

# Synthesis and Solution Properties of Amphiphilic Cyclopolymers and Terpolymers of 4-Methoxycarbonyl-1,1-diallylpiperidinium Chloride, Diallyloctadecylammonium Chloride, and Sulfur Dioxide

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**ABSTRACT:** The cyclooligomerization of a hydrophilic monomer, 4-methoxycarbonyl-1,1-diallylpiperidinium chloride, with a hydrophobic monomer, diallyloctadecylammonium chloride (3–7 mol %), and sulfur dioxide in dimethyl sulfoxide with azobisisobutyronitrile as the initiator afforded a series of water-soluble cationic polyelectrolytes (CPEs) at well over 90% yields. Acidic (HCl) hydrolysis of the ester groups in CPEs to CO<sub>2</sub>H groups gave the cationic acid salts (CASs), which on treatment with 1 equiv of NaOH, furnished polyzwitterions (PZs). Contrary to the well-known behavior that the normal PZs are only soluble in brine, PZ in the absence of the hydrophobe was found to be soluble in salt-free water. The solution properties of the resulting series of interconvertible polymers (CPE → CAS ⇌ PZ) were investigated by viscometric techniques. At a shear rate of 0.36 s<sup>-1</sup>, 2 g/dL solutions of CPE having

0, 3, 5, and 7 mol % hydrophobe in salt-free water at 30°C were found to have apparent viscosity values of 4000, 164,000, 670,000, and 1,430,000 cps, respectively. Polymer–surfactant interactions were investigated with the cationic surfactant cetyltrimethylammonium bromide (CTAB). Tremendous increases in the viscosity values of the CPE having 7 mol % of the hydrophobe were observed in the presence of the surfactant at a shear rate of 0.36 s<sup>-1</sup>; a 0.75 g/dL solution of the polymer in salt-free water was found to have apparent viscosity values of 18,000 and 235,000 cps in the absence and presence, respectively, of 3 mM CTAB. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2951–2958, 2010

**Key words:** cyclooligomerization; polyelectrolytes; water-soluble polymers

## INTRODUCTION

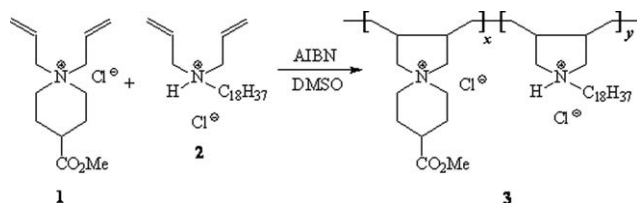
The polymerization reaction of a zwitterionic monomer with charges of both algebraic signs (M<sup>±</sup>) in the same molecular framework leads to polyzwitterions (PZs);<sup>1–3</sup> however, the presence of both M<sup>+</sup> and M<sup>-</sup> in the same polymer chain constitutes a polyampholyte with or without a charge symmetry. Although biopolymers such as proteins or DNA mediate life processes, commercial polyampholytes and PZs, which seem to mimic biopolymers, have offered many new applications. PZs derived from acrylamide- and acrylate-based zwitterionic monomers have been used widely in industries dealing with textiles, medical products, charge-dispersing agents, colloids, and related materials.<sup>4</sup> Butler's cyclooligomerization reaction of zwitterionic diallylammonium monomers or their copolymerizations with sulfur dioxide (SO<sub>2</sub> or M<sub>3</sub>) have been attractive for the synthesis of

PZs.<sup>5–10</sup> Polyampholytes and PZs, unlike polyelectrolytes, exhibit antipolyelectrolyte behavior,<sup>6,11–13</sup> that is, an enhancement in the viscosity and solubility in the presence of added electrolytes (e.g., NaCl), because of the neutralization of the ionically cross-linked network in a collapsed coil conformation of the polymers. There have been some reports<sup>14–19</sup> that described the synthesis of associating ionic copolymers prepared by Butler's cyclooligomerization technique. Above a hydrophobic association concentration (C<sub>HA</sub>\*), interchain associations of the hydrophobic groups led to a more pronounced increase in the viscosity by a reversible formation of the three-dimensional physical crosslinks of the polymer chains.

In pursuit of hydrophobically tailored, pH-responsive polymers, we continued to synthesize a series of cyclopolymers of a hydrophilic monomer, 4-methoxycarbonyl-1,1-diallylpiperidinium chloride (**1** or M<sub>1</sub>), and a hydrophobic monomer, diallyloctadecylammonium chloride (**2** or M<sub>2</sub>), and their terpolymers with SO<sub>2</sub> (Scheme 1). The conversion of the carbomethoxyl pendants to carboxylates (–CO<sub>2</sub>'s) in the polymer backbone would allow us to study polyelectrolyte - to - PZ transitions involving polymers having identical degrees of polymerization.

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Scheme 1

Interactions of hydrophobically modified polymers with surfactants have received considerable interest because of their applications in various industrial fields.<sup>20,21</sup> In this context, we also wanted to study the interactions of the new polymers with both cationic and anionic surfactants.

## EXPERIMENTAL

### Materials

Piperidine-4-carboxylic acid, allyl chloride, diallylamine, and 1-bromooctadecane were obtained from Fluka Chemie AG (Buchs, Switzerland) and were used as received. 2,2'-Azobisisobutyronitrile (AIBN) from Fluka Chemie AG was purified by crystallization from a chloroform-ethanol mixture. Dimethyl sulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a boiling point of 64–65°C (4 mmHg). All of the glassware was cleaned with deionized water. **1**<sup>22</sup> and **2**<sup>15</sup> were prepared with piperidine-4-carboxylic acid/allyl chloride and diallylamine/1-bromooctadecane, respectively, as described previously.

### Physical methods

The melting points were recorded in a calibrated Electrothermal-IA9100 digital melting point apparatus, Electrothermal Engineering Ltd (Essex, UK) at heating rates of 1°C/min in the vicinity of the melting points. Elemental analyses were carried out in a Carlo-Erba elemental analyzer model 1102, (Milan, Italy). IR spectra were recorded on a PerkinElmer

16F PC Fourier transform infrared spectrometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the polymers were measured on a JEOL LA 500-MHz spectrometer. The viscosity measurements were made on an Ubbelohde viscometer (with a viscometer constant of 0.005718 cSt/s at all temperatures) with CO<sub>2</sub>-free water. A gentle stream of N<sub>2</sub> was passed through distilled deionized water at 90°C for 15 min to remove dissolved gases. This water was used in the viscosity measurements in the salt-free and salt (NaCl, 99.9% purity) solutions. A digital Brookfield rotational viscometer with a Ultra Low (UL) adaptor or SC4-18 spindle accessories was used to measure the apparent viscosities at various shear rates.

### General procedure for the cyclocopolymerization of 1 (M<sub>1</sub>)/2 (M<sub>2</sub>)

All of the polymerizations were carried out under the conditions described in Table I. A solution of the monomers (1/2) in DMSO in a round-bottom flask was purged with N<sub>2</sub>. After the required amount of the initiator AIBN was added (as listed in Table I), the mixture was stirred with a magnetic stirring bar in a closed flask at the specified temperature and time. The reaction mixture was dissolved in a minimum amount of methanol and was precipitated in acetone. This process was repeated three times to ensure complete removal of the unreacted monomers. Polymer **3** was then dried to a constant weight at 60°C *in vacuo* and stored in a desiccator.

### General procedure for the terpolymerization of 1/2/SO<sub>2</sub> (Scheme 2)

All of the polymerizations were carried out under the conditions described in Table II. In a typical experiment, SO<sub>2</sub> was absorbed in a solution of monomers **1** (M<sub>1</sub>) and **2** (M<sub>2</sub>) in DMSO in a 25-cm<sup>3</sup> round-bottom flask. The required amount of initiator (AIBN; as listed in Table II) was then added under N<sub>2</sub>, and the closed flask was stirred with a magnetic stirring bar at 60°C for 24 h. The magnetic stirring

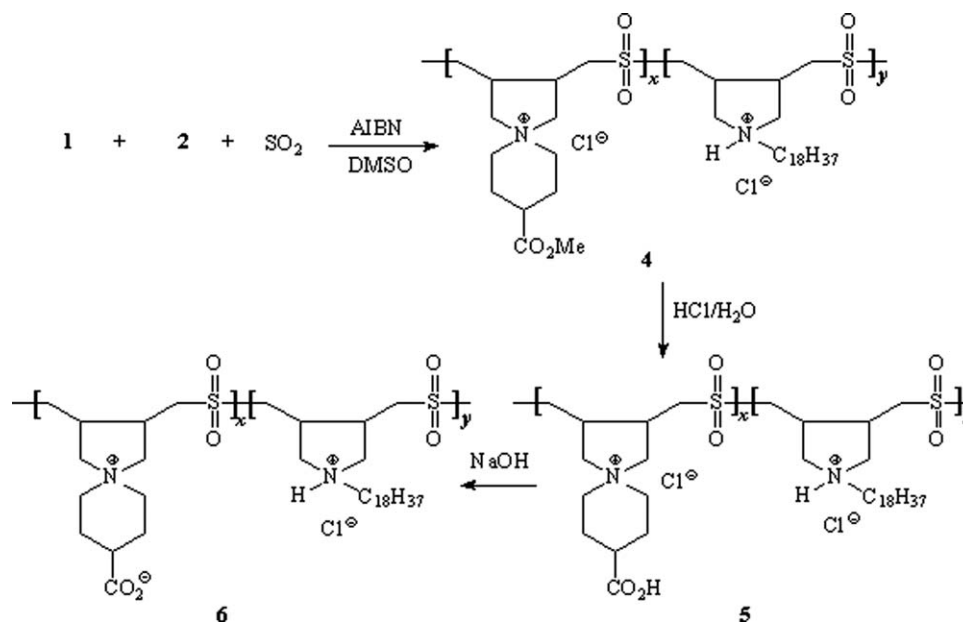
TABLE I  
Cyclocopolymerization of Monomers 1 (M<sub>1</sub>) and 2 (M<sub>2</sub>)

Entry no.	Sample	M <sub>1</sub> (mmol)	M <sub>2</sub> (mmol)	M <sub>1</sub> : M <sub>2</sub> (mol %) <sup>a</sup>		Yield (%)	Intrinsic viscosity (dL/g) <sup>b</sup>
				Feed	Polymer		
1	3-M <sub>2</sub> -0	20.0	0	100 : 0	100 : 0	79	0.264
2	3-M <sub>2</sub> -1.8	19.4	0.6	97 : 3	98.2 : 1.8	75	0.230
3	3-M <sub>2</sub> -2.8	19.0	1.0	95 : 5	97.2 : 2.8	72	0.204
4	3-M <sub>2</sub> -3.7	18.6	1.4	93 : 7	96.3 : 3.7	34	0.190

Polymerization reactions were carried out in DMSO (8.0 g) in the presence of AIBN (100 mg) at 62°C for 48 h.

<sup>a</sup> Determined by <sup>1</sup>H-NMR.

<sup>b</sup> Obtained by the extrapolation of the linear parts of the curves (usually with 0.25–0.0625 g/dL polymer solutions in 0.1N NaCl at 30°C measured with an Ubbelohde viscometer; viscometer constant (K) = 0.005718).



Scheme 2

bar stopped moving within minutes after the addition of the initiator. At the end of the elapsed time, the hard polymeric mass was crushed to a powder, soaked in acetone, filtered, and washed with a liberal excess of hot (50°C) acetone to ensure complete removal of the unreacted monomer (as indicated by <sup>1</sup>H-NMR). The white terpolymer 4 was then dried to a constant weight at 55°C *in vacuo* and stored in a desiccator.

4-M<sub>2</sub>-0 (Table II, entry 1,  $v_{\max}$ , KBr, cm<sup>-1</sup>): 3380, 2952, 1727, 1640, 1454, 1299, 1202, 1116, 928, 771, 523.

#### Acidic hydrolysis of polymer 4

A solution of 4-M<sub>2</sub>-0 (3.24 g, 10 mmol) in 6M HCl (50 cm<sup>3</sup>) was stirred in a closed flask at 50°C for 36 h (or until the hydrolysis of the ester group was

complete, as indicated by the absence of the methoxyl proton signals in the <sup>1</sup>H-NMR spectrum). The cationic acid salt (CAS) 5 was precipitated in acetone, filtered, and dried *in vacuo* at 60°C to a constant weight to give the white polymer 5-M<sub>2</sub>-0 (2.9 g, 94%). The other hydrophobe-containing polymers were hydrolyzed in a similar manner to those of the hydrolyzed polymers in greater than 90% yields.

5-M<sub>2</sub>-0 ( $v_{\max}$ , KBr, cm<sup>-1</sup>): 3419, 2957, 1720, 1455, 1401, 1301, 1202, 1129, 932, 526.

#### Thermal decomposition and elemental analyses of polyelectrolyte 4

There was a closed capillary at onset of thermal decomposition. At 260–265°C, 4-M<sub>2</sub>-0 softened. It darkens upon further heating with expansion at

TABLE II  
Terpolymerization of Monomers 1 (M<sub>1</sub>) and 2 (M<sub>2</sub>) and SO<sub>2</sub>

Entry no.	Sample	M <sub>1</sub> (mmol)	M <sub>2</sub> (mmol)	M <sub>1</sub> : M <sub>2</sub> in the polymer (mol %) <sup>a</sup>	Yield (%)	Intrinsic viscosity (dL/g) <sup>b</sup>		
						CPE 4	CAS 5 <sup>c</sup>	PZ 6 <sup>d</sup>
1	4-M <sub>2</sub> -0	20.0	0	100 : 0	95	0.682	0.476	0.614 <sup>e</sup>
2	4-M <sub>2</sub> -3	19.4	0.60	97 : 3	94	0.732	— <sup>f</sup>	— <sup>f</sup>
3	4-M <sub>2</sub> -5	19.0	1.0	95 : 5	95	— <sup>f</sup>	— <sup>f</sup>	— <sup>f</sup>
4	4-M <sub>2</sub> -7	18.6	1.4	93 : 7	96	— <sup>f</sup>	— <sup>f</sup>	— <sup>f</sup>

Polymerization reactions were carried out in DMSO (6.7 g) containing 20 mmol of SO<sub>2</sub> in the presence of AIBN (100 mg) at 60°C for 24 h.

<sup>a</sup> Determined by <sup>1</sup>H-NMR.

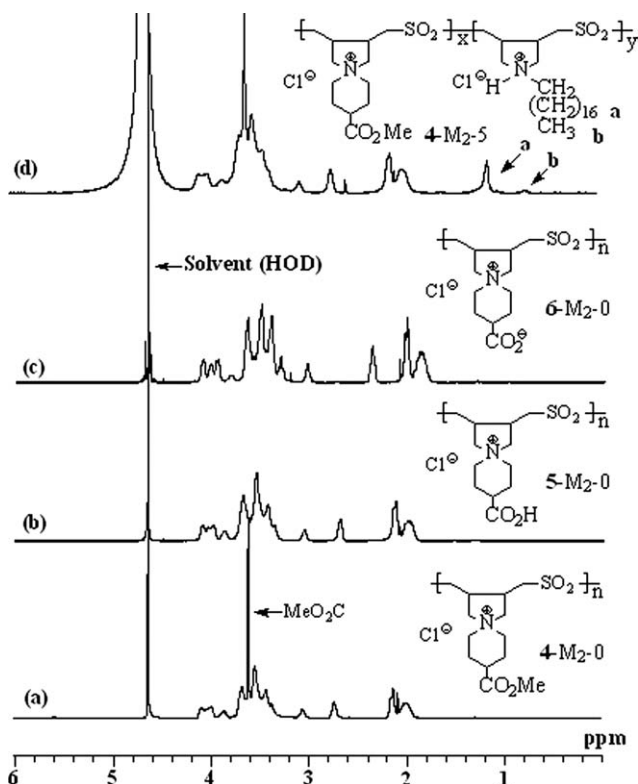
<sup>b</sup> Obtained by the extrapolation of the linear parts of the curves (usually with 0.25–0.0625 g/dL polymer solutions in 0.1N NaCl at 30°C measured with an Ubbelohde viscometer; viscometer constant (K) = 0.005718).

<sup>c</sup> Prepared by acid hydrolysis of the corresponding CPE (4).

<sup>d</sup> Prepared by the treatment of 5 with 1 equiv of NaOH.

<sup>e</sup> 0.660 in 0.5N NaCl and 0.895 in 1.0N NaCl.

<sup>f</sup> Not determined (insoluble).



**Figure 1**  $^1\text{H-NMR}$  spectra for (a) 4- $M_2$ -0, (b) 5- $M_2$ -0, (c) 6- $M_2$ -0, and (d) 4- $M_2$ -5 in  $\text{D}_2\text{O}$ .

275–280°C. At 255–260°C, 4- $M_2$ -5 turned brown, and at 270–275°C, it decomposed and turned blackish.

The elemental analyses ascertained the molar ratio of  $(M_1 + M_2):M_3$  as 1 : 1 for polymer 4. The  $^1\text{H-NMR}$  spectra for 4- $M_2$ -0, 5- $M_2$ -0, 6- $M_2$ -0, and 4- $M_2$ -5 are shown in Figure 1.

The elemental analyses for 4  $[(M_1\text{-SO}_2)_x(M_2\text{-SO}_2)_{1-x}]$  were as follows (the numbers in parentheses represent the calculated values for  $x \leq 1$ ):

- 4- $M_2$ -0: C, 47.9% (48.22%); H, 6.9% (6.85%); N, 4.2% (4.33%); S, 9.7% (9.90%).
- 4- $M_2$ -3: C, 48.4% (48.69%); H, 7.1% (6.97%); N, 4.2% (4.29%); S, 9.6% (9.82%).
- 4- $M_2$ -5: C, 48.8% (49.01%); H, 7.2% (7.05%); N, 4.2% (4.27%); S, 9.5% (9.76%).
- 4- $M_2$ -7: C, 49.1% (49.33%); H, 7.2% (7.12%); N, 4.1% (4.24%); S, 9.5% (9.71%).

## RESULTS AND DISCUSSION

### Synthesis and physical characterization of copolymer 3

Hydrophilic monomer 1 ( $M_1$ ) and hydrophobic comonomer 2 ( $M_2$ ) underwent cyclocopolymerization in the solvent DMSO with AIBN as the initiator to give copolymer 3 in moderate to good yields. The

polymerization conditions and intrinsic viscosities ( $[\eta]$ 's) of the resulting polymers are reported in Table I. Copolymer 3- $M_2$ -2.8 (entry 3, Table I), for instance, indicates the use of 5 mol % of hydrophobe 2 ( $M_2$ ) in the feed, whereas the incorporation was found to be 2.8 mol %, as determined by  $^1\text{H-NMR}$  spectroscopy. The incorporation of the hydrophobic monomers was calculated with  $^1\text{H-NMR}$  integration of the  $\text{CH}_3$  signal of the hydrophobe, which appeared at  $\delta 0.89$  ppm (in  $\text{CD}_3\text{OD}$ ) and was free of any overlapping signals.

The  $[\eta]$ 's in 0.1N NaCl were found to be low in comparison with many other polymers synthesized in our earlier studies.<sup>8–10,15–17</sup> A 2-g/dL solution of polymers 3- $M_2$ -2.8 or 3- $M_2$ -3.7 failed to give any indication of hydrophobic associations, as revealed by viscosity measurements. Because of the poor yields and incorporation of the hydrophobes (the hydrophobe molar percentage in the polymer was found to always be less than that in the feed), we switched our attention to the synthesis of the terpolymers from the polymerization of 1/2/ $\text{SO}_2$ .

### Synthesis and physical characterization of terpolymer 4

Monomer 1 ( $M_1$ ), comonomer 2 ( $M_2$ ), and  $\text{SO}_2$  underwent cyclo-terpolymerization in the solvent DMSO with AIBN as the initiator to give cationic polyelectrolytes (CPEs; 4) at over 90% yields. Terpolymer 4- $M_2$ -5 (entry 3, Table II), for instance, indicated the use of 5 mol % of the hydrophobe ( $M_2$ ) 2 in the feed, whereas the incorporation was also found to be 5 mol %, as determined by  $^1\text{H-NMR}$  spectroscopy (*vide infra*). Cyclocopolymerization of hydrophilic monomer 1 with  $\text{SO}_2$  (in the absence of hydrophobic monomer) under the same conditions was carried out to obtain CPE 4- $M_2$ -0 (entry 1, Table II). Hydrophobe incorporations were found to match closely with the feed ratio. This was expected because the polymers were obtained at high conversions (>90%). The sulfur analyses ascertained the molar ratio of  $(M_1+M_2+M_3) : \text{SO}_2$  as 1 : 1. The 4 CPEs were hydrolyzed in 6M aqueous HCl to produce 5 CASs (at well over 90% yields), which on treatment with 1 equiv of NaOH afforded 6 PZs.

### IR and NMR spectra

The IR spectra of 4- $M_2$ -0 and 5- $M_2$ -0 (Table II, entry 1) indicated the presence of the  $\text{SO}_2$  group by its characteristic strong bands at about 1300 and 1120  $\text{cm}^{-1}$ , which were assigned to the asymmetric and symmetric vibrations of  $\text{SO}_2$  units. The  $^1\text{H-NMR}$  spectra for 4- $M_2$ -0, 5- $M_2$ -0, 6- $M_2$ -0, and 4- $M_2$ -5 are shown in Figure 1. It was evident that the  $\text{CO}_2\text{Me}$  protons, which appeared at  $\delta = 3.6$  ppm (s) for 4-

M<sub>2</sub>-0, were absent in the spectrum of 5-M<sub>2</sub>-0 and 6-M<sub>2</sub>-0; this indicated the complete hydrolysis of the ester groups. The incorporation of the hydrophobic monomers was calculated with <sup>1</sup>H-NMR analysis.<sup>23</sup> The hydrophobic repeating unit had a total of 47 H atoms (excluding NH<sup>+</sup>, which was exchanged to ND<sup>+</sup>); the integrated area (*A*) in the range δ = 0.6–1.65 belonged to 35 H atoms of the hydrophobic tail (CH<sub>2</sub>)<sub>16</sub>CH<sub>3</sub>. The area of a single proton then became *A*/35. The remaining 12 H atoms of the hydrophobic repeating unit then contributed an area of 12*A*/35 to the total area (*B*) under δ = 1.8–4.2, where signals of the entire 22 H atoms of the hydrophilic repeating unit also appeared. The area belonging to a single proton of the hydrophilic repeating unit then equated to [*B* – (12*A*/35)]/22. The hydrophobic incorporation was then determined with the following equation:

$$\text{Hydrophobe (mol\%)} = \frac{A/35}{\frac{A}{35} + \frac{B - (12A/35)}{22}} \times 100$$

#### Solubility, viscosity measurements, and solution properties

To allow meaningful assessment of the associative behaviors of the synthesized polymers, the polymerization conditions were kept as rigorously similar as possible to obtain polymers with similar degrees of polymerizations. In fact, all of the polymerizations were carried out simultaneously with a single oil bath.

All of the CPEs **4** were found to be soluble in salt-free water; whereas 4-M<sub>2</sub>-0 and 4-M<sub>2</sub>-3 were soluble in 0.1*N* NaCl, the polymers having higher hydrophobe contents were insoluble (Table III). The CAS **5** polymers were all soluble in salt-free water, whereas only 5-M<sub>2</sub>-0 was soluble in 0.1*N* NaCl. The PZ **6**-M<sub>2</sub>-0, obtained by treatment of CAS 5-M<sub>2</sub>-0 with 1 equiv of NaOH, was found to be soluble in water or saline media; the other PZs containing the hydrophobes were found to be insoluble in of the salt-free and salt (NaCl)-added media. Contrary to the well-

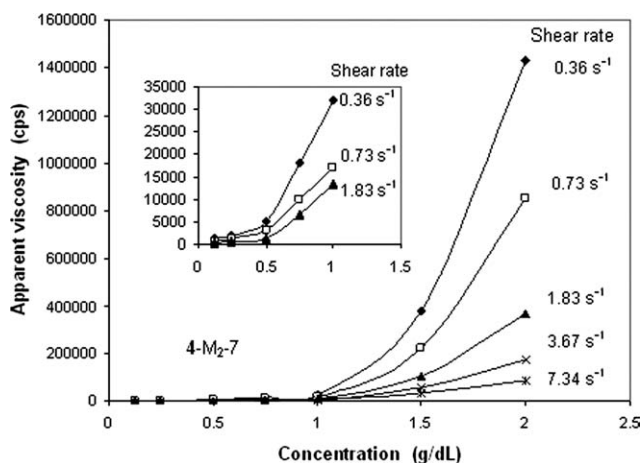
known behavior that normal PZs are only soluble in brine, both CAS 5-M<sub>2</sub>-0 and PZ 6-M<sub>2</sub>-0 were found to be soluble in salt-free water. A considerable number of polycarbobetaines and sulfobetaines were reported to be soluble in salt-free and salt (NaCl)-added solutions.<sup>24,25</sup> The solubility behavior of polycarbobetaines has been found<sup>25</sup> to depend on the number of methylene units between the opposite charges; those having a single methylene unit and carboxyl p*K*<sub>a</sub> values of 2.0 or lower were found to be insoluble in salt-free water but soluble in salt-added solutions. The negative charges on polycarbobetaines, having apparent carboxyl p*K*<sub>a</sub> values greater than 2.0 as a result of the increasing number of methylene spacers between the zwitterions, were expected to be less dispersed and, hence, more hydrated.<sup>8,24,26</sup> In such a scenario, carboxylate groups tend to exhibit weaker Coulombic interactions with the cationic charges;<sup>27</sup> as a result, the polymers become soluble in salt-free water. Sterically crowded cationic charges are also reported to be unable in manifesting effective intramolecular or intermolecular Coulombic interactions; this, thereby, leads to its solubility in salt-free water.<sup>6,28</sup> The temperature and molecular weight also have a say in the solubility behavior of polybetaines.<sup>29</sup> Simply being a PZ is thus not enough to dictate the solubility behavior; there are many other factors, such as those mentioned previously, that needed to be considered to rationalize the solubility behavior of the polymers in this study. Presumably, because of the longer distance of five intervening bonds between the charge centers of the zwitterionic motives and the geometric constraints imposed on an equatorially oriented –CO<sub>2</sub><sup>–</sup> moiety, the dipolar attraction in PZ 6-M<sub>2</sub>-0 was not so effective; this made the polybetaine soluble in salt-free water. Also, the carboxyl p*K*<sub>a</sub> value in PZ 6-M<sub>2</sub>-0 was expected to be much higher than 2.0, which would thus make it soluble in water. However, the reason for the insolubility of the hydrophobically modified PZs **6** in water or 0.1*N* could have been the combined effects of the hydrophobic zwitterionic motifs and the hydrophobic tails in an aqueous environment hostile to the hydrophobic functionalities.

Extrapolation of linear part of the viscosity plots in the concentration range 0.25–0.0625 g/dL permitted us to determine the [η]'s of the polymers in 0.1*N* NaCl (Tables I and II). Polymers 4-M<sub>2</sub>-0 and 4-M<sub>2</sub>-3 were found to have similar [η]'s. The [η]'s of polymers 4-M<sub>2</sub>-0, 5-M<sub>2</sub>-0, and 6-M<sub>2</sub>-0, having similar degrees of polymerizations (because **5** and **6** were directly derived from **4**), were found to be 0.682, 0.476, and 0.614 dL/g, respectively, in 0.1*N* NaCl. The rationale behind the lowest [η] of 5-M<sub>2</sub>-0 was attributed to the presence of intramolecular H-bonding between the CO<sub>2</sub>H groups; this led to a reduced

TABLE III  
Solubility of CPE **4**, CAS **5**, and PZ **6** in Salt-Free-Water and 0.1*N* NaCl at 23°C

Hydrophobe	Salt-free water			0.1 <i>N</i> NaCl		
	<b>4</b>	<b>5</b>	<b>6</b>	<b>4</b>	<b>5</b>	<b>6</b>
M <sub>2</sub> -0	+	+	+	+	+	+
M <sub>2</sub> -3	+	+	–	+	–	–
M <sub>2</sub> -5	+	+	–	–	–	–
M <sub>2</sub> -7	+	+	–	–	–	–

+ = soluble; – = insoluble.

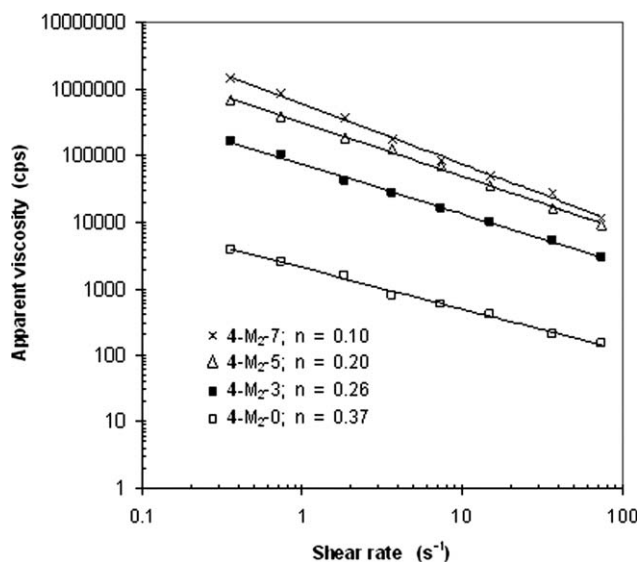


**Figure 2** Variation of the viscosity with the concentration of 4-M<sub>2</sub>-7 at various shear rates in salt-free water at 30°C. The inset shows the variation in the lower concentration range.

hydrodynamic volume of the polymer. Also, ionization of some of the CO<sub>2</sub>H groups resulted in the presence of a certain percentage of the PZ motifs in the polymer backbone, which thereby further reduced the hydrodynamic volume and, hence,  $[\eta]$ .  $[\eta]$  of PZ 6-M<sub>2</sub>-0 in the salt-free, 0.5N NaCl, and 1.0N NaCl were determined to be 0.614, 0.660, and 0.895 dL/g, respectively; this, thereby, indicated the PZ nature of the polymer (Table II, footnote f).

Figure 2 displays the variations of the viscosity with concentration of 4-M<sub>2</sub>-7 at various shear rates in salt-free water. Hydrophobic associations ( $C_{HA}^*$ ), as indicated by exponential increases in the viscosity values, began to manifest around a value of 0.5 g/dL for the polymer. The strong interchain associations contributed significantly to the thickening.<sup>18,30,31</sup>

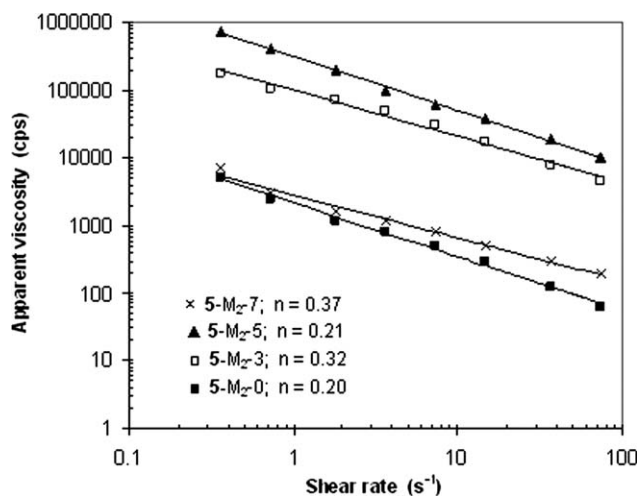
Figure 3 displays the variation of viscosity with shear rates of 2 g/dL solutions of the 4-M<sub>2</sub>-0, 4-M<sub>2</sub>-3, 4-M<sub>2</sub>-5, and 4-M<sub>2</sub>-7 samples in salt-free water at 30°C; at a shear rate of 0.36 s<sup>-1</sup>, the polymers were found to have apparent viscosity values of 4000, 164,000, 670,000, and 1,430,000, cps, respectively. Among the CPEs, polymer 4-M<sub>2</sub>-7 was, thus, found to have the highest viscosity values, higher by a factor of 360 than that that of 4-M<sub>2</sub>-0. The viscosity values of 4-M<sub>2</sub>-3 decreased in 0.1N NaCl; at a shear rate of 0.36 s<sup>-1</sup>, the viscosity in the salt-free water and 0.1N NaCl became 164,000 and 23,000, respectively (not shown in the figure). The increase in the hydrophobe content resulted in an increase in shear thinning, as indicated by the values of the power-law index ( $n$ ), which are shown in Figure 3. The  $n$  values of 4-M<sub>2</sub>-0, 4-M<sub>2</sub>-3, 4-M<sub>2</sub>-5, and 4-M<sub>2</sub>-7 were determined to be 0.37, 0.26, 0.20, and 0.10, respectively. Under high shear, the hydrophobic associations were disrupted; this led to the highest shear thinning for polymer 4-M<sub>2</sub>-7, which contained the



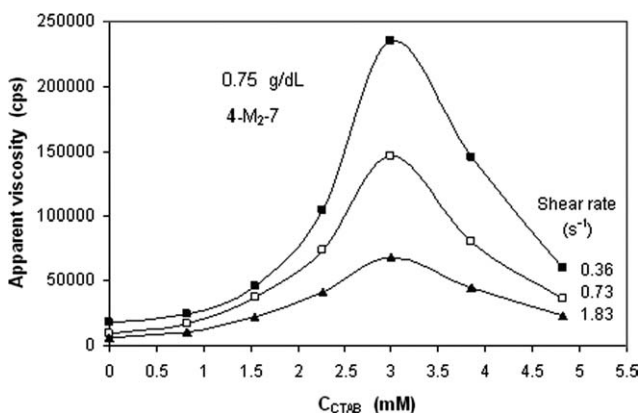
**Figure 3** Variation of the viscosity of 2 g/dL solutions of 4-M<sub>2</sub>-0, 4-M<sub>2</sub>-3, 4-M<sub>2</sub>-5, and 4-M<sub>2</sub>-7 at various shear rates in salt-free water at 30°C.

highest molar percentage of hydrophobes. A simple shear molecular theory<sup>32</sup> led to a power-law expression for high shear rates, with  $n = 0.33$ .

Figure 4 displays the variation of viscosity with shear rates of 2 g/dL solutions of 5-M<sub>2</sub>-0, 5-M<sub>2</sub>-3, 5-M<sub>2</sub>-5, and 5-M<sub>2</sub>-7 samples in salt-free water at 30°C; at a shear rate of 0.36 s<sup>-1</sup>, the polymers were found to have apparent viscosity values of 5000, 174,000, 740,000, and 7000, cps, respectively. Among the CAS 5 polymers, 5-M<sub>2</sub>-5 was, thus, found to have the highest viscosity value. Note the tremendous drop in the viscosity values of 5-M<sub>2</sub>-7 in comparison with 4-M<sub>2</sub>-7 (*vide supra*). This demonstrated the increasing participation of intramolecular micellization, possibly assisted by intrachain and interchain hydrogen-



**Figure 4** Variation of the viscosity of 2 g/dL solutions of 5-M<sub>2</sub>-0, 5-M<sub>2</sub>-3, 5-M<sub>2</sub>-5, and 5-M<sub>2</sub>-7 at various shear rates in salt-free water at 30°C.



**Figure 5** Variation of the viscosity with the CTAB concentration ( $C_{\text{CTAB}}$ ) of a 0.75 g/dL solution of 4-M<sub>2</sub>-7 at different shear rates in salt-free water at 30°C.

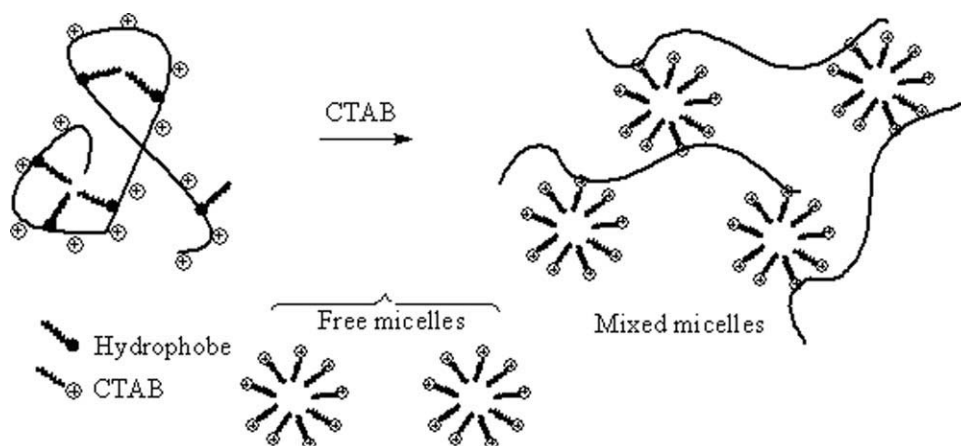
bond interactions between the pendant  $-\text{CO}_2\text{H}$  groups. Polymers with higher hydrophobe contents usually demonstrate higher degrees of intramolecular association. Changing the polymer 4-M<sub>2</sub>-7 to 5-M<sub>2</sub>-7 brought about a drastic change in the hydrodynamic volume of the polymer backbone. The pH of the aqueous environment controlled the direction of equilibration  $\text{CAS } 5 \rightleftharpoons \text{PZ } 6$ ; a hydrophobic CAS sample would be soluble in an acidic medium but recycled by precipitation in an alkaline medium. The  $n$  values of 5-M<sub>2</sub>-0, 5-M<sub>2</sub>-3, 5-M<sub>2</sub>-5, and 5-M<sub>2</sub>-7 were determined to be 0.20, 0.32, 0.21, and 0.37, respectively (Fig. 4). Unlike the CPEs 4, the  $n$  values for the CAS 5 did not seem to follow a well-defined pattern. As discussed previously, the presence of ionizable  $\text{CO}_2\text{H}$  groups in the CAS 5 polymers led to a complicated situation because of possible intramolecular and intermolecular H bonding and associations.

### Polymer-surfactant interactions

An interesting feature of amphiphilic polyelectrolytes with poor water solubility is that redissolution

is greatly facilitated by the addition of surfactants, which indicates the existence of surfactant-polymer interactions, such that surfactant micelles provide the solubilization of the hydrophobic moieties of the amphiphilic polyelectrolyte.<sup>21,33</sup> The interactions are driven by electrostatic attraction and/or association of the hydrophobic groups on the polymers and those of the surfactant molecules. The polymer-surfactant interactions were examined with viscometric measurements on CPE 4-M<sub>2</sub>-7 in the presence of the cationic cetyltrimethylammonium bromide (CTAB) surfactant. Figure 5 illustrates the viscosity behavior of a 0.75 g/dL solution of 4-M<sub>2</sub>-7 in the presence of the cationic surfactant CTAB at various shear rates. A concentration of 0.75 g/dL of 4-M<sub>2</sub>-7 corresponded to a concentration of 1.6 mM octadecyl pendants. Upon the addition of CTAB above its critical micelle concentration of 0.92 mM, the solution of 4-M<sub>2</sub>-7 became more viscous; this indicated the existence of surfactant-terpolymer interactions.

Above a critical complexation concentration of about 1 mM CTAB, the viscosity increased sharply as a result of the formation of mixed micelles of CTAB and octadecyl pendants of the polymer. At a shear rate of  $0.36 \text{ s}^{-1}$ , the polymer 4-M<sub>2</sub>-7 was found to have apparent viscosity values of 18,000 and 46,000 cps in the absence and presence, respectively, of 1.5 mM CTAB. This interaction of CPE with a surfactant of like charge (CTAB) is rather unusual, but it is not unique. Interactions in aqueous solutions of hydrophobically modified polyelectrolytes with surfactants of the same charges have been reported.<sup>34-36</sup> With further increases in the CTAB concentration, the viscosity continued to increase; this suggested gradual polymer restructuring and the formation of mixed-micelle domains, which contained hydrophobic groups belonging to two or more distinct polymer chains. The viscosity attained its maximum value (235,000 cps) at a CTAB concentration of 3 mM, which corresponded to approximately two



**Figure 6** Effect of CTAB on the structural reformation of a CPE.

CTAB molecules per octadecyl pendent of the polymer. Comicellization between the polymer and surfactant provided bridging between the polymer chains (Fig. 6).<sup>37</sup> Further increases in the concentration of CTAB led to the formation of more micelles, and the number of micelles per polymer-bound hydrophobe increased; this eventually disfavored comicellar bridging. Polymer 4-M<sub>2</sub>-7 (1 g/dL) precipitated out upon addition of the anionic surfactant SDS. A possible reason could have been that the anionic head of SDS, being electrostatically attracted toward the positively charged polymer backbone, became the counterion of the quaternary nitrogen and, thereby, made the macromolecule even more hydrophobic. SDS, therefore, might not have gotten a chance to participate in the comicellization process. Polymers 5-M<sub>2</sub>-7 (1 g/dL) and 6-M<sub>2</sub>-7, however, failed to improve their viscosity values or solubility behavior in the presence of CTAB or SDS; the polymers precipitated out in both cases.

### CONCLUSIONS

Interconvertible polymers (4 → 5 → 6) were synthesized at excellent yields, and their solution properties were compared. Contrary to the well-known behavior that normal PZs are only soluble in brine, both CAS 5-M<sub>2</sub>-0 and PZ 6-M<sub>2</sub>-0 were found to be soluble in salt-free water. This study involved an interesting class of interconvertible polymers having identical degrees of polymerization; it, thus, allowed a meaningful assessment of their solution properties. Among the CPEs, polymer 4-M<sub>2</sub>-7 was found to have the highest viscosity values for a 2 g/dL solution, higher by a factor of 360 than that of 4-M<sub>2</sub>-0. The addition of a small amount of CTAB to a solution (0.75 g/dL) of 4-M<sub>2</sub>-7 made the solution very viscous; this indicated polymer-surfactant interactions; at a shear rate of 0.36 s<sup>-1</sup>, a 0.75 g/dL solution of the polymer in salt-free water was found to have apparent viscosity values of 18,000 and 235,000 cps in the absence and presence, respectively, of 3 mM CTAB. The pH of the aqueous environment controlled the direction of the equilibration of CAS 5 ⇌ PZ 6; as such, a hydrophobic CAS sample could be used in an acidic solution and recycled by precipitation in an alkaline medium.

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