampholytic polymers II and IV were more soluble in various salt solutions than they were in deionized water in much the same fashion as has been shown previously for polyampholytic systems [3, 9, 10].

In a continuation of our study regarding ion-pair comonomers of analogous polarities and radical reactivities, it was decided to prepare new systems that additionally had structures of greater simi-
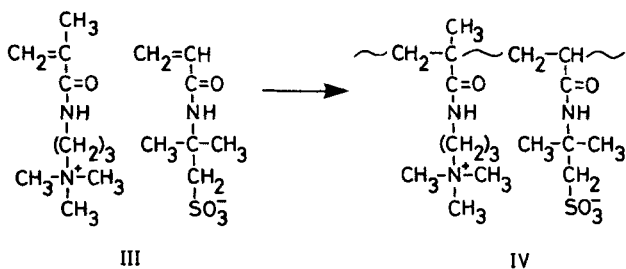
larity than those previously reported. Of particular interest were the ester ion-pair comonomer of 2-methacryloyloxyethyltrimethylammonium 2-methacryloyloxyethanesulfonate (METMA·MES), V, and its resulting homocopolymer VI, as well as the amide ion-pair comonomer of 3-acrylamido-3-methylbutyltrimethylammonium 2-acrylamido-2-methylpropanesulfonate (AMBTMA·AMPS), VII, and its resulting homocopolymer VIII.

```
       CH3          CH3                      CH3        CH3
        |            |                        |          |
 CH2=C       CH2=C                    ~CH2-C ~CH2-C~
        |            |                        |          |
       C=O          C=O        →             C=O        C=O
        |            |                        |          |
        O            O                        O          O
        |            |                        |          |
       CH2          CH2                      CH2        CH2
        |            |                        |          |
       CH2          CH2                      CH2        CH2
        |            |                        |          |
 CH3-N+-CH3   SO3-              CH3-N+-CH3   SO3-
        |                                     |
       CH3                                   CH3

            V                                     VI
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 CH2=CH       CH2=CH                  ~CH2-CH~CH2-CH~
        |            |                        |          |
       C=O          C=O        →             C=O        C=O
        |            |                        |          |
       NH           NH                       NH         NH
        |            |                        |          |
 CH3-C-CH3   CH3-C-CH3          CH3-C-CH3  CH3-C-CH3
        |            |                        |          |
       CH2          CH2                      CH2        CH2
        |            |                        |          |
       CH2          SO3-                     CH2        SO3-
        |                                     |
 CH3-N+-CH3                        CH3-N+-CH3
        |                                     |
       CH3                                   CH3

           VII                                   VIII
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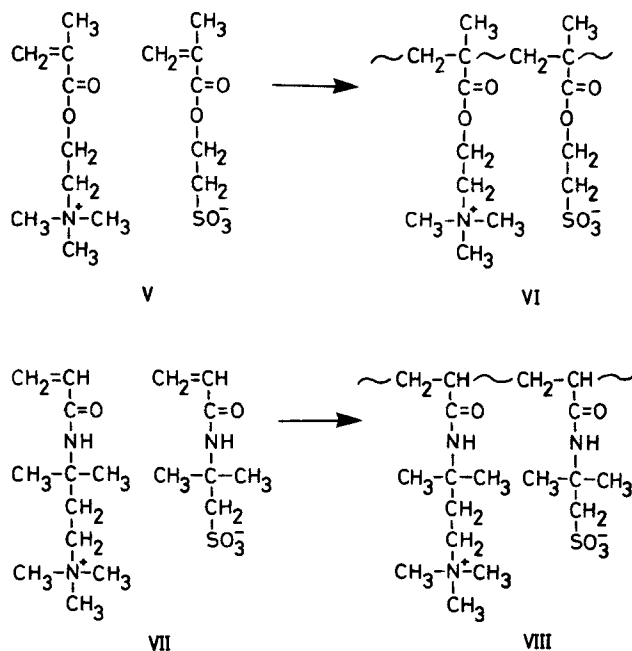
EXPERIMENTAL

Materials

2-Sulfoethyl methacrylate (95% purity) (2-methacryloyloxyethanesulfonic acid) from Polysciences, Inc. was diluted with distilled water and treated three times with activated carbon to remove impurities and polymeric residues. 2-Methacryloyloxyethyltrimethylammonium chloride, supplied by Alcolac Inc. as a 75% active material in water, was treated twice with activated carbon prior to use.

Silver hydroxide was prepared from the reaction of silver nitrate with sodium hydroxide or potassium hydroxide in water at ambient

temperature under light-shielded conditions. 2-Acrylamido-2-methyl-propanesulfonic acid and 3-acrylamido-3-methylbutyltrimethylammo-nium chloride were both supplied from Lubrizol Corp. and recrystal-lized before use.

4,4'-Azobis(4-cyanovaleric acid) (ACVA) and 2,2'-azobisisobutyro-nitrile (AIBN) were recrystallized twice from water and methanol, re-spectively.

Solvents and other reagents were used after purification by ordinary methods.

Synthesis of 2-Methacryloyloxyethyltrimethyl-ammonium 2-Methacryloyloxyethanesulfonate, V

To a light-shielded suspension of 16.0 g (0.128 mol) of silver hydrox-ide in 50 mL water was added dropwise with stirring 80 mL aqueous solution containing 20.0 g (0.103 mol) of 2-methacryloyloxyethanesul-fonic acid at 20-25°C. The reaction was then continued for another 3-4 h at room temperature. After filtration to remove the remaining sil-ver hydroxide, the filtrate was treated twice with charcoal, giving a yellowish solution of silver 2-methacryloyloxyethanesulfonate. To this solution was added drop by drop 110 mL of a 20% aqueous solution of 2-methacryloyloxyethyltrimethylammonium chloride while stirring at room temperature. The white precipitate of silver chloride formed almost immediately and the mixture was stirred for about 2 h after addition. Thereafter, the precipitate was filtered and the yellowish filtrate was treated with activated carbon followed by lyophilization. Extraction of the solid residue with anhydrous benzene gave very pale yellow crystals of METMA·MES (yield: 32-35% based on starting 2-methacryloyloxyethanesulfonic acid). This ion-pair comonomer was then purified by recrystallization twice from anhydrous benzene to give colorless crystals, with mp 94-95°C.

Analysis: Calculated for $C_{15}H_{27}O_7NS$: C, 49.30%; 7.45%; N, 3.83%; S, 8.77%. Found: C, 49.37%; H, 7.48%; N, 3.82%; S, 8.71%. ^{13}C-NMR (D_2O): δ 18.14 ($CH_2=C(CH_3)-COO-$), δ 50.48 ($-COO-CH_2-CH_2-S-$), δ 54.73 ($-COO-CH_2-CH_2-\overset{+}{N}(CH_3)_3$), δ 59.40 ($COO-CH_2-CH_2-N-$), δ 61.10 ($-COO-CH_2-CH_2-S-$), δ 65.59 ($COO-CH_2-CH_2-N-$), δ 127.87 ($CH_2=C(CH_3)-COO-CH_2-CH_2-S-$), δ 128.50 ($CH_2=C(CH_3)-COO-CH_2-CH_2-N-$), δ 135.96 ($CH_2=C(CH_3)-COO-CH_2-CH_2-N-$), δ 136.57 ($CH_2=C(CH_3)-COO-CH_2-CH_2-S-$), δ 169.02 ($-COO-CH_2-CH_2-N-$), and δ 169.94 ($-COO-CH_2-CH_2-S-$).

Synthesis of 3-Acrylamido-3-methylbutyltrimethyl-ammonium 2-Acrylamido-2-methylpropanesulfonate, VII

A suspension containing 2.07 g (0.010 mol) or 2-acrylamido-2-methylpropanesulfonic acid and 2.35 g (0.010 mol) of 3-acrylamido-

3-methylbutyltrimethylammonium chloride in dry methylene chloride, to which was added 1.0 mL (0.83 g, 0.014 mol) of propylene oxide, was shaken overnight. The resulting solution was filtered of traces of undissolved material and evaporated to a colorless oil that solidified on standing. By means of triturations with acetone and hexane, respectively, there was obtained pure material in two crops, 2.45 g, mp 118-120°C, and 1.49 g, mp 116-118.5°C (total yield: 3.94g, 97%). An analytical sample was obtained by recrystallization twice from absolute ethanol, mp 120.5-121°C.

Analysis: Calculated for $C_{18}H_{35}O_5N_3S$: C, 53.31%; H, 8.70%; N, 10.36%; S, 7.91%. Found: C, 53.20%; H, 8.76%; N, 10.31%; S, 7.80%. ^{1}H-NMR (D_2O_2): δ 1.32 (s, 6H, $-NH-C(C\underline{H}_3)_2-CH_2-CH_2-N-$), δ 1.46 (s, 6H, $-NH-C(C\underline{H}_3)_2-CH_2-S-$), δ 2.32-2.35 (m, 2H, $-C\underline{H}_2-CH_2-N-$), δ 3.04 (s, 9H, $-\overset{+}{N}(C\underline{H}_3)_3$), δ 3.31-3.37 (m, 2H, $-CH_2-C\underline{H}_2-N-$), δ 3.37 (s, 2H, $-C\underline{H}_2-S-$), δ 4.73 (s, 2H, $-N\underline{H}-$), δ 5.66-5.69 (m, 2H, vinyl C$\underline{H}$), and δ 6.11-6.20 (m, 4H, vinyl C$\underline{H}_2$).

Polymerization

In a polymerization ampule, a solution of the cationic-anionic monomer pair with or without initiator was prepared. The ampule was evacuated by the freeze-thaw technique and then placed in a thermostated bath at 60°C. After an appropriate polymerization time, the aqueous solutions were dialyzed exhaustively against distilled water followed by lyophilization. In the cases of organic media, the precipitated polymer was collected by filtration and dried. This polymer was then purified by redissolving it in distilled water, dialyzed against distilled water, followed by lyophilization. The conditions and results of the polymerization of both METMA·MES and AMBTMA·AMPS pairs are summarized in Table 1.

^{13}C-NMR of homocopoly(METMA·MES) (in 1.8 M LiCl-D_2O at 90°C): δ 16.92-22.45 ($-CH_2-C(\underline{C}H_3)-COO-$), δ 45.69 ($-\underline{C}H_2-\overset{|}{C}(CH_3)-COO-$), δ 49.99 ($-COO-CH_2-\underline{C}H_2-S-$), δ 53.05 ($-CH_2-\overset{|}{\underset{+}{C}}(CH_3)-COO-$), δ 54.79 ($COO-CH_2-CH_2-\overset{+}{N}(\underline{C}H_3)_3$), δ 59.64 ($COO-\underline{C}H_2-CH_2-N-$), δ 61.46 ($-COO-CH_2-\underline{C}H_2-S-$), δ 64.9$\overline{8}$ ($-COO-CH_2-\underline{C}H_2-N-)^-$, and δ 177.11-180.90 ($-COO-\overline{\underline{C}}H_2-CH_2-$).

^{13}C-NMR of homocopoly(AMBTMA·AMPS) (in D_2O at 90°C): δ 27.30 ($-CO-NH-\overset{|}{C}(\underline{C}H_3)_2-CH_2-$), δ 33.19 ($-C(CH_3)_2-\underline{C}H_2-CH_2-N-$), δ 34.25-40.13 ($-\underline{C}H_2-\overset{|}{C}H-CO-NH-$), δ 41.40-46.13 ($-CH_2-\overset{|}{\underline{C}}H-CO-NH-$), δ 53.33 ($-CO-NH-\overset{|}{C}(CH_3)_2-\underline{C}H_2-$), δ 54.12 ($-C(CH_3)_2-CH_2-CH_2-\overset{+}{N}$ ($\underline{C}H_3)_3$), δ 59.70 ($-CO-NH-\overset{|}{C}(CH_3)_2-\underline{C}H_2-S-$), δ 64.01 ($-C(CH_3)_2-\underline{C}H_2-$ $\underline{C}H_2-N-$), and δ 175.67-178.13 ($-\underline{C}H-\underline{C}O-NH-C(CH_3)_2-$).

TABLE 1. Spontaneous and Radical Homocopolymerization of Ion-Pair Comonomers

Monomer pair		Solvent		Initiator		Temperature, °C	Time, h	Conversion, %	Elemental analysis, %			
Type	g	Type	mL	Type	mol/L $\times 10^3$				C	H	N	S
METMA·MES	0.90	H_2O	9.0	-	-	60	15.0	70.0	48.16	7.52	3.70	8.52
	1.10	C_6H_6	11.0	-	-	80	64.0	25.0	48.09	7.54	3.68	8.35
	1.10	DMF	11.0	-	-	60	145.0	17.4	48.13	7.64	3.63	8.35
	1.10	CH_3OH	11.0	-	-	60	14 d	0	-	-	-	-
	2.19	H_2O	22.0	ACVA	1.14	60	8.5	77.6	48.08	7.57	3.69	8.49
	2.19	C_6H_6	65.0	AIBN	2.23	80	6.0	86.7	48.03	7.57	3.73	8.54
	2.19	DMF	22.0	AIBN	2.20	60	18.0	91.3	48.07	7.61	3.63	8.30
						Calc for $C_{15}H_{27}O_7N$ S:			49.30	7.45	3.83	8.77
AMBTMA·AMPS	0.60	H_2O	6.0	ACVA		60	20.0	62.6	51.99	8.76	10.04	7.66
						Calc for $C_{18}H_{35}O_5N_3S$:			53.31	8.70	10.36	7.91

Measurements

^{13}C-NMR spectra were recorded on a JEOL PFT-100 MHz spectrometer at room temperature and 90°C for monomers and polymers, respectively, using deuterium oxide as the solvent and p-dioxane as the internal reference.

The thermal properties of both comonomers and their homocopolymers were studied with a Perkin-Elmer DSC-2C Model differential scanning calorimeter in a nitrogen atmosphere. Linear programmed heating rates of 10, 20, 40, and 80°/min were used, and the temperature was calibrated against indium (mp 429 K) and crystals of stearic acid (mp 345 K).

The viscosity measurements were made using an Ubbelohde viscometer maintained in a bath at 25°C.

RESULTS AND DISCUSSION

Monomer Preparations

The previous preparations of ion-pair comonomers utilized three different pathways to effect their syntheses. In the first instance, which is illustrated by the preparation of 4-vinylpyridinium p-styrenesulfonate, I, a protonation of an amine is achieved by a strong acid in an organic solvent giving the insoluble cationic-anionic monomer pair [1]. For the preparation of quaternary derivatives, two different methods have been employed, namely ion-exchange chromatography and acid-base titration. Such syntheses have been utilized for 3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulfonate, III, [4] wherein, for ion-exchange chromatography, one of the monomers is placed on the resin, followed by elution with its counterpart. This process proved to be very tedious and, consequently, is no longer used. However, a relatively facile method is to convert the quaternary ammonium compound to its hydroxide form, followed by neutralization with a strong acid. From the latter two processes, the aqueous solutions are lyophilized and the ion-pair comonomers can then be recrystallized from an appropriate organic solvent. For the current investigation for the preparation of METMA· MES and AMBTMA·AMPS monomer pairs, two additional, facile techniques for their syntheses are presented.

The preparation of the METMA·MES ion-pair comonomer was performed in two steps, that is, the conversion of 2-methacryloyloxyethanesulfonic acid to its silver salt in the first step and reaction of the resulting salt with 2-methacryloyloxyethyltrimethylammonium chloride in the second step. The first reaction, however, can also be considered as a purification stage since 2-methacryloyloxyethanesulfonic acid can be purified through an aqueous solution of its salts

[11]. After completion of both reactions, the monomer pair was iso-
lated by lyophilization of the aqueous solution followed by extraction
with hot, anhydrous benzene. These procedures left a dark brown
residue, which appeared to be composed of a large amount of polymer,
especially a polyion from 2-methacryloyloxyethanesulfonic acid and
its silver salt (both monomers have a high tendency to polymerize
spontaneously). This residue was dissolved in water, giving a highly
viscous, transparent solution, whose viscosity decreased with increas-
ing amounts of added salt, such as NaCl, suggesting its polyelectro-
lyte character.

The METMA·MES ion-pair comonomer obtained is a colorless,
fine crystal having a melting point of 94-95°C, and shows elemental
analysis results that agree very well with the theoretical values. More-
over, the formation of this ion-pair comonomer was also character-
ized by IR and ^{13}C-NMR spectroscopies. For the NMR measurements,
the assignment of all resonances were performed by comparing their
chemical shifts with those of peaks determined for the individual cat-
ionic and anionic monomers. It was found that the ion-pair comonomer
spectrum revealed good resolution of all carbon atoms except the un-
derstandable overlapping of resonances due to the two α-methyl car-
bons at 18.14 ppm.

In the preparation of the AMBTMA·AMPS ion-pair comonomer,
propylene oxide was added as an acid scavenger in the reaction of the
quaternary monomeric chloride with the monomeric free sulfonic acid.
This reaction was conducted utilizing propylene oxide with 3-acryl-
amido-3-methylbutyltrimethylammonium chloride dissolved in methyl-
ene chloride followed by the addition of one equivalent of suspended
2-acrylamido-2-methylpropanesulfonic acid. The reaction was con-
veniently followed by the disappearance of undissolved material, and
after workup gave purified AMBTMA·AMPS as a crystalline solid in
nearly quantitative yield. This synthetic pathway to the ion-pair co-
monomer exploits the well-known capacity of epoxides to react essen-
tially completely and irreversibly with hydrogen halides (to form halo-
propanol derivatives) [12, 13], thereby driving the otherwise ionic
equilibrium to the desired ion-pair comonomer. Of key importance to
the observed selectivity is the low nucleophilicity of the sulfonate ion
which does not compete significantly in the ring opening. This method
thus avoids the use of an excess of either monomeric component or
the reliance on special solubility characteristics in reactants or
products.

Both ion-pair comonomers prepared were found to be hygroscopic
and water-soluble. Moreover, the METMA·MES pair dissolved easily
in polar solvents such as methanol, ethanol, propanol, benzyl alcohol,
methylene chloride, chloroform, acetonitrile, formic acid, dimethyl-
formamide, and dimethylsulfoxide. It also dissolved slowly in hot sol-
vents of acetone, 2-butanone, ethyl acetate, tetrahydrofuran, p-dioxane,
benzene, toluene, and xylene, but was insoluble in tetrachloromethane,
diethyl ether, petroleum ether, n-hexane, and cyclohexane. The
AMBTMA·AMPS pair, on the other hand, also showed similar solubili-

ties in these solvents except that it dissolved in chloroform only at high temperature and was insoluble in ethyl acetate, benzene, toluene, and xylene.

The thermal behavior of the monomer pairs obtained was also studied by differential scanning calorimetry in a nitrogen atmsophere at a heating rate of $20°C/min$. For METMA·MES and AMBTMA·AMPS monomer pairs, endothermic peaks corresponding to melting points were observed at 93-95°C and 118-120°C, respectively, which are comparable with the temperatures measured on a capillary melting point apparatus. Moreover, it is of interest to note that a very strong exothermic peak was detected immediately after the melting peak on the DSC thermograms, thereby indicating that these monomer pairs can polymerize easily in the molten state.

Polymer Preparations

The results of spontaneous and radical homocopolymerization of both ion-pair comonomers are collected in Table 1. Inspection of the data in Table 1 reveals that METMA·MES was moderately prone to polymerize spontaneously in water and that its radical polymerization proceeded with a much higher rate as compared with AMBTMA·AMPS under similar conditions. For the METMA·MES comonomer, it was also found that the polymerization reactivity decreased from water to benzene, to dimethylformamide, and to methanol by either spontaneous or radical-initiated polymerization. With respect to the elemental analysis data of these homocopolymers, it is observed that the carbon contents are about 1.3% lower than the theoretical values. The hydrogen contents are slightly higher, whereas the contents of either nitrogen or sulfur are slightly decreased. These deviations can be considered to be caused by the high sensitivity of polymers to moisture. Assuming that these homocopolymers absorbed some water, the differences in the elemental contents were calculated to correspond to 2.4-2.6 wt% of water of hydration in the polymers. Indeed, the hygroscopic character of polymers was also confirmed by a strong absorption due to water at 3400-3600 cm^{-1} in their IR spectra.

The ^{13}C-NMR measurements of homocopoly(METMA·MES) (VI) and homocopoly(AMBTMA·AMPS) (VIII) were performed at 90°C in 1.8 M LiCl-D_2O solution and D_2O, respectively. In both cases, no resonance peaks attributed to vinyl or vinylidene groups could be detected, implying the absence of any unpolymerized monomeric moieties. The most outstanding distinction between the polymers from METMA· MES and AMBTMA·AMPS is found for the resonance peaks owing to the carbonyl groups, and this is caused by the different sensitivity of the carbonyl groups on an ester or on an amide. Furthermore, the ester carbonyl resonance also shows a slight resolution corresponding to the dyad sequences of the two monomer units. On the other hand, the amide carbonyl resonance, which is known to show no splitting according to microstructure [14, 15], provides two separate peaks which may

be considered to result from individual cationic and anionic compo-
nents. In addition to the similar polymerization behavior of the
cationic and anionic moieties, these spectra seem to suggest that the
polymers prepared are random homocopolymers.

Differential scanning calorimetry was also carried out in order to
study the thermal behavior of both homocopolymers derived from
METMA·MES and AMBTMA·AMPS comonomer pairs. In general, the
samples showed a strong, broad, endothermic peak in the range of
100-200°C during the first heating. However, because the occurrence
of this peak is not reproduced on the second or further heating, it
does not seem to correspond to a melting or any transitions of the
polymers. Contrarily, this peak seems to indicate that water, which
was absorbed by the polymer and decreased the carbon contents de-
termined by elemental analysis (Table 1), is eliminated at this tem-
perature range; as a result, it disappears during further heating.

Beside this endothermic peak, no pronounced shift of the DSC base-
line was discernible over a temperature range of -30 to 300°C. The
T_g's, if present, are expected to be very high for the present homo-
copolymers.

Solution Properties

The polymer from METMA·MES pair is soluble in formic acid and
insoluble in almost all organic solvents. In water, it can be dissolved
at low concentration ($< 5\%$) giving a turbid solution, but at higher con-
centration it precipitates easily. However, this solubility is greatly
enhanced by addition of inert salts such as LiCl, NaCl, KCl, etc., in
much the same fashion as has been shown for other polyampholytes
[3, 9, 10]. In contrast with this, the AMBTMA·AMPS polymer in
water produces a transparent solution even without added salts. From
these observations, it is likely that the METMA·MES polymer consists
either of a higher degree of ionic interaction than homocopoly(AMBTMA·
AMPS), or that it is substantially higher in molecular weight, and/or
that the ester polymer is less hydrogen bonded than the amide polymer
to water.

It has been of interest to investigate the dilute solution properties
of a polyampholyte, wherein no small molecules of counterions are
present [3, 0]. For this purpose, the viscosity study on homocopoly-
(METMA·MES) was carried out in 0.5, 1.0, and 2.0 M KCl aqueous solu-
tions at 25°C. The plots of concentration, c, versus reduced viscosity,
η_{sp}/c, are given in Fig. 1, from which the intrinsic viscosity, $[\eta]$, the
Huggins' constant, k', and the correlation coefficient are computed and
are shown in Table 2.

From Fig. 1 it is apparent that the reduced viscosity increases with
increasing concentration of added electrolyte, which is an opposite
tendency for usual polyelectrolytes. This abnormal behavior for poly-
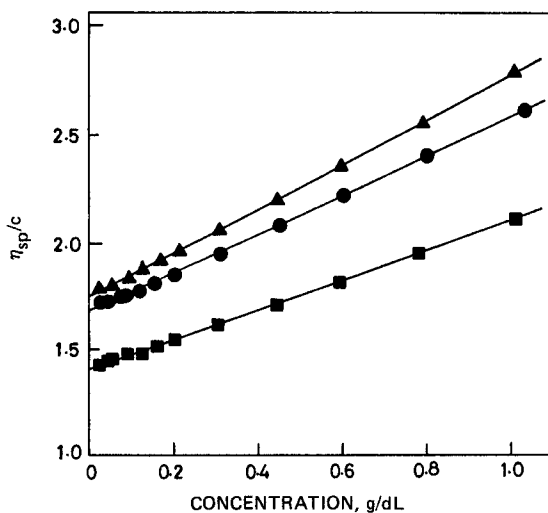ampholytes was also observed for poly(vinylimidazolium sulfopropyl-

FIG. 1. Reduced viscosity of homocopoly(METMA·MES) as a function of polymer concentrations in aqueous KCl solutions: (■) 0.50 M, (●) 1.00 M, (▲) 2.00 M KCl.

TABLE 2. Effect of Salt Concentration on the Viscosity Behavior of Homocopoly(METMA·MES) at 25°C.

[KCl] (M)	Correlation coefficient	Slope	Intercept $[\eta]$ (dL/g)	k'
0.50	1.0	0.71	1.40	0.36
1.00	1.0	0.92	1.66	0.33
2.00	1.0	1.02	1.75	0.33

betaine) [9], poly(2-vinylpyridinium sulfopropylbetaine) [10], and poly(2-methacryloyloxyethyldimethylammonium sulfopropylbetaine) [10], but not for the homocopolymer derived from the 3-methacryl-amidopropyltrimethylammonium 2-acrylamido-2-methylpropane-sulfonate monomer pair, wherein no distinct salt effect on viscosity was detected [3]. For the present homocopolyampholyte, it is ex-pected that the added electrolyte would disrupt the intra- and inter-molecular interactions of the ammonium and sulfonate groups, which caused the low solubility of the polymer, thus allowing the polymer to behave more freely. Therefore, the increase in the reduced vis-

cosity could be related to the increased interactions between polymer and solvent, as reflected by a slight decrease in the Huggins' constant, and/or by the electrostatic repulsive forces between the unshielded ions. Further studies on this polymer are currently in progress in order to clarify the effects of salt on viscosity and molecular weight.

ACKNOWLEDGMENTS

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