

# Preparation and Characterization of Polyelectrolyte Copolymers Containing Methyl Methacrylate and 2-Hydroxyethyl Methacrylate. I. Polymers Based on Methacrylic Acid

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## SYNOPSIS

Acidic polyelectrolyte copolymers containing 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and methacrylic acid (MAA) were prepared by free radical polymerization to high conversion in solution. Copolymer yields were obtained by gravimetry (all in the 30–50% range), relative molecular weights estimated by intrinsic viscosity measurements (all in the 50–70 cc/g range), tacticity by  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy (all polymers predominantly syndiotactic with some atactic content), and composition by acid/base titrations in conjunction with  $^1\text{H}$ -NMR spectroscopy (all close to the monomer charge ratios). Acid strengths or apparent  $\text{pK}_a$ 's were examined as a function of extent of ionization. Measurements performed in water indicated that the compact/extended coil transformation in predominantly syndiotactic polymethacrylic acid occurs also in copolymers of similar tacticity containing moderate to high concentrations of MAA. The apparent  $\text{pK}_a$  of such polymers containing only small amounts of MAA did not vary with extent of ionization, indicating a low degree of interaction between the acid groups. In copolymer pairs containing similar amounts of MAA but differing HEMA and MMA contents, the polymer containing more HEMA appeared the stronger acid, presumably due to a better solvation of that polymer which would increase the net spatial charge-charge separation and decrease cooperative effects that lead to suppressed ionization.

## INTRODUCTION

Polyelectrolyte polymers, both natural and synthetic, have been the object of intense scrutiny by the scientific community for many years. For example, naturally occurring polyelectrolytes form the building blocks of life itself and have been the major impetus for the development of such important disciplines as molecular biology and biochemistry. The simpler synthetic polyelectrolytes, first championed by Fuoss and other pioneers,<sup>1,2</sup> although less important overall, still contribute both industrially (e.g., as the basis of ion-exchange resins) and academically as simpler model systems used to gain an

understanding of the more sophisticated natural polymers.

The solution behavior of polymethacrylic acid, especially as a function of degree of ionization, has interested many polymer chemists, who, presumably, see in the secondary hydrophobic network driven compact-extended coil transformation at about 25% ionization,<sup>3,4</sup> a situation thought to have some parallel in natural systems.

We have recently become interested in the preparation and polyelectrolyte complexation (or perhaps more correctly, complex coacervation) of polyelectrolyte copolymers containing methacrylic acid (MAA) and comonomers such as 2-hydroxyethyl methacrylate (HEMA) and/or methyl methacrylate (MMA). As a preliminary to this work, we thought it advisable to investigate (and report here) relationships between polymerization conditions and

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polymer microstructure and molecular weight; to study briefly the influence of acid group content on the "acid strength" of these predominantly syndiotactic polymers as a function of degree of ionization, conveniently measured as apparent pK<sub>a</sub>; and finally, to rationalize the effect of altering the hydrophobic/hydrophilic balance of uncharged 'mers on the "acid strength" of dissolved polymer containing similar amounts of ionizable methacrylic acid monomer.

## MATERIALS AND METHODS

### Reagents for Polymerization and Characterization

Azobisisobutyronitrile (AIBN, Polysciences Inc.), methyl methacrylate (MMA, Aldrich), and 2-hydroxyethyl methacrylate (HEMA, Kodak) were all purified as described in a previous communication.<sup>5</sup> Ethanol (HPLC grade, Fisher Scientific) was used as received. Methacrylic acid was double distilled under reduced pressure before use. All monomers were stored at -20°C and used within 24 h of the last distillation. AR grade dimethyl formamide (Kodak) and anhydrous lithium bromide (Aldrich) were used in the intrinsic viscosity experiments. Deuterated, methanol, water, acetone, and chloroform; other deuterated species such as sodium deuterioxide; and miscellaneous items such as tetramethyl silane, for use in NMR spectroscopic measurements, were all purchased from the Aldrich Chemical Company. Standard 1.0 *N* and 10.0 *N* sodium hydroxide and hydrochloric acid solutions, for use in acid-base titrations, were purchased from Fisher Scientific.

### Polymer Synthesis

Polymers were synthesized by solution polymerization in ethanol solvent under a flowing nitrogen atmosphere in a wide-mouthed reaction kettle equipped with pressure equalizing addition funnel, mechanical stirrer, reflux condenser outlet, and thermometer well. Solvent was brought to temperature and monomer was charged, and when the system had reestablished temperature equilibrium, the initiator, AIBN, was added in a small volume of solvent to commence reaction. At the appropriate time, the reactor was chilled to room temperature, polymer was precipitated by addition to a large excess of low-boiling-point petroleum ether, redissolved in a minimum volume of ethanol, and reprecipitated in an excess of distilled water previously made acid by the

addition of some hydrochloric acid. Recovered polymer was extensively vacuum dried before weighing and use. Polymer yields were obtained by simple gravimetry.

Small quantities of poly(2-hydroxyethyl methacrylate) (PHEMA), poly(methyl methacrylate) (PMMA), and polymethacrylic acid (PMAA) were prepared as reference materials for NMR spectroscopy and the titration experiments. These were prepared under conditions identical to those employed in the preparation of the copolymers, except those polymers were made in smaller quantity.

### Intrinsic Viscosity Measurements

Polymer intrinsic viscosities were measured in dimethyl formamide containing 0.2% (wt/vol) of lithium bromide to suppress polyelectrolyte effects.<sup>6</sup> Measurements were performed at 35 ± 0.05°C, taking the usual precautions,<sup>7</sup> in previously described dilution viscometers.<sup>8</sup>

### Nuclear Magnetic Resonance (NMR) Spectroscopy

Carbon 13 (<sup>13</sup>C) spectra of polymers were obtained in dimethyl sulfoxide (DMSO) solvent at 35°C. Proton (<sup>1</sup>H) spectra were obtained either in deuterated DMSO at 60°C or in deuterated (*d*<sub>4</sub>) methanol at 40°C. All measurements were performed using the Varian XL-300 spectrometer.

### Acid-Base Titrations

Polymer (1.00 g) was dissolved either in distilled water or in a mixed methanol/water (50/50 by volume) solvent over a period of days. The solution pH was kept above 8.0 by the careful addition of small droplets of 10 *N* NaOH to ionize acidity in the polymer and encourage dissolution. Upon complete dissolution, the solution was made up to 100 mL and transferred to a three-necked flask with stir bar. Nitrogen was introduced through the first neck, titrant through the second, and the calomel combination electrode through the third neck of the flask. After an equilibration period, the solution pH was raised to 12-13 units by the careful addition of small amounts of 10 *N* NaOH solution and the polymer back-titrated by the subsequent addition of small aliquots of 1.0 or 0.5 *N* HCl. Solution pH's were recorded as millivolt signals fed to a flat-bed recorder. All measurements were performed using an Orion SA 720 pH meter.

## RESULTS AND DISCUSSION

## Polymer Preparation and Characterization

Ten co- and terpolymers were prepared by solution polymerization of monomer charges to high conversion. In each case, a combined mixture of 200 g was polymerized in 2 l of ethanol for 4 h at  $70 \pm 0.05^\circ\text{C}$  using 0.1 mol % of azobisisobutyronitrile (AIBN) as free radical initiator. Monomer charges, as summarized in Table I, were adjusted to produce polymers containing a broad range of methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA), and methyl methacrylate (MMA) content. In Table I, feed mixtures are arranged so that the acid content of the polymer feed mixture increases from the top to the bottom of the table. When two entries contain the same acid level, that containing more HEMA is placed below that containing more MMA, and so on.

Polymer yields and intrinsic viscosities are reported in Table II. No marked trend could be distinguished in either set of data. Polymer yields appeared to increase a little with HEMA content in the feed mixture and ranged from approximately 30 to 50% conversion. Polymer intrinsic viscosities varied even less, ranging from just under 60 cc/g to just over 70 cc/g. Of course, polymer molecular weights may vary by a larger margin depending on the appropriate Mark-Houwink-Sakurada constants that must be applied to each system. However, as a first approximation, the data would imply a low spread of molecular weights.

Polymer tacticities have long been known to exert a major influence on solution dimensions. For this

Table I Monomer Charges

Polymer #	Monomer Charge (mol %)		
	MAA	HEMA	MMA
1	10	45	45
10	10	90	—
3	25	25	50
2	25	50	25
5	40	20	40
4	40	40	20
8	60	10	30
9	60	30	10
6	75	—	25
7	75	25	—

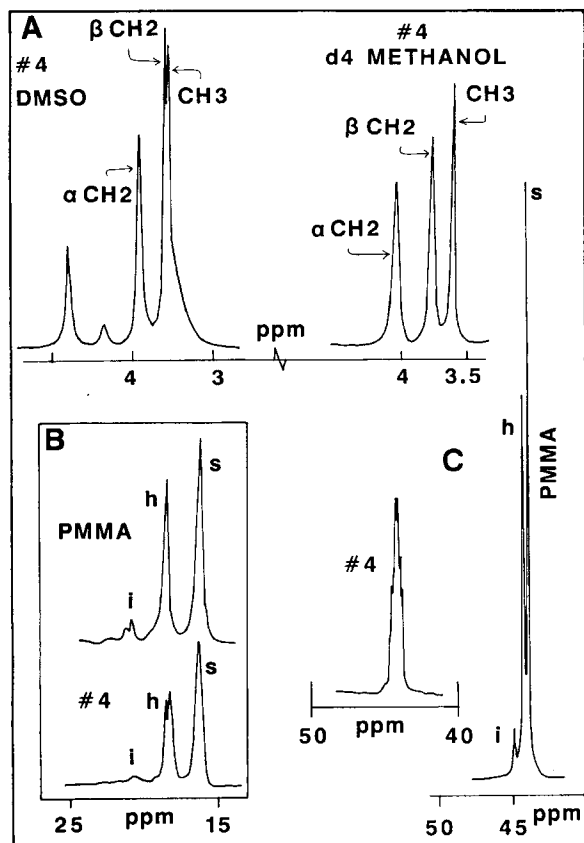
MAA: methacrylic acid, HEMA: 2-hydroxyethyl methacrylate, MMA: methyl methacrylate.

Table II Polymer Yields and Intrinsic Viscosities

Polymer #	Yield (%)	Intrinsic Viscosity (cc/g)
1	30.7	60.4
10	45.1	72.0
3	35.9	56.6
2	34.7	60.3
5	40.0	56.0
4	41.3	65.1
8	42.7	59.4
9	48.0	70.2
6	42.4	64.7
7	51.0	60.8

reason, we employed NMR spectroscopy to measure the tactic distributions of the co- and terpolymers prepared for this study in case such would be needed to explain results of the acid/base titrations. We were unable to utilize proton signals from the in-chain methyl groups at 0.9–1.4 ppm, the preferred method with methacrylate homopolymers,<sup>5</sup> because of signal broadening in the structurally more complex copolymers. Likewise, we were unable to utilize carbon 13 signals from the tertiary in chain carbon, at about 40–50 ppm, to estimate tacticity of the co- and terpolymers. Typical signals from a methacrylate homopolymer (PMMA) and a copolymer (#4) are shown in Figure 1(C). We were, however, able to utilize carbon 13 signals from in-chain methyl groups at 15–25 ppm to estimate polymer tacticities. Some typical spectra are reproduced in Figure 1(B). Signals from the three homopolymers studied (PMMA, PHEMA, and PMAA) were well enough resolved to rely on machine integration to determine the tactic distributions. Signals from the co- and terpolymers were less well resolved, and we had to resort to the cutting out and weighing of traces to estimate the isotactic content of such polymers.

Polymer tacticities, as determined by this method, are reproduced in Table III, from which it can be seen that all lie between expected limits for polymers prepared by free radical polymerization at  $70^\circ\text{C}$ ,<sup>5,9</sup> namely, 50–70% syndiotactic, 30–40% heterotactic, and 1–6% isotactic. The tacticities of all copolymers were similar to those exhibited by the three homopolymers prepared under the same conditions. This low spread of tacticity is essential for a proper comparison of the potentiometric behavior of these copolymers, as it is well known that the acid and (presumably) the base strength of thermoplastic polyelectrolyte polymers are profoundly affected by this variable. It is generally agreed that such differences



**Figure 1** Representative portions of NMR spectra. (A) Proton signals used to ratio the HEMA/MMA contents of terpolymers. (B) Carbon 13 signals generated by in-chain methyl carbons and used to determine polymer tacticity. (C) Carbon 13 signals from tertiary in chain carbons.

originate in the solution conformations of the isotactic [helical (compact)] and syndiotactic (extended) forms of the polymer. (Isotactic forms of methacrylate polymers are found to be weaker polyelectrolytes than are syndiotactic forms, presumably due to a more cooperative process of ionization in the more compact isotactic coil<sup>10</sup>.)

The determination of copolymer composition by NMR spectroscopy was made difficult by the absence of any unique and quantifiable signal associated with the methacrylic acid residue in the polymer. Of course, MAA content could always be obtained by difference, by comparing the intensity of, for example, proton signals from ethyls, alpha (4.70 ppm), or beta (4.04 ppm) to the hydroxyl functionality of HEMA and the signal at ca. 3.55 ppm from the methyl ester protons of MMA, with the integrated intensity at about 1 ppm from in-chain methyls in the polymer. However, the breadth of the latter sig-

nal would make such comparison of doubtful value. Attempts to split carbon 13 signals (in particular, those originating from in-chain methyls at 15–25 ppm) by the addition of sodium deuterioxide in D<sub>2</sub>O to polymer in *d*<sub>4</sub> methanol at levels approximating 2–3 times above that required to cause complete ionization of acid functionality in the polymer proved unsuccessful. Changes were, of course, observed in the carbonyl region of the spectrum, but those changes could not be quantified.

As an alternative, the methacrylic acid content of co- and terpolymers was determined by titration in either water or a mixed methanol/water solution of the polymer using a protocol developed more fully later in this communication. The MAA level in copolymers (nos. 6, 7, and 10) was determined by this method and the comonomer level determined by difference. The MAA level in all other terpolymers (nos. 1–5, 8, and 9) was also obtained by this method and the levels of HEMA and MMA obtained from inspection of proton NMR spectra.

Although intrinsically simple spectra, some small mention must be made of solvent effects on peak positions in the proton NMR spectrum of copolymers containing both MMA and HEMA. As seen in Figure 1 (A), signals from the beta methylene group of HEMA, and those from the methyl ester of MMA, overlap extensively when obtained in *d*<sub>6</sub> dimethyl sulfoxide (DMSO) as solvent. In contrast, the greater solvating power of *d*<sub>4</sub> methanol shifts both the alpha and beta ethyl signals from the HEMA residue downfield, making the process of signal integration a relatively simple affair. MMA and

**Table III** Polymer Tacticities

Polymer	% Isotactic	% Heterotactic	% Syndiotactic
PMMA	5.3	39.9	54.7
PMAA	2.6	30.4	67.0
PHEMA	5.2	37.6	57.2
1	4	41	55
10	3	38	59
3	3	40	57
2	3	37	60
5	3	36	61
4	4	35	60
8	3	37	60
9	4	38	58
6	2	31	67
7	—	37	63

PMMA: polymethyl methacrylate, PHEMA: poly 2-hydroxyethyl methacrylate, PMAA: poly methacrylic acid.

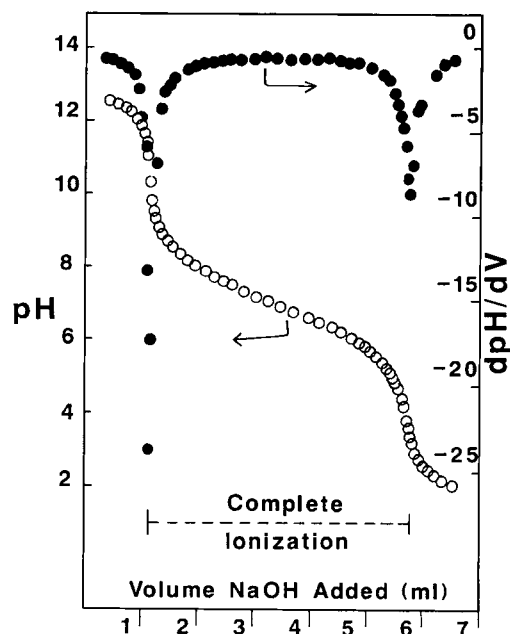
HEMA ratios and levels were all determined from proton spectra run in  $d_4$  methanol.

Co- and terpolymer compositions, as measured by these methods, are summarized in Table IV. Of course, the high conversions observed preclude any discussion of reactivity ratio or other such quantitative relation of feed mixture composition to copolymer structure; however, some observations may be made. For example, MAA levels in these polymers are consistently lower than in the corresponding feed mixture (Table I), indicating a greater tendency of both MMA and HEMA to enter into the co- or terpolymer. Surprisingly, MMA appears to enter more readily into terpolymers than does HEMA. A determination of reactivity ratios from systems prepared to low conversion would yield invaluable insight into the process, but such was not attempted here.

### Acid Strengths

The acid strength, or ease of ionization, of a polyacid differs from that of a simple acid in that each successive charge becomes more difficult to remove as the Coulombic field builds up around the polymer coil. The acid strength of a polyacid has been conveniently represented by "apparent" pKa that has been related to "alpha" or  $a$ —the extent of ionization—through the equation:  $\text{pKa} = \text{pH} + \log[(1 - a)/a]$ .<sup>3,4</sup> The measurement of polymer pKa becomes, therefore, a simple manipulation of the data pair (pH,  $a$ ).

The determination of alpha ( $a$ ) for a polymeric substance is complicated by the fact that one is never sure that the starting material is 100% covalent, although some success may be had using an appropriate ion-exchange column. For example, we found that the simple exercise of collecting MAA-contain-



**Figure 2** Representative titration and rate curves for polymer 9.

ing polymer on copper mesh ionized the polymer to the copper salt. As a compromise, therefore, we decided to completely ionize the polymer and follow the back titration to the covalent form.

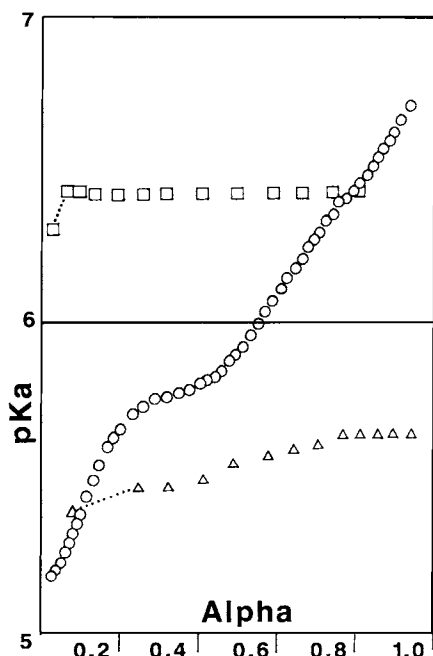
In brief, polymer was titrated to complete ionization using 10 *N* NaOH and back-titrated to the covalent form using 1.0 or 0.5 *N* HCl. A representative titration is depicted in Figure 2, omitting some of the data points for clarity. Also shown is the derivative curve that was constructed using simple spreadsheet programming. The rate maximum on the left was taken as corresponding to 100% ionization ( $a = 1$ ), and that on the right, as  $a = 0$ . It became, therefore, a simple matter to continue the spreadsheet program to generate values of pKa as a function of alpha using the given equation. The positions of these rate maxima are reproducible in a given solvent, and their separation (in terms of added acid) varies less than 2% between solvents (in this instance, water and water/methanol mixtures). Even so, it is unlikely that the rate maxima correspond to the absolute beginning and end of the ionization process. For example, the titration of carefully dried polymethacrylic acid (PMMA) in mixed solvent by this method undervalued the acid content by a correction factor of 13% and in distilled water by a correction factor of 16%, both of which were factored into the structural calculations discussed in the previous section. The choice of solvent in the titrations used to determine MAA level was

**Table IV** Polymer Compositions

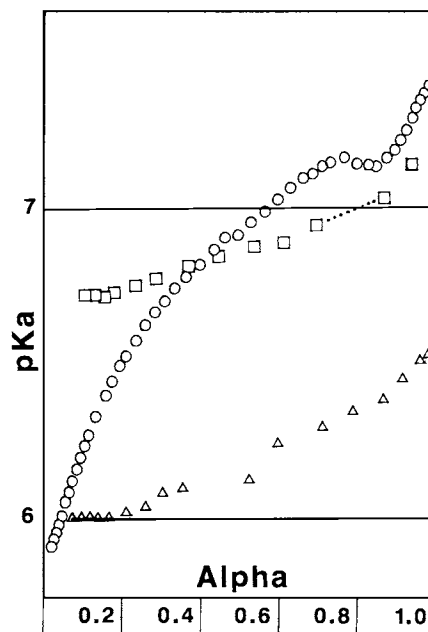
Polymer #	Mol % MAA	Mol % HEMA	Mol % MMA
1	9	42	48
10	10	90	—
3	22	25	53
2	21	53	26
5	36	20	44
4	31	46	23
8	54	10	36
9	54	34	12
6	71	—	29
7	64	36	—

determined by its solvating power. In general, titrations in mixed solvent were used except where, for example, in the case of polymer 8, some precipitation is observed on neutralization of the acid groups. In the acid strength experiments, we were more interested in trends than in absolute numbers, so we felt safe in using the uncorrected rate maxima as reproducible beginning and endpoints of the titration.

The compact/extended coil transformation of PMAA at about 25% ionization is extensively documented.<sup>3,4</sup> Essentially, the "unraveling" of the polymer coil on ionization is hampered by the secondary hydrophobic attractions of the in-chain methyl groups of the polymer. This results in a premature loss of acid strength that is regained at higher extents of ionization, as electrostatic repulsions overcome attractive forces and the coil abruptly expands in solution. The net result of this effect produces a localized maxima or plateau in the pKa curve that is not observed in the absence of in chain methyls (i.e., with polyacrylic acid<sup>11</sup>). We were interested in whether this effect carried through to the copolymers, and so we performed experiments in distilled water. We were, however, concerned that this effect could mask important trends, and so we performed experiments in a mixed methanol/water solvent (50/50 by volume) that suppresses the transformation. In the following discussion, results are



**Figure 3** pKa titration curves in water: polymethacrylic acid (open circles), polymer 10 (open triangles), polymer 1 (open squares).



**Figure 4** pKa titration curves in mixed water/methanol: Polymethacrylic acid (open circles), polymer 10 (open triangles), polymer 1 (open squares).

grouped so as to simplify comparison and best illustrate points of interest.

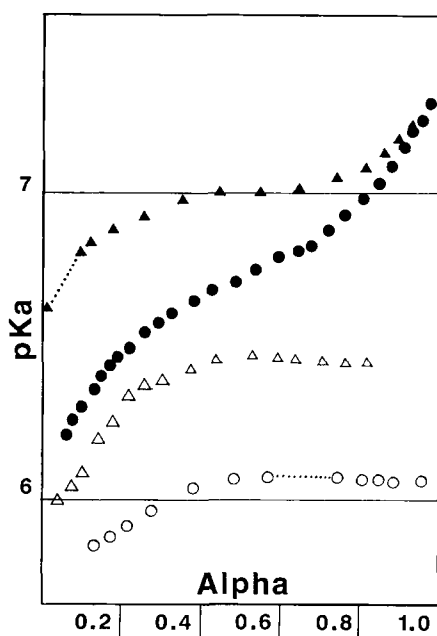
In Figure 3 we illustrate pKa curves for PMAA, and polymers 1 and 10, all in distilled water. The high charge density of PMAA results in a rapid decrease of acid strength with extent of ionization. In contrast, the acid groups in polymers 1 and 10 (which contain a low  $\approx$  10 mol % acid content) appear to behave as isolated units, producing pKa curves with little or no slope. It is interesting to note that the more hydrophilic polymer 10 appears to be a stronger polyacid than does polymer 1, presumably because of a higher degree of compatibility with the solvent (water) that would result in a more extensible conformation and a higher spatial separation of ionized groups. In making this statement, the authors do realize that it somewhat contradicts that previously made concerning the cooperative nature of the ionization process.

In Figure 4, the same polymers are examined in water/methanol solvent. As expected, all polymers became weaker acids in the presence of methanol, which is less able to stabilize the ionized acid groupings in the polymer and which encourages a more compact solution conformation.<sup>12</sup> An inflection in the pKa curve of PMAA at about 80% ionization may be due to a conformational transformation, but such would have to be checked by dilute solution viscometry to be made a firm assignment. As before,

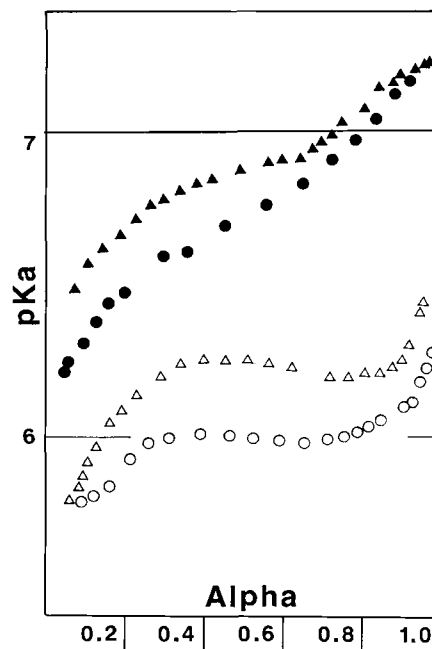
the more hydrophilic polymer 10 is shown to be a stronger polyacid than is polymer 1. The pronounced slope of both pKa curves would indicate a higher degree of charge-charge interaction, possibly resulting from a more compact solution conformation in the mixed solvent.

In Figure 5, we observe the variation of acid strengths of polymers 2 and 3 in both water and water/methanol. As both polymers contain about the same amount of MAA functionality ( $\approx 20$  mol %), we can attribute changes in acid strength to differences in the hydrophilicity of the uncharged residues of those polymers. From the figure it would appear that the more hydrophilic polymer 2 is the stronger polyacid in water, we suppose as a result of a more extended solution conformation. It would also appear that both polymers undergo some sort of conformational transition occurring over a broad range of ionization. Both polymers are again weaker acids in the mixed solvent, we presume for reasons discussed previously. Conformational transitions are not observed in mixed solvent, and, again, the more hydrophilic polymer 2 appears the stronger acid.

The behavior of polymers 4 and 5 in water and in mixed solvent is contrasted in Figure 6. Although the intent here was to contrast the behavior of polymers containing a similar intermediate level of acidity ( $\approx 40$  mol %), but with differing comonomers,



**Figure 5** pKa titration curves for polymer 2 in water (open circles) and in water/methanol (shaded circles) and for polymer 3 in water (open triangles) and in mixed water/methanol (shaded triangles).

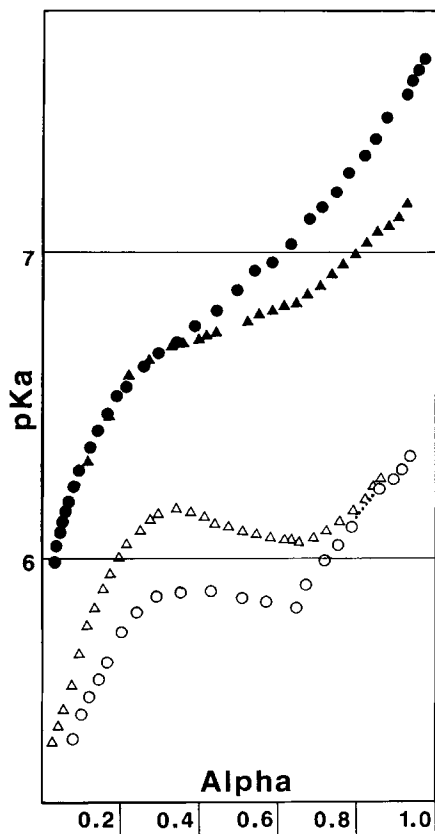


**Figure 6** pKa titration curves for polymer 4 in water (open circles) and in water/methanol (shaded circles) and for polymer 5 in water (open triangles) and in water/methanol (shaded triangles).

the situation was made more complex by the discovery that polymer 4 in reality contained measurably less MAA than did polymer 5 (Table IV). Even so, we contend that the greater observed acid strength of polymer 4, both in water and in mixed solvent, is a result of its larger HEMA content and, therefore, more easily extensible solution conformation in both solvents. The pKa curves for both copolymers in water again appear to suggest the presence of some conformational transition at intermediate degrees of ionization.

The pKa curves of polymers 8 and 9 in distilled water, as illustrated in Figure 7, appear to follow the same trend. The interpretation of the data in this instance is simplified by the similar acidities of both polymers (both 54 mol %). Again, the more hydrophilic polymer 9 appears the stronger acid, with both polymers appearing to undergo a pronounced conformational transformation at intermediate degrees of ionization. The behavior of polymers 6 and 7 (not shown) is very similar to that exhibited by polymers 8 and 9.

In mixed solvent, both polymers 8 and 9 exhibit similar acidities at low degrees of ionization. However, at higher degrees of ionization, polymer 8 (the more hydrophobic of the two) appears the stronger acid, in contrast to our previous trends. We believe



**Figure 7** pKa titration curves for polymer 8 in water (open triangles) and in water/methanol (shaded triangles) and for polymer 9 in water (open circles) and in water/methanol (shaded circles).

that this reversal may be related to the partial precipitation of polymer 8 during the titration. The same trend of acidity and precipitation is observed with polymers 6 and 7.

## CONCLUSIONS

(Applying to polymers with tacticity as described here.)

1. The acid strength of copolymers containing MAA, MMA, and HEMA is less in a mixed water/methanol solvent than in water itself.
2. The acid strength of copolymers containing medium to high levels of MAA, along with HEMA and MMA, decreases through cooperative interaction, at increased levels of ionization in both water and water/methanol mixtures. Such polymers appear to undergo a conformational transition in water (but not in water/methanol) at intermediate levels of ionization.

3. The ionization of acid functionality in copolymers containing low levels of MAA (10 mol % or less) proceeds as with simple acids. In mixed methanol/water solvent, however, cooperative effects gain in importance and acidity decreases with extent of ionization.
4. The acid strength of copolymers containing similar amounts of MAA becomes a function of the hydrophobic/hydrophilic balance of the uncharged portion of the polymer. Both in water and in mixed water/methanol solvent, polymers containing HEMA (or higher levels of HEMA) appear to be stronger acids than do polymers containing MMA (or higher levels of MMA). This we presume to be a direct consequence of the degree of compatibility of the copolymer with the solvent, and, hence, the ease with which the partly ionized coil may expand in solution to minimize charge-to-charge repulsion effects.

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