Preparation and Characterization of Polyelectrolyte Copolymers Containing Methyl Methacrylate, and 2-Hydroxyethyl Methacrylate. II. Polymers Based on Dimethylaminoethyl Methacrylate

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SYNOPSIS

Co- and terpolymers containing dimethylaminoethyl methacrylate (DMAEMA), methyl methacrylate (MMA), and 2-hydroxyethyl methacrylate (HEMA) were prepared by solution polymerization, and characterized by dilute solution viscometry and proton and carbon-13 nuclear magnetic resonance spectroscopy. Polymers were prepared containing 75, 60, 40, 25, and 10 mol % DMAEMA but with differing levels of MMA and HEMA. Polymer solutions were titrated under nitrogen to obtain variations of pKb with alpha (the extent of protonation of the DMAEMA residue). From these experiments, we were able to show that, as expected, the cooperative nature of the ionization process decreased as the level of DMAEMA in the polymer was reduced from 75 mol % to 10 mol %. By comparing polymers containing similar amounts of DMAEMA monomer, we were also able to show that base strength increased with the polarity of the uncharged portion of the polymer, in other words, that polymers containing higher levels of HEMA were stronger bases than polymers containing higher levels of MMA. This effect was rationalized by assuming that higher contents of the more polar HEMA monomer facilitated the coil expansion that accompanied the process of ionization, thus increasing charge separations at corresponding values of alpha and increasing base strength.

INTRODUCTION

Water-soluble synthetic polyelectrolyte polymers are of interest both industrially, where they are used, e.g., as flocculants and complexing agents for heavy metals, and in the academic sphere, where interest has, for the main part, focused on relationships between structure/charge density and solution conformation.[1,2] Although much is known about the behaviour of polyelectrolyte homopolymers, much less is understood about structure/property relationships in polyelectrolyte co- and terpolymers, in which both charge density and a hydrophobic/hydrophilic balance may be altered by the addition of uncharged 'mers with differing polarities and hy-

drogen bonding capability. In this, the second part of a series,[3] we detail the influence of copolymerized methyl methacrylate (MMA, a nonpolar hydrophobic monomer) and 2-hydroxyethyl methacrylate (HEMA, a monomer capable of extensive hydrogen bonding) upon the base strength of copolymerized dimethylaminoethyl methacrylate (DMAEMA).

EXPERIMENTAL

Chemicals and Reagents

Reagents for preparation and characterization of polymers were handled in much the same manner as detailed in the first part of this series.[3] Reagents not mentioned there include dimethylaminoethyl methacrylate (Kodak), which was double distilled under rotary pump vacuum with small cuts (10% top, 20% bottom) immediately before use, and deu-

terated chloroform solvent for nuclear magnetic resonance (NMR) measurements, purchased from the Aldrich Chemical Company.

Polymer Synthesis

For a detailed account of the methods involved, refer to part I of this series.[3] In brief, polymers were synthesized by solution polymerization under nitrogen, in ethanol solvent, using a standard wide-mouthed reaction kettle assembly. Azobisisobutyronitrile (AIBN) was used as initiator at a concentration of 1 mol % with respect to the combined monomer charge; polymerizations were conducted for 4 h at $70 \pm 0.05°C$, using monomer with a combined weight of 200 g in 2 L solvent. Polymer was recovered by precipitation, first in low-boiling point petroleum ether, then in water that had been made mildly basic by the addition of sodium hydroxide. A small quantity of polydimethylaminoethyl methacrylate (PDMAEMA) was prepared for comparison with the co- and terpolymers, using a scaled-down version of the protocol outlined above.

Intrinsic Viscosity Measurements

Polymer intrinsic viscosities were measured in modified Ubbelhode viscometers at $35 \pm 0.05°C$ using dimethyl formamide solvent containing 0.2% (wt/vol) lithium bromide to suppress polyelectrolyte effects.[3]

NMR Spectroscopy

Carbon 13 (^{13}C) spectra of polymers were obtained in dimethyl sulfoxide (DMSO) solvent at 35°C. Proton (^{1}H) spectra were obtained in deuterated chloroform at the same temperature, using tetramethyl silane (TMS) as a lock agent. All measurements were performed on a Varian XL-300 NMR spectrometer.

Acid-Base Titrations

Acid-base titrations were performed as previously outlined.[3] Polymer (1 g) was dissolved in 100 mL distilled water or a mixed water/methanol solvent. The solution pH was kept acidic by the addition of small amounts of $5.0N$ HCl acid to encourage dissolution of the polymer. Titrations were performed under nitrogen and a record of solution pH made using an Orion SA 720 pH meter connected to a flat bed recorder. The solution pH was first lowered to about 2 and raised thereafter by the addition of small

aliquotes of NaOH. The base concentration (usually 0.5 or $1.0N$) was determined by the content of DMAEMA in the polymer and was adjusted so the neutralization portion of the titration curve spanned the addition of 4–8 mL titrant.

RESULTS AND DISCUSSION

Polymer Preparation and Characterization

Our rationale for this work was to elucidate trends governing the relationships between the structure of some water-soluble basic co- and terpolymers and base strength as measured by pKb. In particular, we were interested in the effect on pKb of ultimate charge density, as a reflection of DMAEMA content. We were also interested in the effect on pKb of the hydrophilic–hydrophobic balance in such polymers, reflected in the relative contents of MMA and HEMA.

With this in mind, we prepared a series of polymers covering a range of DMAEMA content. Two polymers were prepared at each DMAEMA loading, but with differing contents of MMA and HEMA. Monomer charges are detailed in Table I. Polymer yields, as measured by simple gravimetry, are reproduced in Table II, where it is shown that, *in general*, for polymers containing a similar amount of DMAEMA but differing levels of HEMA and MMA (e.g., polymers 12 and 17), the polymer prepared with a higher content of HEMA is produced in higher yield. This effect is most evident in polymer pairs containing low levels of DMAEMA and high levels of HEMA and MMA, and is indicative of the higher reactivity of the HEMA monomer.[4]

Polymer intrinsic viscosities were obtained as an

Table I   Monomer Charges

Polymer	Monomer Charge (mol %)		
	MMA	HEMA	DMAEMA
18	45	45	10
20	—	90	10
11	50	25	25
19	25	50	25
12	40	20	40
17	20	40	40
13	30	10	60
14	10	30	60
16	25	—	75
15	—	25	75

Table II **Polymer Yields and Intrinsic Viscosities**

Polymer	Yield (wt %)	Intrinsic Viscosity (cc/g)
18	64.0	20.6
20	71.8	26.2
11	45.6	14.9
19	61.4	23.0
12	22.4	18.8
17	53.4	22.2
13	24.1	19.4
14	42.0	19.2
16	45.7	12.5
15	46.1	17.3

indication of molecular weight. As reported in Table II, intrinsic viscosities varied from about 10–25 cc/ g polymer. In each polymer pair containing similar levels of DMAEMA, the member containing the higher level of HEMA possessed the higher intrinsic viscosity. This difference is most evident when comparing polymers containing high levels of HEMA and MMA, and is a simple consequence of the presence in the HEMA monomer of ethylene glycol dimethacrylate, a dimethacrylate containing impurity that is reduced but not eliminated by the monomer purification scheme.[4] If we *assume* that dimethyl formamide is a good solvent for these polymers (a reasonable assumption) and if we, therefore, *assume* Mark–Houwink–Sakurada constants of a = 0.7 and K = 0.02,[5] then we would obtain an (order of magnitude) viscosity average molecular weight range of about 10,000–30,000 Daltons. These low molecular weights are entirely consistent with the relatively low monomer concentrations and high levels of initiator used in the synthesis reaction.[6]

The volume occupied by a solvated polyelectrolyte polymer coil has a direct bearing on the acid or base strength of the polymer due to the effect of the former on the spatial separations of the developing charges. Polymer tacticity has been shown to influence hydrodynamic volumes and ionization equilibria.[7] As such, we determined the tactic distribution of these polymers by NMR spectroscopy. The tacticity of methacrylate type polymers is usually measured by signal splitting of either carbon-13 or proton resonances associated with the in-chain methyl groups.[8] We showed in an earlier publication that the presence of methacrylic acid comonomer broadened proton resonances to the extent that the isotactic (i), heterotactic (h), and syndiotactic (s) triads could not be reliably separated for analysis. In contrast, most of the polymers examined here
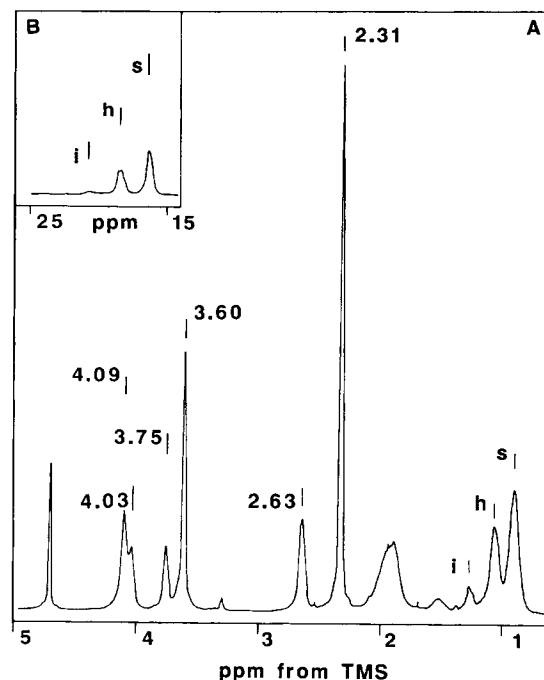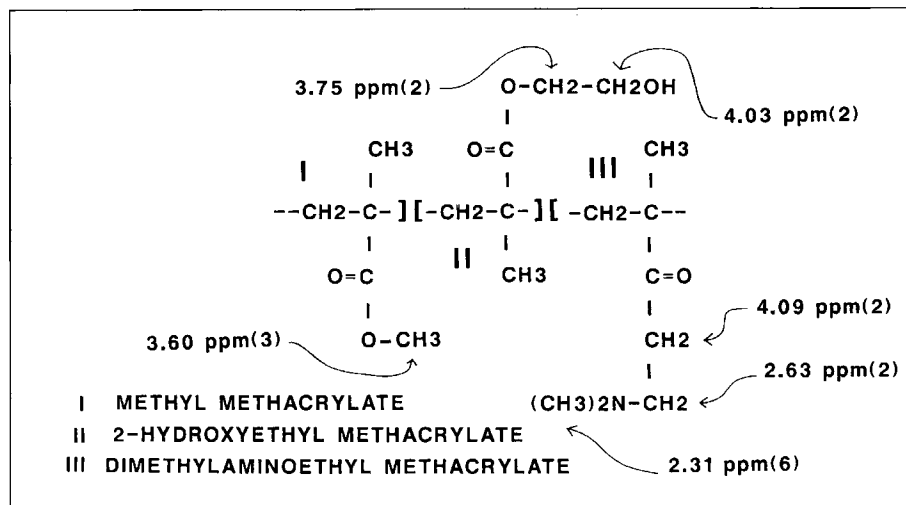

Figure 1 (a). Proton NMR spectrum of polymer 12 (38 mol % DMAEMA, 22 mol % HEMA, 40 mol % MMA). (B) Carbon-13 NMR spectrum of the same polymer. i, isotactic; h, heterotactic; s, syndiotactic in chain methyl resonances.

produced well-defined proton resonances in deuterated chloroform. See, e.g., the proton NMR spectrum of polymer 12, reproduced in Figure 1(a). The triads centered around 1 ppm are well defined with only a little overlap, and could be integrated to yield a qualitative distribution of tacticity. However, we chose to determine tacticity from corresponding signals in the carbon-13 spectrum around 20 ppm. These signals, as reproduced in Figure 1(b), are completely separated for better resolution. Polymer

Table III **Polymer Tacticities**

Polymer	% Isotactic	% Heterotactic	% Syndiotactic
18	3	38	59
20	2	40	58
11	4	39	57
19	3	39	58
12	3	38	59
17	3	38	59
13	2	38	60
14	3	38	59
16	2	37	61
15	2	39	59

3.75 ppm(2) —⟋ O-CH2-CH2OH
                                    4.03 ppm(2)
                | |
               CH3   O=C   CH3
        | | | III |
     --CH2-C-] [-CH2-C-] [-CH2-C--
                | | |
               O=C   II CH3   C=O
                | | |
                                        CH2   4.09 ppm(2)
     3.60 ppm(3)   O-CH3 | 2.63 ppm(2)
                                    (CH3)2N-CH2

     I   METHYL METHACRYLATE
     II 2-HYDROXYETHYL METHACRYLATE
     III DIMETHYLAMINOETHYL METHACRYLATE   2.31 ppm(6)

Figure 2   Monomer residue structures and associated proton NMR signals applicable to a compositional analysis.

tacticities obtained by this method are reproduced in Table III. The high syndiotactic content of these polymers (55–60%), moderate heterotactic content (35–40%), and low isotactic content (2–4%), is characteristic of polymers prepared by free radical solution polymerization at this temperature.[4] The narrow *distribution* of the data sets would indicate that differences in solution dimensions and, therefore, base strengths, could not be attributed to any variation of tacticity.

Polymer compositions were obtained from proton (P) NMR spectroscopy of the copolymers. Signals associated with the three monomer units were identified by comparison of homopolymer and copolymer spectra, and were integrated and ratioed to provide a compositional analysis. Monomer residue structures and relevant PNMR signals are illustrated in Figure 2. The proportion of DMAEMA in these

polymers was obtained from the relative intensity of the well-defined and isolated signal at 2.31 ppm from the N-methyl group on the DMAEMA residue. The proportion of MMA in the polymer was obtained from the relative intensity of the signal at 3.60 ppm from the methyl ester protons, while the proportion of HEMA was obtained from the relative intensity of the signal at 3.75 ppm produced by methylene protons beta to the hydroxyl group. Polymer compositions obtained by this method are summarized in Table IV. Of interest is the close relationship between polymer composition and the corresponding monomer feed mixture for each copolymer (Table I). Take, e.g., polymer 12: feed mixture, 40 mol % MMA, 20 mol % HEMA, 40 mol % DMAEMA; composition, 40 mol % MMA, 22 mol % HEMA, 38 mol % DMAEMA. Considering the high conversions involved (Table II), it would be safe to say that DMAEMA, MMA, and HEMA co- and terpolymerize as a random system under these conditions.

Base Strengths

The base strength of a tertiary amine derivative such as DMAEMA is conveniently measured by the equilibrium constant for the protonation reaction, usually designated as K_b. In contrast with simple amines, the base strength of a polymeric amine derivative such as PDMAEMA is a function of the degree of ionization of the polymer, the placement of each successive charge on the polymer requiring more work due to the buildup of the localized coulombic field around the polymer coil. This charge

Table IV   Polymer Compositions

Polymer	Mol % MMA	Mol % HEMA	Mol % DMAEMA
18	44	47	9
20	xx	92	8
11	50	27	23
19	25	54	21
12	40	22	38
17	20	46	34
13	28	12	60
14	10	31	59
16	24	xx	76
15	xx	28	72

buildup dilates the solvated polymer coil and increases the average rms separation of the charges. This dilation is opposed by entropic effects and aided if structures on the polymer coil are heavily solvated by the water, in other words, if the balance of the copolymer is hydrophilic in nature.

If we define alpha as the proportion of basic functionality on the polymer that has been protonated, then, as a first approximation, values of K_b for those systems containing a low concentration of DMAEMA should be greater than for corresponding systems containing a higher proportion of the basic monomer at similar values of alpha. In a similar vein, the upward slope of the K_b (or, more correctly, the pKb) vs alpha curve, which indicates the degree of charge–charge interaction, should be less for those systems that contain a low concentration of DMAEMA. In copolymeric systems, the situation is, of course, complicated by interactions of the uncharged portion of the polymer with the solvent, which may help or hinder the protonation reaction by aiding or hindering the expansion process.

Acidic polyelectrolyte polymers have been subjected to intense scrutiny as models of the more complicated natural polyelectrolyte polymers. In particular, polymethacrylic acid has attracted attention due to the well-documented compact/extended coil transformation that occurs at about 25% ionization. This transformation has been followed by corresponding changes in solution viscosity and by the more convenient measurement of acid strength, which temporarily increases with the abrupt expansion of the polymer coil,[9,10] using the convenient relationship:

$$pKa = pH + \log[(1 - alpha)/alpha],$$

in which alpha or "a" represents the proportion of the acid groups that have been ionized. In our case, we would use the corresponding relationship:

$$pKb = pOH + \log[(1 - a)/a],$$

in which a is defined as the proportion of basic functionality that has been protonated. In common with most workers in this area, we have neglected to include corrections for solution activity in our working equation.[9,10]

To compensate for possible contamination and premature protonation of our polymers prior to the titration, and to aid in the analysis of those polymers that become soluble only when partially ionized, we chose to back titrate from a low-solution pH, where we may assume 100% protonation of the amine

groups in the polymer, to a high pH, at which we may assume complete deprotonation of the amines in the polymer. Titrations were performed in both distilled water and a 50/50 (vol/vol) mixture of water and methanol, the latter to examine the effect on pKb of increasing the solvent power toward the uncharged portion of the polymer. When comparing results obtained in the two solvent systems, the reader must, of course, be aware of uncertainties associated with pH measurements made in partially nonaqueous solvent systems.[11] All titrations were performed using 1% polymer solutions that were diluted less than 10% during the experiment. To help visualize the experiment, we reproduced in Figure 3 a typical titration curve. Raw data was manipulated by spreadsheet programming to produce a rate curve [dpH/dvol] used to identify the two rate maxima that we thereafter identified with $a = 0$ and $a = 1$, as shown in the figure. Having defined the limits of the experiment, it became a simple matter to tabulate values of pKb vs. a. It must be emphasized here that although the two rate maxima are very distinct (and reproducible) it is unlikely that they represent the *exact* onset and end points of the reaction. As such, data obtained by this method was used for internal comparison and for the identification of trends, rather than for the exact determination of polymer pKbs.
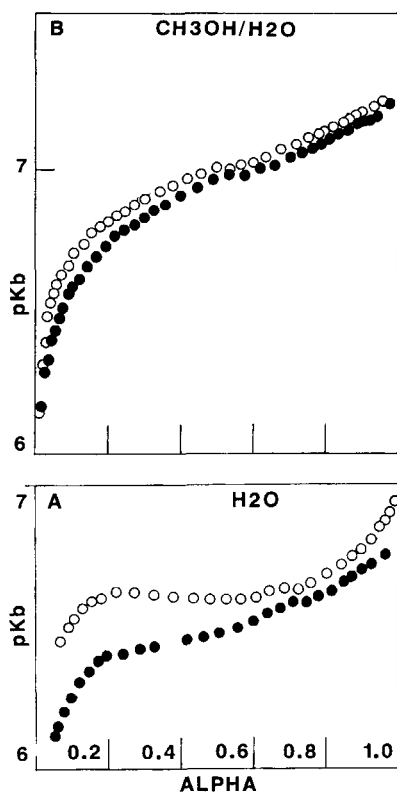
To facilitate comparison of the data, we have chosen to discuss systems in order of decreasing
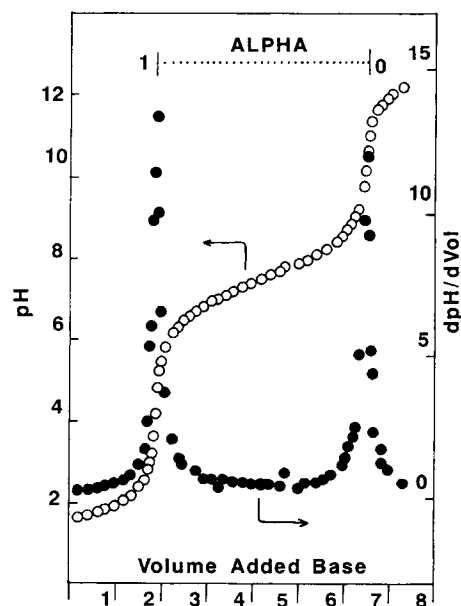
Figure 3 Back titration and rate curves for polymer 15 (72 mol % DMAEMA, 28 mol % HEMA) using 1.0M NaOH titrant.
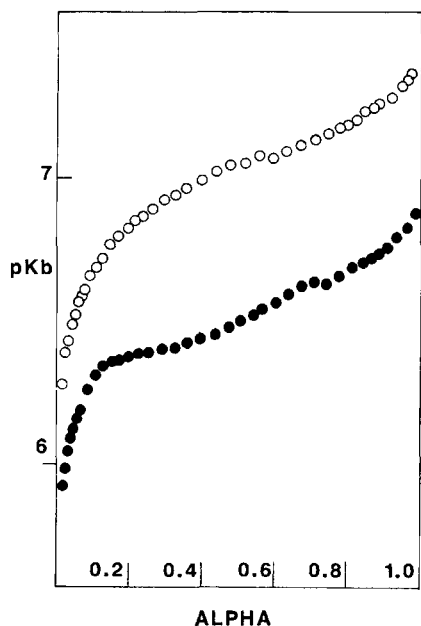
Figure 4 Variation of pKb with extent of ionization for PDMAEMA in distilled water (shaded circles) and 50/50 (vol/vol) methanol/water solvent (open circles).
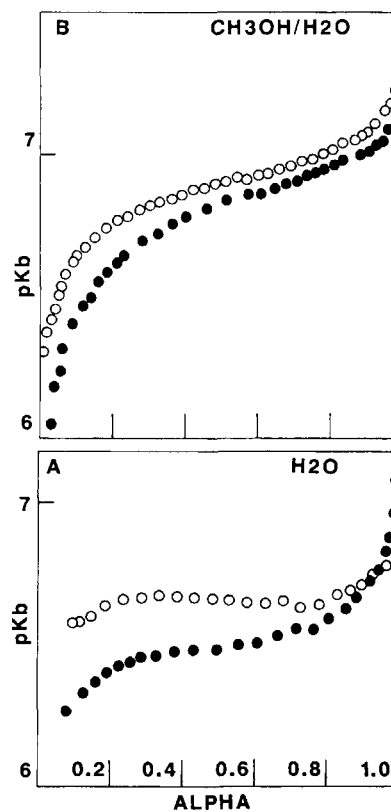
DMAEMA content, beginning with poly-DMAEMA and ending with a comparison of polymers 18 and 20.

The behaviours of poly-DMAEMA in both distilled water and in the methanol/water solvent mixture are compared in Figure 4. As expected, the basicity of the polymer drops off in both solvents with increasing extent of ionization, evidenced by the upward slope of the pKb curve. In common with other polymers discussed here, we could not detect any discontinuity in the pKb curve that could be attributed to the sort of conformational change attributed to polymethacrylic acid.[9,10] Remembering that pKb $= -\log K_b$, it can be seen that the basicity of the polymer is almost an order of magnitude larger in water than in the mixed solvent. From this, it would appear that stabilization of the developing charges (which would be more efficient in pure water) is a more powerful driving force than solubilization of the polymer backbone (which would be more efficient in the solvent mixture).
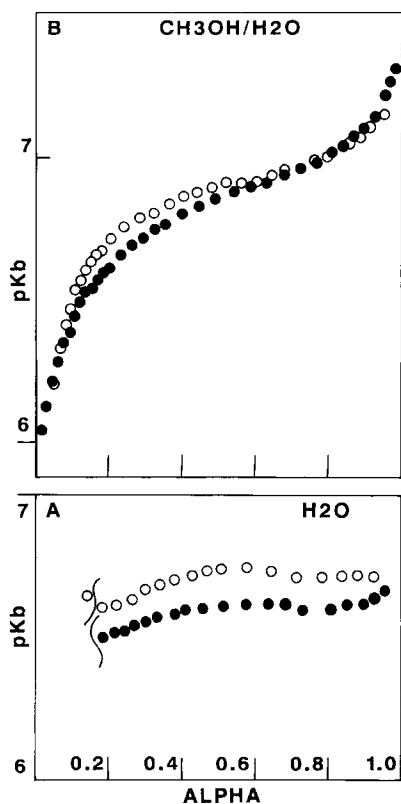
The behaviour of polymers 15 and 16 are compared and contrasted in Figure 5. Both polymers

Figure 5 Variation of pKb with extent of ionization for polymers 15 (shaded circles) and 16 (open circles), both containing about 75 mol % DMAEMA monomer.
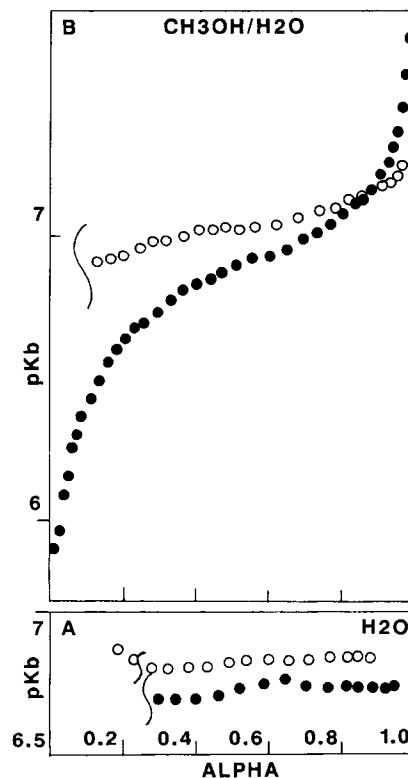

Figure 6 Variation of pKb with extent of ionization for polymers 13 (open circles) and 14 (shaded circles), both containing about 60 mol % DMAEMA monomer.

contain about 75 mol % DMAEMA, so differences in behaviour may be attributed to the comonomer. Polymer 15 is the stronger base in both distilled water and in the mixed solvent, with the difference more evident in pure water. We assume this to be due to the better solvation of the HEMA comonomer in both solvents, which would increase base strength by facilitating the coil expansion that accompanies the ionization process. The base strength of polymer 15 is close to that of poly-DMAEMA, indicating a similar degree of charge–charge interaction.

Polymers 13 and 14 are compared in Figure 6. Both polymers contain about the same amount of DMAEMA (circa 60 mol %), so differences in behaviour may again be attributed to the composition of the remainder of the polymer. Polymer 14, with the higher content of the more hydrophilic HEMA monomer, is again the stronger base in both solvents, with the difference more evident in pure water. Comparisons with poly-DMAEMA showed a slight decrease in the curve slope, indicating a correspondingly small decrease in the extent of cooperative interaction between charges.
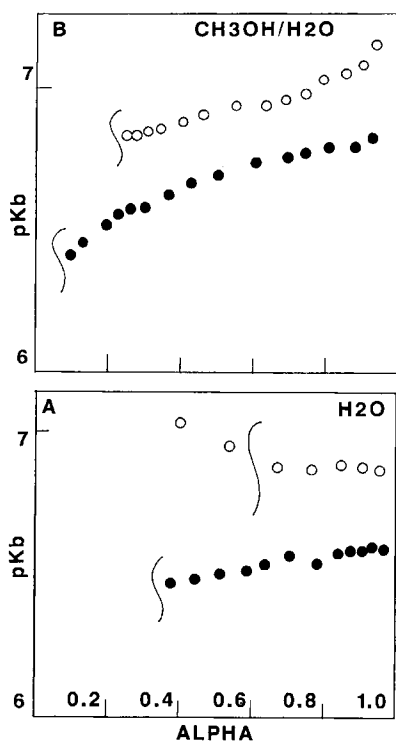

Figure 8   Variation of pKb with extent of ionization for polymers 18 (open circles) and 19 (shaded circles), both containing about 25 mol % DMAEMA monomer.

The behaviour of polymers 12 and 17, both containing about 40 mol % DMAEMA, is compared in Figure 7. Polymer 17, possessing the more hydrophilic backbone (in other words, the higher HEMA content) is the stronger base in distilled water, with the difference much less evident in the mixed solvent. From the essentially horizontal slope of the titration curve, it would appear that charged groups on the polymer act in isolation at this concentration of DMAEMA. Sigmoidal lines are used in the figure to indicate the cloud points of both polymers, beyond which we have chosen not to report data due to lack of accuracy. In *all* cases in which a cloud point was observed, the base strength was seen to drop off rapidly at lower extents of ionization. This could not be attributed to removal of material from solution, as the proportion of colloidal polymer formed just after the cloud point is minute. We must, therefore, attribute this behaviour to hypercoiling of the bulk of the polymer chains in solution, a hypothesis that lends support to our other discussions that primarily center on the effect of polymer coil dimensions on base strength.

The behaviour of polymers 11 and 19 (25 mol % DMAEMA; Fig. 8) and 18 and 20 (10 mol %

Figure 7   Variation of pKb with extent of ionization for polymers 12 (open circles) and 17 (shaded circles), both containing about 40 mol % DMAEMA monomer.

Figure 9   Variation of pKb with extent of ionization for polymers 18 (open circles) and 20 (shaded circles), both containing about 10 mol % DMAEMA monomer.

DMAEMA; Fig. 9) follow the same pattern as that set by polymers 12 and 17 in Figure 7. In each comparison, the polymer containing more HEMA monomer is the stronger base. Not unexpectedly, the cloud point in distilled water shifts to larger values of alpha as the proportion of DMAEMA in the polymer is reduced from 40 (Fig. 7) to 25 (Fig. 8) and 10 mol % (Fig. 9). The extent of interaction between charges on the polymer as reflected in the slope of the pKb curves for these polymers, especially in water, is shown to be negligible in polymers containing 25 mol % or less of DMAEMA monomer. In the extreme case of polymers 18 and 20 (10 mol % DMAEMA), the cloud point for the polymer containing the higher level of HEMA (polymer 20) occurs at a lower value of alpha in both solvent systems.

CONCLUSIONS

1. The base strength of co- and terpolymers containing DMAEMA, MMA, and HEMA is

less in a mixed water/methanol solvent than in distilled water.
2. The degree of interaction between protonated amino groups in these polymers decreases with the proportion of DMAEMA in the polymer.
3. Abrupt conformational changes, such as are observed in systems containing methacrylic acid, are not seen in these systems.
4. At similar levels of DMAEMA, polymers containing a more hydrophilic comonomer, or mixture of comonomers, are stronger bases in polar solvent; we presume, due to better solvation of the polymer, which would lead to a more expanded coil, less charge–charge interaction and a greater ease of protonation.

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