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Water Soluble Polymers. 76. Electrolyte Responsive Cyclocopolymers with Sulfobetaine Units Exhibiting Polyelectrolyte or Polyampholyte Behavior in Aqueous Media

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ABSTRACT: Copolymers of *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride (DADMAC) and the zwitterionic monomer 3-(*N*,*N*-diallyl-*N*-methylammonio)propanesulfonate (DAMAPS) have been prepared in a 0.5 M NaCl aqueous solution using 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) as the free-radical photoinitiator. The feed ratio of DADMAC:DAMAPS was varied from 100:0 to 0:100 mol % with the total monomer concentration held constant at 2.5 M. ^{13}C NMR data indicate that the resulting polymers maintain the five-membered ring structure in the cis conformation common to diallylammonium salts. Reactivity ratio studies indicate that the sulfobetaine monomer is incorporated randomly along the polymer backbone. Laser light scattering provided molecular weights and second virial coefficients, which varied from 5.16×10^4 to 8.42×10^4 and 5.54×10^{-4} to 1.89×10^{-4} mL mol g^{-2}, respectively. Solution behavior is dependent upon ionic strength as determined by low shear viscosity and dynamic light scattering experiments. For cyclocopolymers containing <40 mol % sulfobetaine, classical polyelectrolyte behavior is shown by viscosity decreases with increasing ionic strength. However, for polymers containing ≥ 40 mol % sulfobetaine, chain expansion occurs as the ionic strength is increased above that required for the Donnan equilibrium.

Introduction

The synthesis of electrolyte-tolerant, water-soluble polymers that contain ionic pendent groups has been the goal of academic and industrial laboratories for the past several years.[1−4] Such polymers have applications in water treatment, remediation, drag reduction, petroleum recovery, viscosification, formulation of coatings, cosmetics, and pharmaceutics. In striving to synthesize polymers that show tolerance in the presence of added electrolytes, we have recently focused our attention on polyampholytes, polymers that possess both cationic and anionic pendent groups.[5−9] The ionic groups may be located on separate monomer units or may be incorporated into one zwitterionic monomer. Polyampholytes can be tailored for enhancement in viscosity and solubility in the presence of added electrolytes due to shielding of coloumbic (dipole−dipole) attractions.[10−13] Thus, these polymers are promising for formulation in the presence of electrolytes and surfactants.

Polyzwitterions containing the sulfonate functionality have been thoroughly studied beginning with the pioneering work of Hart and Timmerman.[14] In that work, zwitterionic monomers were prepared by the reaction of 2- and 4-vinylpyridine with 1,4-butane sultone. Polysulfobetaines are typically insoluble in deionized water and require a relatively high content of hydrophilic comonomer or the addition of a critical concentration of electrolyte to achieve solubility and viscosity enhancement. Polysulfobetaines have also been synthesized from acrylic,[15−22] acrylamido,[23,24] and vinylimidazolium[22,25−27] monomers, and more recently polysulfobetaine block copolymers have been reported.[28,29]

In this contribution we expand an initial report[37] describing the synthesis and characterization of a series of copolymers based upon the copolymerization of *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride (DADMAC) with the sulfobetaine monomer, 3-(*N*,*N*-diallyl-*N*-methylammonio)propanesulfonate (DAMAPS). These monomers undergo an intramolecular−intermolecular cyclopolymerization yielding five-membered rings and a cationic charge common to polymerized diallylammonium salts, as first discovered by Butler.[30−32] The purpose of the present work is to elucidate the compositional effects of zwitterionic comonomer incorporation on the aqueous solution properties of the resulting polyelectrolytes. In particular, the solution behavior as a function of concentration and added electrolytes has been studied by viscometric and dynamic light scattering methods. The results are compared to aqueous solution behavior typically exhibited by polyelectrolytes and polyampholytes.

Experimental Section

Materials. All reagents were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. *N*,*N*-Diallyl-*N*-methylamine (DAMA) was synthesized as previously described.[33]

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-300. ^{13}C NMR spectra of the cyclocopolymers were obtained at 50.3 MHz using 10−15 wt % 1.0 M NaCl aqueous (D_2O) polymer solutions with 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt DSS, as a reference. DEPT135 experiments confirmed peaks assignments for both monomer and polymer samples. A recycle delay of 8 s, 90° pulse length, and inverse gated decoupling to remove all NOE were used for quantitative spectral analysis. Experimental error for the inverse gated decoupled ^{13}C NMR was <5%. Elemental analysis was performed by MHW Laboratories, Phoenix, AZ. Molecular weight studies were performed with a Brookhaven Instruments 128-channel BI-2030 AT digital correlator using a Spectra Physics He−Ne laser operating at 632.8 nm. Weight-average molecular weights (M_w) were determined through analysis of the Berry plots.[34−36] Hydrodynamic radii were determined using the cumulants analysis of the autocorrelation function obtained at 90°. Refractive index measurements were carried out using a Chromatix KMX-16 differential

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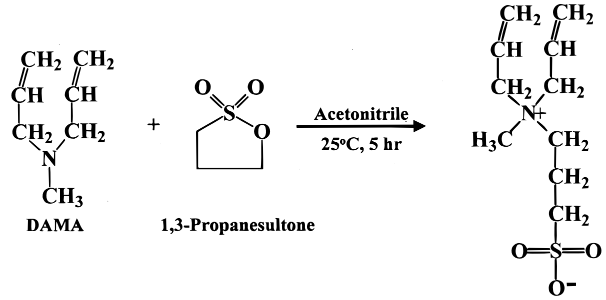
Scheme 1. Synthetic Pathway for Preparation of 3-(*N*,*N*-Diallyl-*N*-methylammonio)propanesulfonate (DAMAPS)



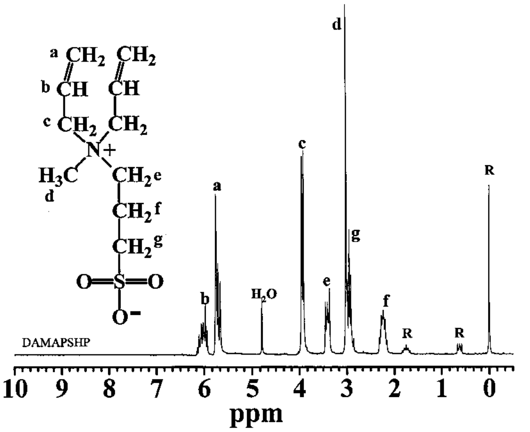


Figure 1. ^{1}H NMR spectrum of 3-(*N*,*N*-diallyl-*N*-methylammonio)propanesulfonate (DAMAPS) in D_2O. (R = 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt, as a reference.)

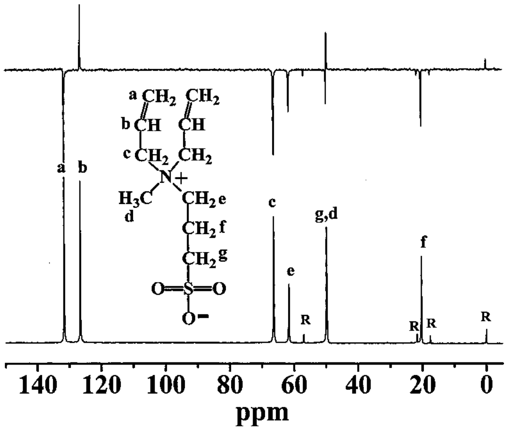
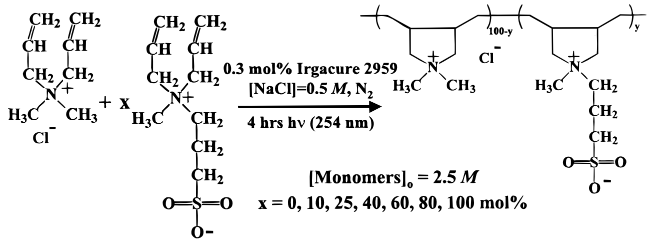


Figure 2. ^{13}C NMR and DEPT135 spectra of 3-(*N*,*N*-diallyl-*N*-methylammonio)propanesulfonate (DAMAPS) in D_2O. (R = 3-trimethylsilyl)-1-propanesulfonic acid, sodium salt, as a reference.)

refractometer. Dilute solution viscometric studies were conducted with a Contraves LS-30 low-shear rheometer at a constant shear rate of 5.96 s^{-1} at 25 °C. Optical microscopy was performed with a Nikon OPTIPHOTO2 POL light microscope.

Synthesis of 3-(*N*,*N*-Diallyl-*N*-methylammonio)propanesulfonate (DAMAPS).[37-39] *N*,*N*-Diallyl-*N*-methylamine (DAMA) (0.45 mol) and 1,3-propane sultone (0.5 mol) were reacted in 200 mL of acetonitrile with stirring at room temperature for 5 h. During this period, the product formed as a white precipitate. This was then filtered and washed with three 200 mL aliquots of diethyl ether. DAMAPS was obtained in 72% yield. Mp 169−170 °C. Analysis for $C_{10}H_{19}NSO_3$. Calculated: C, 51.48%; H, 8.21%; N, 6.00%; S, 13.74%. Found: C, 51.59%; H, 8.10%; N, 5.89%; S, 13.64%.

Scheme 2. Synthetic Pathway for Preparation of DADMAC-*co*-DAMAPS Cyclocopolymers



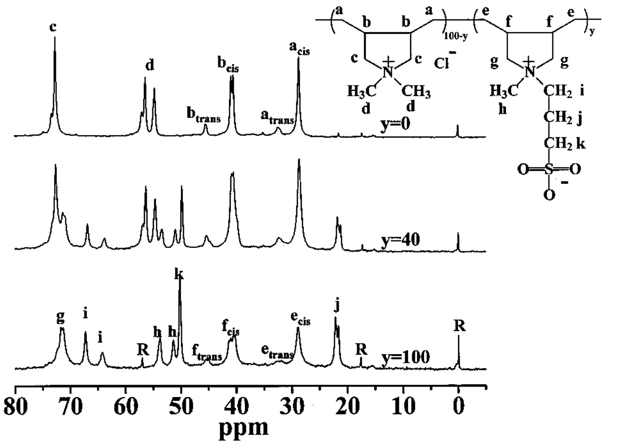


Figure 3. Representative inverse gated decoupled ^{13}C NMR spectra of the DADMAC-*co*-DAMAPS cyclocopolymers in D_2O (1 M NaCl). (R = 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt, as a reference.)

Table 1. Reaction Parameters and Polymer Composition for the Copolymerization of DADMAC (M_1) and DAMAPS (M_2)

sample	rxn time (h)	% conv	M_2 feed (mol %)	M_2 in copolymer (mol %)[a]	cis isomer (mol %)[a]
DADMAC	4.0	41	0	0[b]	89
DADS11	4.0	35	10	11	90
DADS23	4.0	43	25	23	90
DADS40	4.0	40	40	40	89
DADS55	4.0	37	60	55	88
DADS82	4.0	38	80	82	89
DAMAPS	4.0	69	100	100[b]	89

[a] From inverse gated decoupled ^{13}C NMR (D_2O). [b] Theoretical value.

Synthesis of Copolymers of DAMAPS with DADMAC. Homopolymers of DAMAPS and DADMAC and the copolymers of DAMAPS with DADMAC were synthesized by free radical photopolymerization in a 0.5 M aqueous NaCl solution under a nitrogen atmosphere at 35 °C using 0.3 mol % 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959) (Ciba) as the photoinitiator. The feed ratio of DADMAC/DAMAPS was varied from 100/0 to 0/100 mol % with the total monomer concentration held constant at 2.5 M. The 0.5 M NaCl was maintained in the reaction medium to ensure that polymers with high DAMAPS content remained soluble during polymerization. The polymerizations were carried out in a Rayonet photoreactor (Southern New England Ultraviolet Co.) operating at 300 nm for 4 h under a nitrogen atmosphere. A low-conversion sample was obtained for reactivity ratio studies. The reaction was usually terminated at <50% conversion as a precaution against copolymer drift. The copolymers were purified by dialyzing against deionized water with 6000−8000 MWCO dialysis tubing (Spectrapor). The dialysis was carried out for 2 weeks with frequent changing of the permeate. The copolymers were recovered by lyophilization. Conversions were determined gravimetrically.

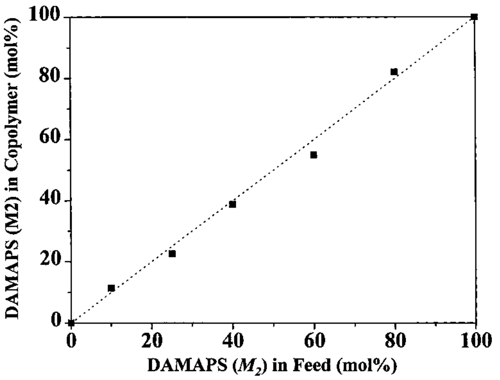


Figure 4. Mole percent sulfobetaine incorporation as a function of mole percent sulfobetaine in the feed as determined by inverse gated decoupled ^{13}C NMR.

Table 2. Classical Light Scattering Data for the Copolymers of DADMAC (M_1) with DAMAPS (M_2) in 1 M NaCl

sample	M_2 in copolymer (mol %)	dn/dc (mL/g)	$M_w \times 10^{-4}$ (g mol^{-1})	$A_2 \times 10^4$ (mL mol g^{-2})	DP$_w$ × 10^{-2}
DADMAC	0[b]	0.171 ± 0.003	5.16	5.54	3.2
DADS11	11	0.168 ± 0.003	5.97	4.75	3.6
DADS23	23	0.173 ± 0.001	6.51	3.90	3.6
DADS40	40	0.157 ± 0.003	7.28	2.24	3.8
DADS55	55	0.158 ± 0.001	7.22	1.89	3.5
DADS82	82	0.157 ± 0.001	7.87	2.07	3.6
DADS100	100[b]	0.153 ± 0.001	8.42	2.14	3.6

[a] From inverse gated-decoupled ^{13}C NMR (D_2O). [b] Theoretical value.

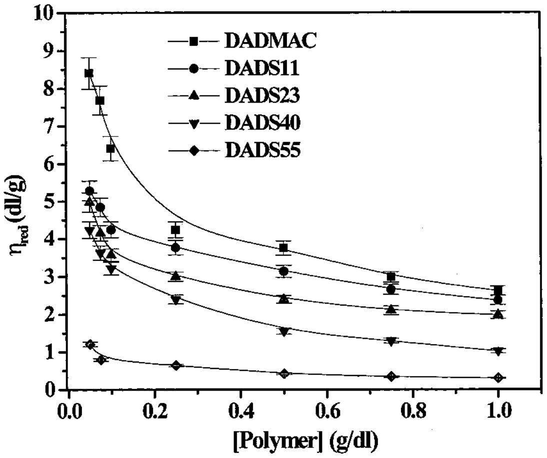


Figure 5. Reduced viscosity as a function of polymer concentration for the homopolymer of DADMAC and copolymers of DADMAC and DAMAPS in deionized water (T = 25 °C, γ = 5.96 s^{-1}).

Results and Discussion

Monomer Synthesis. 3-(N,N-Diallyl-N-methyl ammonio)propanesulfonate (DAMAPS) was synthesized by the ring-opening reaction of 1,3-cyclopropane sultone with N,N-diallyl-N-methylamine as shown in Scheme 1. Monomer structure was confirmed by elemental analysis, ^{1}H, ^{13}C NMR, and DEPT135 as shown in Figures 1 and 2.

Synthesis and Compositional Analysis of Cyclocopolymers. The copolymerization of DADMAC with DAMAPS was conducted photochemically as depicted in Scheme 2. The water soluble photoinitiator utilized was 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959). This initiator undergoes a Norrish type I cleavage leading to the formation of the initiating species. This mechanism of photoinitiation was chosen since facile production of high concentrations of radicals occurs in short lengths of time, an attribute that is not typically observed in classical thermal polymerization of the diallylammonium salts. No phase separation or precipitation of the polymers occurred during polymerization, indicating homogeneous polymerization conditions persisted throughout the reaction.

Representative inverse gated decoupled ^{13}C NMR spectra are shown in Figure 3. Peak assignments were confirmed through DEPT135 analysis. (Data are not shown.) The five-membered ring structure found in poly(DADMAC)[40] was retained for each copolymer regardless of the incorporation of the sulfobetaine mer unit. Also, the cis conformation, which is the primary isomer found in the DADMAC homopolymer,[40] was also confirmed in the sulfobetaine copolymers by analysis of the backbone carbon resonances at 28.8 and 40.7 ppm for the cis isomer and 32.6 and 45.7 ppm for the trans isomer. (Data summarized in Table 1.)

Copolymer compositions were determined by inverse gated decoupled ^{13}C NMR according to eq 1, where I_i, I_a, I_e, I_b, I_f, I_c, and I_g represent the integrated intensities corresponding to carbons i, a, e, b, f, c, and g, respectively (Figure 3).

$$\text{mol \% DAMAPS (M2)} = \frac{2I_i}{3}\left(\frac{1}{I_a+I_e}+\frac{1}{I_b+I_f}+\frac{1}{I_c+I_g}\right) \quad (1)$$

From the experimentally determined compositions of the low-conversion samples, reactivity ratios of $r_1 = 1.14 \pm 0.05$ and $r_2 = 0.96 \pm 0.05$ for DADMAC(M_1)/DAMAPS(M_2) were determined by a nonlinear least-squares method.[41] The experimentally measured values of copolymer composition as a function of feed compositions are shown in Figure 4; the dashed line represents ideal incorporation. Random (nearly ideal) incorporation was expected due to the identical polymerizable moieties present in DADMAC and DAMAPS.

Multiangle Laser Light Scattering. Table 2 shows the weight-average molecular weights determined by Berry plots at 25 °C in 1 M NaCl. The molecular weights vary from 5.16×10^4 to 8.42×10^4 g mol^{-1}. While these values might seem low for free radical polymerizations, these are typical for diallylammonium salt monomers. The likely reason for moderate molecular weight polymers is chain transfer to monomer involving the labile allylic hydrogen atoms. The second virial coefficients (A_2) for this copolymer series in 1 M NaCl lie between 5.54×10^{-4} and 1.89×10^{-4} mL mol g^{-2}. It is important to note that the range of the degree of polymerization for this copolymer series remains narrow, $(3.2-3.8) \times 10^2$, for otherwise identical copolymerization conditions. Therefore, the kinetic chain length appears quasi-independent of the monomer feed ratio, a feature which is in good agreement with $r_1 \sim r_2 \sim 1$ and provides further support for the identical polymerization behavior of the two monomers. Also, since the values obtained for the DP$_w$ for each copolymer are similar, any differences in solution properties are a result of changes in chemical composition and not due to the length of the copolymer chain.

Dilute Solution Behavior. Effects of Copolymer Composition and Added NaCl. During initial solubil-

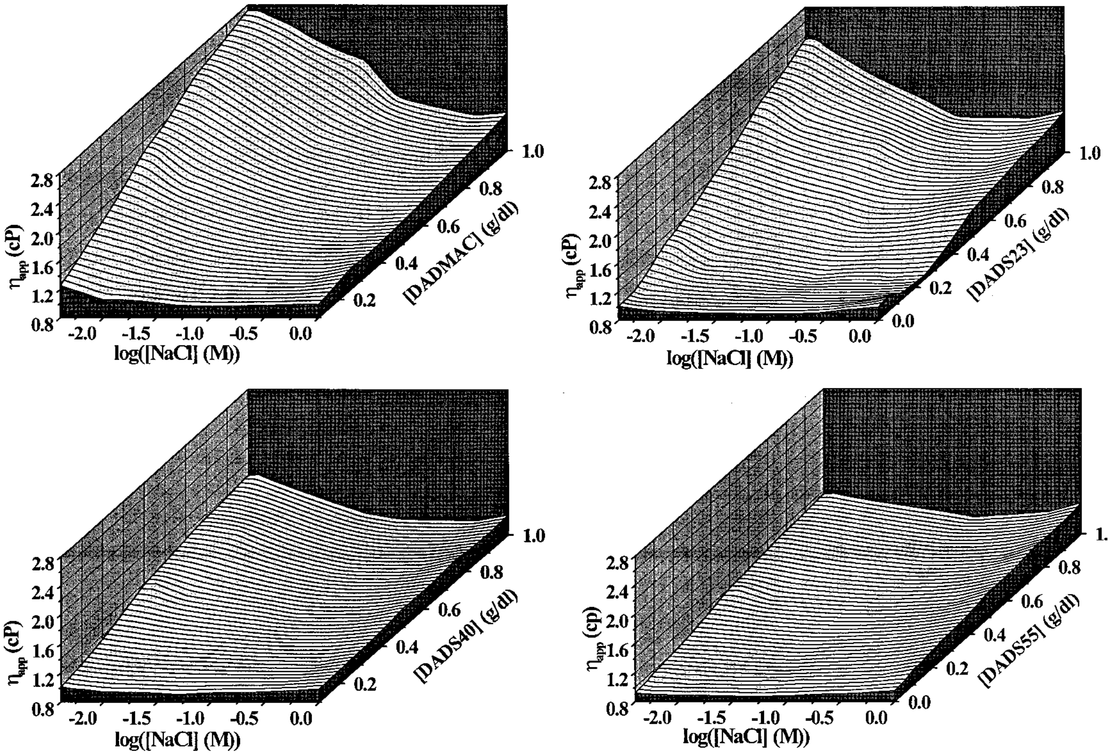


Figure 6. Apparent viscosity for the homopolymer of DADMAC and three copolymers of DADMAC and DAMAPS as functions of NaCl and polymer concentrations ($T = 25$ °C, $\gamma = 5.96$ s^{-1}).

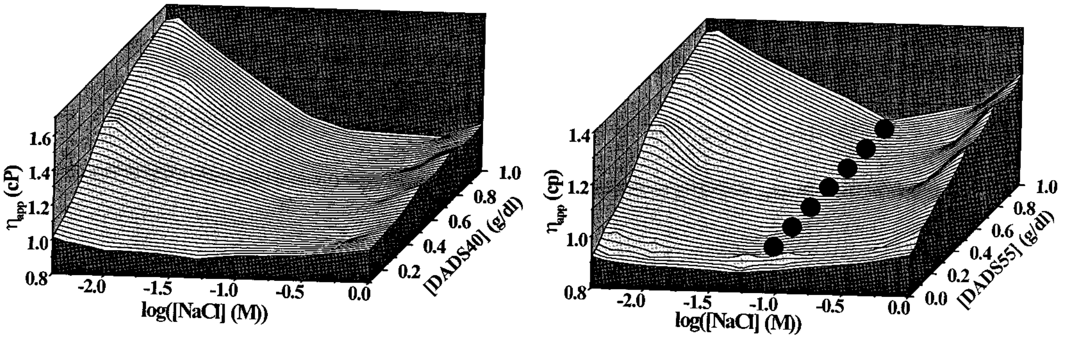


Figure 7. Apparent viscosity for DADS40 and DADS55 as functions of NaCl and polymer concentrations ($T = 25$ °C, $\gamma = 5.96$ s^{-1}). (● represents regions of macroscopic phase separation.)

ity experiments, it was discovered that copolymers containing ≤55 mol % of the sulfobetaine moiety were soluble in deionized water, a characteristic not commonly attributed to polysulfobetaines. In this case, the charge–charge repulsion of the excess positive charges along the polymer backbone (DADMAC mer units) allows the polymer to assume an expanded conformation in deionized water. This is illustrated in Figure 5, which shows the reduced viscosity of the DADS series in deionized water as a function of polymer concentration. It may be seen from Figure 5 that the DADS series exhibits classical polyelectrolyte solution behavior—in that the reduced viscosity increases dramatically as the polymer concentration decreases. However, the magnitude of the response diminishes with increased incorporation of the sulfobetaine mer units due to the replacement of an ionic charge with a dipole. It is likely that chain collapse occurs due to dipole–dipole intramolecular interactions between sulfobetaine moieties. (μ of the zwitterionic moiety has been determined to be 23.0 D for triethylammoniopropanesulfonate.[42]) Also, it should be noted that the reduced viscosity decreases as the incorporation of the sulfobetaine moiety increases, again from the intramolecular aggregation brought about by dipole–dipole interactions.[23] This collapse is also observed in light scattering by a decrease in the polymer–solvent interaction parameter, A_2, as the mole percent sulfobetaine increases (Table 2).

The aqueous solution properties of this copolymer series were further evaluated by observing apparent viscosity changes with increasing polymer concentration and ionic strength (Figure 6). Data for the homopolymer of DADMAC and three copolymers of DADMAC and DAMAPS are plotted. The apparent viscosities of the polymer solutions decrease as the molar incorporation of the sulfobetaine moiety increases for selected values of ionic strength. Also, as the ionic strength of the aqueous medium is increased, the apparent viscosity of each polymer solution decreases, a characteristic common to polyelectrolytes. However, for copolymers with higher incorporations of the sulfobetaine, an increase in the apparent viscosity at elevated NaCl concentrations is observed. Evidently, the initial decrease in apparent viscosity is due to the shielding of the charge–

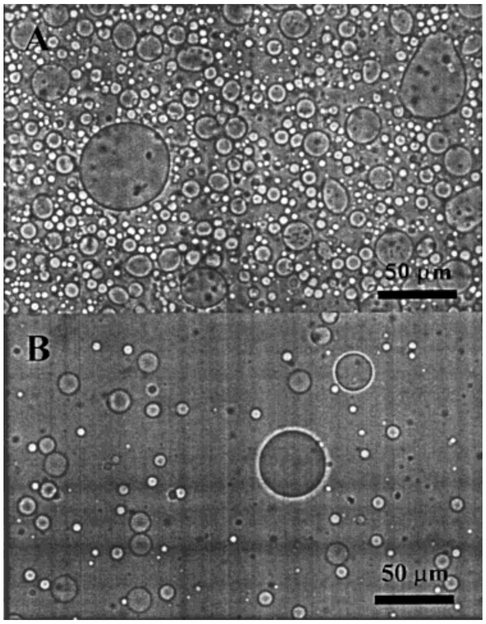


Figure 8. Optical micrographs of aqueous solutions of DADS55 in (A) 0.1 and (B) 0.5 M NaCl ($T = 25$ °C, [DADS55] = 1.0 g/dL).

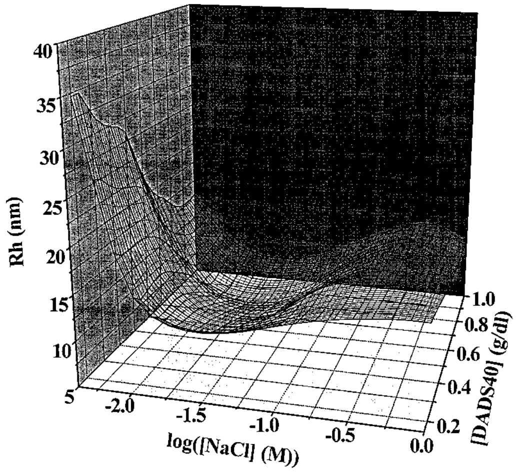


Figure 9. Hydrodynamic radius of DADS40 as functions of NaCl and polymer concentrations ($T = 25$ °C).

charge repulsions along the polymer backbone. When these repulsive forces are diminished, the dipole–dipole interactions allow the copolymer to assume a collapsed conformation, which is manifested by a minimum in the apparent viscosity. As the ionic strength of the medium is increased further, the dipole–dipole interactions are minimized, and chain expansion occurs. The increase in apparent viscosity is better visualized by replotting the data on a smaller scale as depicted in Figure 7.

It must be pointed out that, for DADS55 at 0.075 M < [NaCl] < 0.5 M, the dipole–dipole associations are sufficiently prevalent to bring about macroscopic phase separation. Figure 8 clearly illustrates the presence of polymer-rich and polymer-poor phases at [NaCl] = 0.1 and 0.5 M. Above and below this critical concentration range, a macroscopically homogeneous solution is observed.

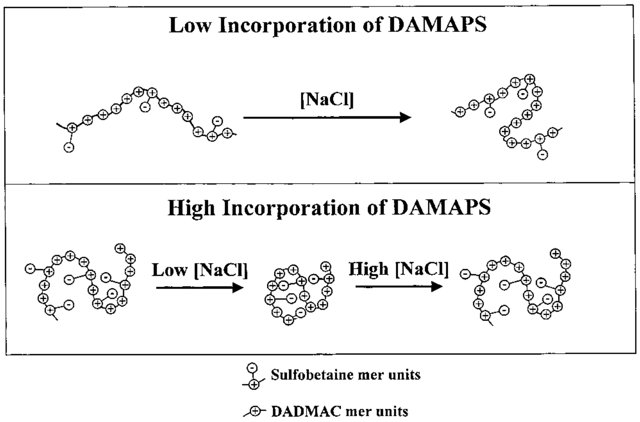


Figure 10. Proposed polymer conformational changes for copolymers of DADMAC and DAMAPS as a function of NaCl concentration.

To study the above macroscopic events on the molecular level, dynamic light scattering experiments were preformed on the DADS40 copolymer as a function of NaCl and polymer concentrations. DADS40 is especially interesting since it maintains macroscopic homogeneity throughout the NaCl and polymer concentration ranges studied and exhibits a large increase in viscosity at elevated NaCl concentrations. Figure 9 is a three-dimensional plot of the hydrodynamic radius of the DADS40 copolymer as functions of NaCl and polymer concentrations. As can be discerned from the figure, for any given polymer concentration, as the ionic strength of the medium is increased, the hydrodynamic radius initially decreases, reaches a minimum, and then increases. This correlates directly with the apparent viscosity data illustrated in Figure 8.

On the basis of the low-shear viscosity and dynamic light scattering data, an association model for the copolymers of DADMAC and DAMAPS as a function of NaCl concentration is presented in Figure 10. For copolymers with a low molar incorporation of the sulfobetaine moiety, classical polyelectrolyte behavior is observed. As the ionic strength of the medium is increased, the small molecule electrolyte by-ions shield the backbone cationic repulsions, allowing the polymer to assume a more random conformation. For copolymers containing 40–55 mol % DAMAPS, the polymer chain assumes a compact conformation due to intramolecular dipole–dipole interactions. However, a sufficient number of excess positive charges along the copolymer backbone allow solubility. As the ionic strength is further increased, the charge–charge repulsion of the excess positive charge is diminished, and a further collapse of the polymer chain is realized. (This collapse leads to macroscopic phase separation of the DADS55 copolymer.) As the ionic strength is increased further, the dipole–dipole interactions of the sulfobetaine mer units are diminished, allowing an expansion of the polymer coil.

The above model is consistent with recent theoretical efforts devoted to understanding the conformations of linear polyampholyte chains.[43–46] For a polyampholyte with excess positive or cationic charge, the electrostatic interactions can be characterized by an excluded volume:

$$\nu^* = -\frac{\pi(f l_B)^2}{\kappa_s} + \frac{4\pi l_B \Delta f^2}{\kappa_s^2} \qquad (2)$$

where l_B is the Bjerrum length, f is the total fraction of charged monomers, and κ_s is the usual Debye–Hückel screening parameter. The first term of eq 2 describes the screening of attractive polyampholyte interactions, and the second term describes the screening of repuslive interactions between excess charges. The electrostatic excluded volume is positive at low ionic strength, inducing a stretching of the chain. As the ionic strength is increased, the screening of Coulombic repulsions is stronger than the screening of the polyampholyte attractions, and the excluded volume becomes negative, thus inducing chain collapse. As the ionic strength is increased, the chain swells again because of the screening of the attractive polyampholyte interactions.

Conclusions

A sulfobetaine monomer, 3-(*N*,*N*-diallyl-*N*-methylammonio)propanesulfonate, has been synthesized and copolymerized with *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride. The resulting polymers maintain the five-membered ring structure common to diallylammonium salts. The solution behavior is dictated by two opposing forces: cationic charge−charge repulsion along the polymer backbone from DADMAC mer units and the dipole−dipole attractive forces created by the presence of the sulfobetaine DAMAPS unit. Stimuli-responsive behavior including phase separation can be realized by adjusting ionic strength.

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