Water-soluble copolymers: 57. Amphiphilic cyclocopolymers of diallylalkoxybenzylmethylammonium chloride and diallyldimethylammonium chloride

Yihua Chang and Charles L. McCormick*
The University of Southern Mississippi, Department of Polymer Science, Southern Station, Box 10076, Hattiesburg, MS 39406-0076, USA
(Received 19 August 1993; revised 15 January 1994)

Water-soluble cyclocopolymers of *N*,*N*-diallyl-*N*-alkoxybenzyl-*N*-methylammonium chloride (alkyl = hexyl and octyl) and *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride were prepared by free radical polymerization at 50°C in aqueous solution. The copolymer compositions were determined by ^{1}H n.m.r. and u.v. measurements. The solution properties of the copolymers were studied as a function of the length and concentration of pendent hydrophobic groups, copolymer concentration and electrolyte or surfactant concentration, utilizing rheological and fluorescence methods. The copolymers in dilute solutions exhibit primarily intramolecular hydrophobic associations in both pure water and electrolyte solutions. The shear-thickening behaviour observed for these copolymer in dilute and semidilute solutions is interpreted in terms of intramolecular and intermolecular associations. Addition of sodium dodecyl sulfate (SDS) to the copolymer solutions results in a large increase in the viscosity at SDS concentrations below the critical micelle concentration. Fluorescence studies suggest that the viscosity enhancement is caused by interpolymer association of polymer–SDS domains.

(Keywords: water-soluble cyclopolymers; ammonium salts; free radical polymerization)

INTRODUCTION

Cationic quaternary ammonium polyelectrolytes have been the subject of increased research efforts in recent years owing to their diverse commercial applications[1]. Among the most prominent technological, water-soluble, cationic ammonium polymers is poly(diallyldimethylammonium chloride) (PDADMAC). Butler and Ingley[2] first reported the free radical polymerization of diallyldimethylammonium bromide yielding a water-soluble polymer. Later, Butler and coworkers[3,4] proposed and confirmed the formation of a linear cyclopolymer via intra-intermolecular polymerization, now termed cyclopolymerization. Although six-membered rings are thermodynamically more stable, ^{13}C n.m.r. studies[5,6] indicated that five-membered rings are predominant in PDADMAC for kinetic reasons.

PDADMAC exhibits typical polyelectrolyte behaviour in aqueous solution; however, complete or partial substitution of methyl groups in the DADMAC monomer with long hydrocarbon chains can substantially alter the solution properties. For example, introduction of hydrophobic side chains can result in the formation of polymeric micelles or polymeric aggregates under specified conditions[7–10]. Cyclopolymers of diallyldidodecylammonium bromide have recently been studied for possible vesicle formation[11,12].

Research in our laboratories has focused on tailoring amphiphilic copolymers to gain a fundamental understanding of the nature of associations in aqueous media as dictated by polymer microstructure[13–16]. Previous studies indicated that the distribution of the hydrophobic groups along the polymer chain significantly affects the associative properties of those polymers with a flexible backbone[14,15,17]. When the hydrophobic groups are arranged in a 'microblocky' manner with long intervening hydrophilic sequences, concentration-dependent intermolecular associations are promoted. Polymers with random distributions of the same units, on the other hand, exhibit largely intramolecular associative behaviour.

In this paper, we report the synthesis and solution properties of cyclocopolymers of diallylalkoxybenzylmethylammonium chloride and diallyldimethylammonium chloride. The formation of ring structures along the polymer backbone is expected to increase the rigidity of the polymer chains in comparison to previously studied amphiphilic acrylamide copolymers[17]. Here we examine whether the distribution of the hydrophobic groups has a similar effect on the associative properties. The introduction of phenyl groups allows a precise determination of copolymer composition by u.v. spectroscopy[18,19]. The effects of hydrophobe length and concentration, electrolytes, surfactants and shear stress were studied by viscometric and photophysical measurements.

---

* To whom correspondence should be addressed

0032-3861/94/16/3503-10

EXPERIMENTAL

Materials

All chemicals and reagent-grade solvents were purchased commercially and used as received. The deionized water used in the studies had a resistance of 18 MΩ and a surface tension of 70.8 mN m^{-1}.

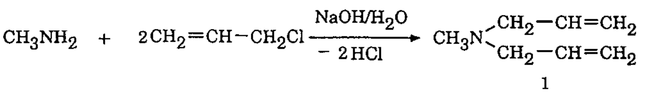
Monomer synthesis

N,N-*Diallyl*-N-*methylamine* ***1***. A modified literature procedure[20] for the reaction of methylamine with allyl chloride was followed for the synthesis of diallylmethylamine (*Scheme 1*). A 78.0 g portion of a 40% aqueous solution of methylamine (31.1 g, 1.00 mol) in a three-necked round-bottomed flask (1 l) was placed in an ice bath and agitated vigorously with a mechanical stirrer. Allyl chloride (168.4 g, 2.2 mol) and a solution of sodium hydroxide (100.0 g, 2.50 mol) in 100 ml of water were added separately over a 1 h period. A thick, white precipitate was formed. The slurried mixture was then heated at 36°C for 3 h and at 60°C for an additional 3 h. The mixture was cooled and the precipitate was filtered. The organic layer was separated and the aqueous phase was extracted with three 150 ml portions of ether. The organic extracts were combined, dried over 50 g of NaOH and fractionally distilled at atmospheric pressure through a 19 cm Vigreux distilling column. The product (68 g, 61%) was collected at 109.5–111.5°C as a colourless oil. ^{1}H n.m.r. (acetone-d$_6$) δ (ppm) 2.13 (s, 3H), 2.95 (d, 4H), 5.05–5.92 (m, 6H). ^{13}C n.m.r. (acetone-d$_6$) δ (ppm) 42.0, 60.9, 117.0, 137.2. *FT*i.r. (cm^{-1}) 3078 (C=$\underline{\text{C–H}}$), 2980 (aliphatic C–H stretch), 2781 (N–$\underline{\text{C–H}}$), 1643 (C=C), 1152 (C–N).

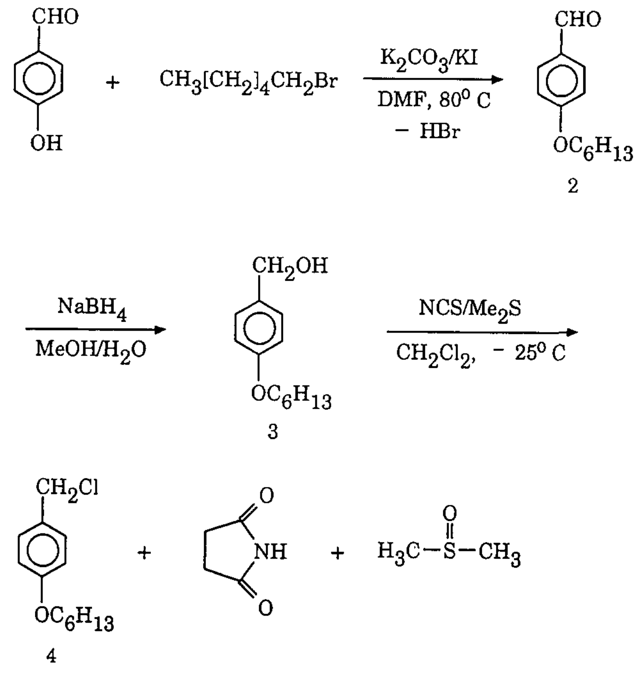
4-Hexyloxybenzaldehyde ***2***. The synthesis of 4-hexyloxybenzaldehyde is illustrated in *Scheme 2*.

4-Hydroxybenzaldehyde (24.5 g, 0.200 mol), bromohexane (36.0 g, 0.210 mol), potassium carbonate (30.0 g, 0.221 mol) and potassium iodide (2.0 g) in 60 ml of anhydrous dimethylformamide (DMF) were heated at 80°C for 11 h in a three-necked, round-bottomed flask (250 ml). The mixture was cooled and poured into 500 ml of water. The oily phase was separated and the aqueous phase was extracted once with 100 ml of ether. The organic solutions were combined and the solvent was removed on a rotary evaporator. Vacuum distillation yielded a colourless oil (38.9 g, 94%), b.p. 160–162°C at 0.5 mmHg. ^{1}H n.m.r. (CDCl$_3$) δ (ppm) 0.909 (t, 3H), 1.19–1.58 (m, 6H), 1.80 (p, 2H), 4.02 (t, 2H), 6.97 (d, 2H), 7.79 (d, 2H), 9.86 (s, 1H). ^{13}C n.m.r. (CDCl$_3$) δ (ppm) 14.0, 22.6, 25.6, 29.0, 31.5, 68.4, 114.7, 129.8, 131.9, 164.3, 190.7. *FT*i.r. (cm^{-1}) 2804, 2735 (O=$\underline{\text{C–H}}$), 1691 (C=O), 1601, 1577, 1510 (aromatic C–C stretch), 1258, 1019 (C–O–C), 833 (aromatic C–H bend).

1-Hydroxymethyl-4-hexyloxybenzene ***3***. The reduction of 4-hexyloxybenzaldehyde **2** is shown in *Scheme 2*.



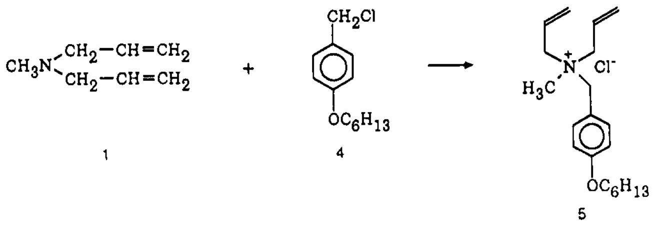
Scheme 1 Synthesis of *N*,*N*-diallyl-*N*-methylamine



Scheme 2 Synthesis of 4-hexyloxybenzyl chloride

4-Hexyloxybenzaldehyde (37.0 g, 0.179 mol) in 170 ml of methanol was treated with a solution of sodium borohydride (2.57 g, 0.0679 mol NaBH$_4$ in 35 ml of 0.25 M aqueous sodium hydroxide solution) at 19–23°C in a three-necked, round-bottomed flask (500 ml). When no further rise in the temperature was observed, the addition was stopped. Removal of methanol was performed with a rotary evaporator. Water (90 ml) and ether (70 ml) were then added and the mixture was stirred overnight. The ether layer was dried with anhydrous magnesium sulfate. After removal of the ether, the product was collected as white crystals, m.p. 38–39.5°C. A quantitative yield was obtained. ^{1}H n.m.r. (CDCl$_3$) δ (ppm) 0.896 (t, 3H), 1.21–1.58 (m, 6H), 1.72 (p, 2H), 3.68 (b, 1H), 3.86 (t, 2H), 6.78 (d, 2H), 7.13 (d, 2H). ^{13}C n.m.r. (CDCl$_3$) δ (ppm) 14.0, 22.6, 25.7, 29.3, 31.6, 64.3, 68.0, 114.4, 128.5, 133.1, 158.5. *FT*i.r. (cm^{-1}) 3333 (O–H), 1612, 1584, 1512, 1474 (aromatic C–C stretch), 1254 (C–O–C), 1050 (C–OH), 835 (aromatic C–H bend).

4-Hexyloxybenzyl chloride ***4***. A literature method[21] was modified for the preparation of 4-hexyloxybenzyl chloride **4** (*Scheme 2*). Dimethyl sulfide (12.0 g, 0.194 mol) was added dropwise to a solution of *N*-chlorosuccinimide (24.2 g, 0.178 mol) in 300 ml of anhydrous methylene chloride at 0°C in a three-necked, round-bottomed flask (500 ml). The temperature was then lowered to −25°C and 1-hydroxymethyl-4-hexyloxybenzene **3** (33.6 g, 0.162 mol) in 50 ml of anhydrous methylene chloride was added dropwise such that the temperature was maintained below −20°C. After the addition was complete, the suspension was stirred for 12 h at 0°C. The mixture was then poured into 400 ml of iced water. The organic layer was washed three times with saturated NaCl solution and then dried with MgSO$_4$. After removal of the methylene chloride, a slightly yellow oil was obtained (35.8 g, 98%). Vacuum distillation gave a colourless oil, b.p. 115°C at 0.5 mmHg. The purity was determined to be >99.7% by gas chromatography (g.c.). ^{1}H n.m.r. (CDCl$_3$) δ (ppm) 0.897 (t, 3H), 1.21–1.54 (m, 6H), 1.75 (p, 2H), 3.91 (t, 2H), 4.52 (s, 2H), 6.83 (d, 2H), 7.25 (d, 2H). ^{13}C n.m.r. (CDCl$_3$) δ (ppm) 14.0, 22.6, 25.7, 29.2, 31.6, 46.3, 68.0, 114.6, 129.4, 130.0, 159.3. *FT*i.r. (cm^{-1})



Scheme 3 Synthesis of *N*,*N*-diallyl-*N*-(4-hexyloxybenzyl)-*N*-methylammonium chloride

3036 (aromatic C–H), 2931 (aliphatic C–H), 1612, 1586, 1514, 1470 (aromatic C–C stretch), 1246 (C–O–C), 831 (aromatic C–H bend), 665 (C–Cl).

N,N-*Diallyl*-N-*(4-hexyloxybenzyl)*-N-*methylammonium chloride* **5** (Scheme 3). Diallylmethylamine **1** (14.3 g, 0.128 mol) was added at 0°C to 4-hexyloxybenzyl chloride **4** (29.1 g, 0.128 mol) in a round-bottomed flask (100 ml) through a syringe under nitrogen. The solution was stirred at room temperature for 2 days to give a slightly yellow gel. Precipitation in ether yielded a hygroscopic white solid in quantitative yield. The purity was determined to be $>99.5\%$ by high performance liquid chromatography (h.p.l.c.). ^1H n.m.r. ($CDCl_3$) δ (ppm) 0.905 (t, 3H), 1.22–1.58 (m, 6H), 1.77 (p, 2H), 3.09 (s, 3H), 3.94 (t, 3H), 4.10–4.31 (2q, 4H), 4.89 (s, 2H), 5.66–6.28 (m, 6H), 6.88 (d, 2H), 7.62 (d, 2H). ^{13}C n.m.r. ($CDCl_3$) δ (ppm) 13.6, 21.9, 25.2, 28.9, 31.1, 45.6, 62.1, 64.2, 67.4, 114.3, 117.7, 123.6, 128.4, 134.0, 160.1.

N,N-*Diallyl*-N-*(4-octyloxybenzyl)*-N-*methylammonium chloride* **6**. The synthesis of **6** started with the reaction of bromooctane with 4-hydroxybenzaldehyde. The reaction conditions, purification procedures and subsequent reaction steps in this preparation were the same as in the synthesis of the hexyl analogue.

4-Octyloxybenzaldehyde: ^1H n.m.r. ($CDCl_3$) δ (ppm) 0.890 (t, 3H), 1.19–1.55 (m, 10H), 1.80 (p, 2H), 4.02 (t, 2H), 6.97 (d, 2H), 7.81 (d, 2H), 9.86 (s, 1H); ^{13}C n.m.r. ($CDCl_3$) δ (ppm) 14.1, 22.7, 26.0, 29.1, 29.2, 29.3, 31.8, 68.4, 114.7, 129.8, 131.9, 164.3, 190.7; *FT*i.r. (cm^{-1}) 2802, 2733 ($O{=}\underline{C{-}H}$), 1692 (C=O), 1601, 1578, 1510, 1468 (aromatic C–C stretch), 1257, 1020 (C–O–C), 831 (aromatic C–H bend).

1-Hydroxymethyl-4-octyloxybenzene: ^1H n.m.r. ($CDCl_3$) δ (ppm) 0.886 (t, 3H), 1.17–1.54 (m, 10H), 1.75 (p, 2H), 2.88 (b, 1H), 3.90 (t, 2H), 4.47 (s, 2H), 6.82 (d, 2H), 7.18 (d, 2H); ^{13}C n.m.r. ($CDCl_3$) δ (ppm) 14.1, 22.7, 26.1, 29.3(2), 29.4, 31.9, 64.7, 68.1, 114.5, 128.6, 133.0, 158.6; *FT*i.r. (cm^{-1}) 3420 (O–H), 1613, 1512, 1472 (aromatic C–C stretch), 1256 (C–O–C), 1049 (C–OH), 835 (aromatic C–H bend).

4-Octyloxybenzyl chloride: ^1H n.m.r. ($CDCl_3$) δ (ppm) 0.884 (t, 3H), 1.18–1.54 (m, 10H), 1.76 (p, 2H), 3.92 (t, 2H), 4.52 (s, 2H), 6.83 (d, 2H), 7.26 (d, 2H); ^{13}C n.m.r. ($CDCl_3$) δ (ppm) 14.1, 22.7, 26.1, 29.3(2), 29.4, 31.9, 46.3, 68.1, 114.7, 129.5, 130.0, 159.3; *FT*i.r. (cm^{-1}) 1612, 1587, 1513, 1483 (aromatic C–C stretch), 1253 (C–O–C), 833 (aromatic C–H bend), 665 (C–Cl).

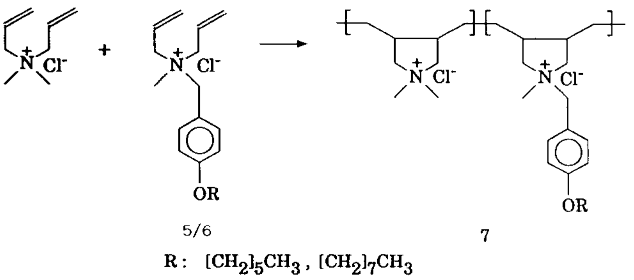
N,*N*-Diallyl-*N*-(4-octyloxybenzyl)-*N*-methylammonium chloride: ^1H n.m.r. ($CDCl_3$) δ (ppm) 0.889 (t, 3H), 1.17–1.56 (m, 10H), 1.79 (p, 2H), 3.12 (s, 3H), 3.95 (t, 2H), 4.03–4.36 (2q, 4H), 4.90 (s, 2H), 5.78–6.27 (m, 6H), 6.90 (d, 2H), 7.62 (d, 2H); ^{13}C n.m.r. ($CDCl_3$) δ (ppm) 13.5, 22.0, 25.4, 28.5, 28.7, 31.1, 45.8, 62.3, 64.2, 67.5, 114.3, 118.1, 124.2, 128.5, 134.1, 160.2.

Cyclocopolymerization of amphiphilic diallyl monomers 5 and 6 with diallyldimethylammonium chloride

The synthesis of the cyclocopolymers **7** from *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride and *N*,*N*-diallyl-*N*-(4-alkoxybenzyl)-*N*-methylammonium chloride is illustrated in *Scheme 4*. To a three-necked, round-bottomed flask (250 ml) equipped with a mechanical stirrer, a nitrogen inlet and an outlet were added 60 ml of a 60 wt% aqueous DADMAC solution and a desired amount of a 50 wt% aqueous solution of **5** or **6**. The solution was purged with nitrogen for 1 h at 50°C. A solution of potassium persulfate was introduced through a syringe. The total monomer to initiator molar ratio used in this study was kept constant at 500. The copolymer was precipitated into an ethanol–actone mixture and dried under vacuum. Purification of the copolymer was performed by redissolving the sample in water and dialysing against water using a membrane with a 12 000–14 000 molecular weight cut-off. The polymer was recovered by freeze drying.

Characterization methods

^1H and ^{13}C n.m.r. spectra were recorded using a Bruker AC-200. A Mattson 2020 Galaxy Series *FT*i.r. spectrometer was used to obtain i.r. spectra. The purity of liquid samples was determined by g.c. utilizing a Hewlett–Packard 5890 Series II gas chromatograph equipped with an Alltech AT-5 capillary column. A Hewlett–Packard model 1050 was used to determine the purity of solid samples by h.p.l.c. A Waters Bondapak C18 column was employed with methanol as the mobile phase. Classical light-scattering studies were performed with a Chromatix KMX-6 low angle laser light scattering spectrophotometer with a 2 mW He–Ne laser operating at 633 nm. Refractive index increments (d*n*/d*c*) were obtained using a Chromatix KMX-16 differential refractomer. The molecular weight of poly(diallyldimethylammonium chloride) was measured in 0.5 M NaCl solution. For hydrophobically modified copolymers, methanol was used as a solvent in the light-scattering studies to disrupt hydrophobic associations and to keep the copolymers from interacting with the filter. Steady-state fluorescence measurements were made with a Spex Fluorolog-2 fluorescence spectrometer and corrected for the wavelength dependence of the detector using an internal correction function provided by the manufacturer. Intensities for pyrene probe measurements (I_1/I_3) were taken at 372 nm (I_1) and 384 nm (I_3). The I_1/I_3 ratios were reproducible over the concentrations



Scheme 4 Copolymerization of diallyl monomers to give cyclocopolymers 7-C6 and 7-C8

investigated to ±0.1 units. Viscosity measurements were conducted with a Contraves LS-30 low shear rheometer at a constant shear rate of $1.28\,s^{-1}$ at 25°C, unless otherwise noted.

Sample preparation

The appropriate amount of dried polymer was weighed and then dissolved in water in a volumetric flask from which further dilutions of this stock solution could be made. The solutions were allowed to stand for 1 week prior to viscosity measurement.

RESULTS AND DISCUSSION

Monomer synthesis and copolymerization

One synthetic objective of this work was to prepare chromophore-containing monomers which could be copolymerized with diallyldimethylammonium chloride to yield cyclopolymers having a relatively rigid backbone. The synthetic procedure for the preparation of monomer **5** is shown in *Schemes 1–3*. The reaction of methylamine with allyl chloride (*Scheme 1*) is straightforward. Utilization of a slight excess of allyl chloride gave the diallylmethylamine **1** as the major product. The multistep synthesis of 4-alkoxybenzyl chloride **4** (*Scheme 2*) proved to be easy with a yield in each step greater than 90%. The hydrophobic group length can be altered as desired by choosing appropriate alkyl halides. Finally, the reaction of **1** with **4** generates the hydrophobically substituted quaternary monomer **5** (*Scheme 3*). Monomer **6** is prepared in a similar way and is described in the Experimental.

The amphiphilic monomers **5** and **6** have the necessary properties for the purpose of our investigations. The presence of the diallylamine functionality ensures the formation of the ring structure in the backbone. The phenyl ring in both monomers in this study provides a chromophore by which the concentration in the copolymers can be determined by ^{1}H n.m.r. and u.v. spectroscopy and serves as a hydrophobic moiety along with the long alkyl groups. Although the monomers contain two benzylic hydrogens which appear accessible to abstraction by free radical processes, no difficulty was encountered in the copolymerization with diallyldimethylammonium chloride, as indicated by the reasonably high molecular weight (*Table 1*). Successful cyclopolymerization of other diallyl monomers containing benzylic hydrogens has also been reported[22,23].

Previous kinetic studies indicate that in the cyclopolymerization of diallyl quaternary ammonium monomers, the optimum monomer concentration is 50–65 wt% for high conversion, high molecular weight and low residual double bonds[24]. Furthermore, cyclocopolymerization of DADMAC and a hydrophobic diallyl monomer in such a high concentration has been reported to yield a random copolymer rather than a 'microblocky copolymer', even though the hydrophobic monomer possesses surfactant properties[10]. In our work, the monomer concentrations were controlled at 50–60 wt%. ^{1}H n.m.r. shows that the cyclocopolymers contain negligible numbers of double bonds (*Figure 1*). The cyclocopolymerization reactions in this study were conducted to low conversion to minimize drift in the copolymer composition and to control, to the degree possible, molecular weight distribution[25].

Table 1 Structural parameters of the copolymers

Sample	Conversion (mol%)	Hydrophobe content (mol%) ^{1}H n.m.r.	Hydrophobe content (mol%) U.v.	$10^{-5}M_w$ (g mol^{-1})
PDADMAC	6.1	0	0	1.65
7-C6-3	5.8	3	3.8	1.61
7-C6-7	5.1	7	5.6	2.34
7-C6-10	6.8	10	11.2	2.27
7-C6-24	9.0	24	21.3	2.17
7-C8-3	7.2	3	2.8	1.71
7-C8-5	3.6	5	4.4	2.53
7-C8-10	7.8	10	12.5	2.00
7-C8-27	8.1	27	23.3	2.02

The compositions and weight-average molecular weights, M_w, of the copolymers are presented in *Table 1*. Cyclocopolymers **7** (*Scheme 4*) are designated with C6 or C8 to indicate hexyl or octyl substitution. The final number represents the mole percentage incorporation of hydrophobic monomer. Under similar copolymerization conditions (initiator and monomer concentrations, reaction conversion, etc.), M_w values for the 7-C6 series vary from 1.61 to $2.34\times10^5\,g\,mol^{-1}$ and from 1.71 to $2.53\times10^5\,g\,mol^{-1}$ for the 7-C8 series. These similar molecular weights allow meaningful assessments of the effects of copolymer composition on solution behaviour.

Copolymer composition

The cyclocopolymers (**7**-C6 and **7**-C8 series) were synthesized by varying the feed ratios of DADMAC to **5** or **6** from 95:5 to 70:30 mol%. The aromatic and aliphatic resonances in the cyclocopolymers are distinct in the ^{1}H n.m.r. spectra and may be used for the estimation of copolymer composition (*Figure 1*). The molar fractions of diallyl monomers in the **7**-C6 copolymers were determined from

$$\frac{F_1}{F_2}=\frac{N-7M}{4M} \tag{1}$$

where F_1 and F_2 are the molar fractions of DADMAC and **5**, respectively, in the copolymer. M is the total integration number of aromatic protons and N is the total integration number of aliphatic protons.

The copolymer compositions of the **7**-C8 copolymers were determined from

$$\frac{F_1}{F_2}=\frac{N-8M}{4M} \tag{2}$$

where F_1 and F_2 are the molar fractions of DADMAC and **6**, respectively, in the copolymer, M is the total integration number of aromatic protons and N is the total integration number of aliphatic protons. The copolymer compositions are reported in *Table 1*. For comparison, the results obtained by u.v. measurements are also included in *Table 1*. The data from both methods agree favourably.

Dilute solution properties

Rheological and photophysical methods were employed to study the solution behaviour of the copolymers. The two methods are complementary: rheological measurements study solution properties at the macroscopic level, and the fluorescence techniques provide information

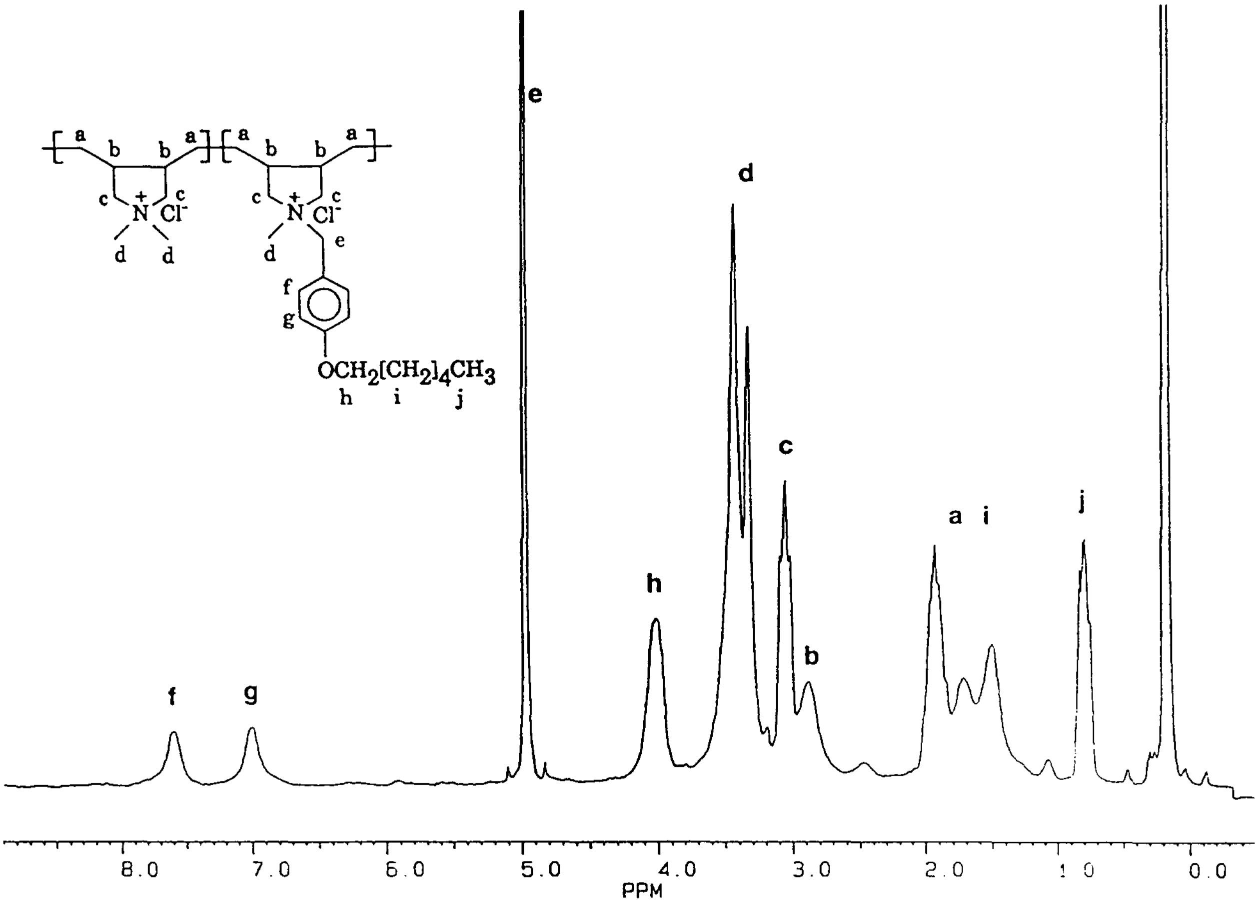


Figure 1 ^{1}H n.m.r. spectrum for 7-C6-7

regarding the polymer conformation at the microscopic level.

Rheological studies

Effect of copolymer composition. In order to assess the effects of hydrophobic monomer concentration on the copolymer conformation in deionized water, the intrinsic viscosity was first determined utilizing the Fuoss relationship[26]. The viscometric studies were performed at a low shear rate (1.28 s^{-1}) to minimize shear-dependent conformational changes. *Figure 2* shows the change in intrinsic viscosity as a function of hydrophobic group content for the copolymer series 7-C6 and 7-C8. The intrinsic viscosities decrease continuously with increasing hydrophobe concentration for both hexyl and octyl copolymers. Similar behaviour has been observed for hydrophobically modified poly(4-vinylpyridine)s[27–29]. These data imply that these copolymers form mainly intramolecular hydrophobic associations. This is consistent with our previous studies which indicated that random copolymers have a tendency towards intramolecular association in dilute solution[17]. The decrease in intrinsic viscosity for both 7-C6 and 7-C8 with increasing hydrophobe content reflects the increasing compactness of these amphiphilic systems in aqueous media.

Effect of copolymer concentration. The dependence of η_{red} on copolymer concentration for the 7-C6 series is shown in *Figure 3*. For all samples, η_{red} decreases with increasing concentration, which is typical polyelectrolyte behaviour. Note that the copolymers with a higher hydrophobe content show a less marked concentration dependence owing to the increased compaction of the polymer coil. Similar behaviour is observed for the 7-C8 copolymers (*Figure 4*).

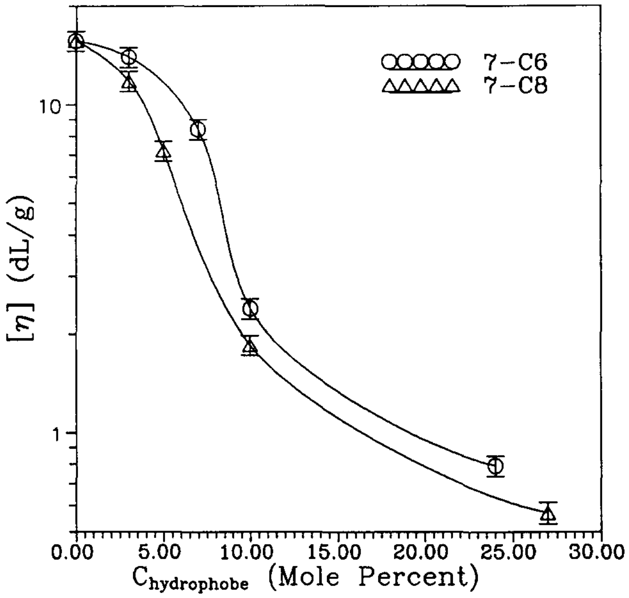


Figure 2 Effects of hexyl and octyl group content on the intrinsic viscosity [η] of copolymers 7-C6 and 7-C8 in deionized water at 25°C

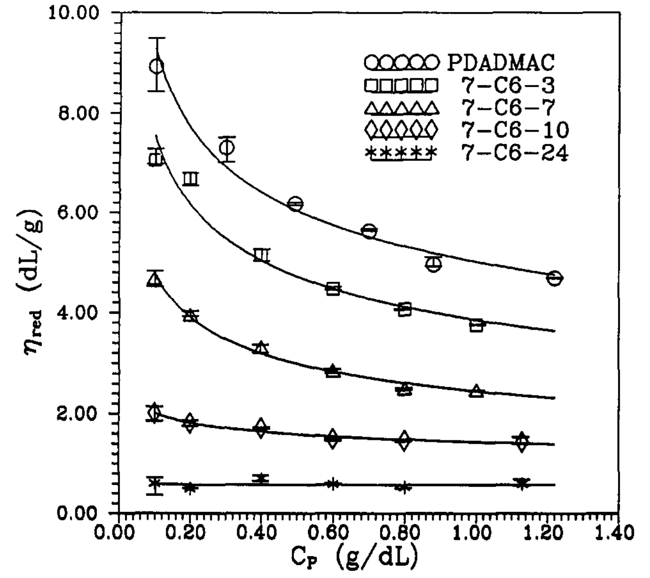


Figure 3 Variation in η_{red} for the 7-C6 series as a function of copolymer concentration (shear rate = 1.28 s^{-1}, T=25°C)

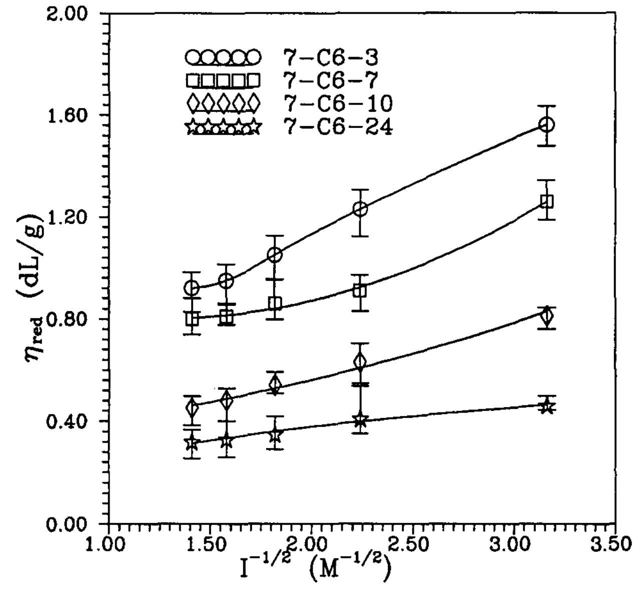


Figure 5 Variation in η_{red} as a function of ionic strength for the 7-C6 copolymers (shear rate = 1.28 s^{-1}, T=25°C)

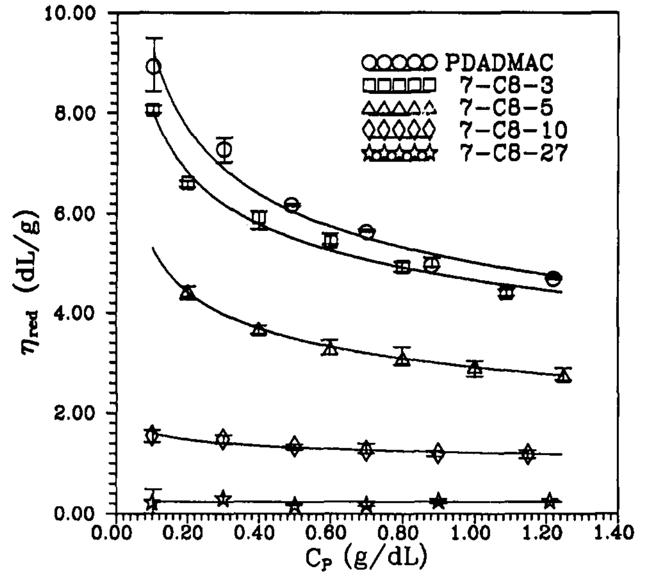


Figure 4 Variation in η_{red} for the 7-C8 series as a function of copolymer concentration (shear rate = 1.28 s^{-1}, T=25°C)

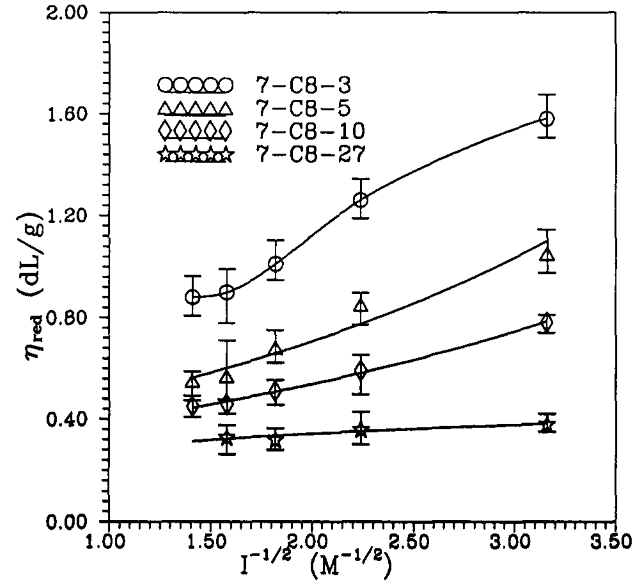


Figure 6 Variation in η_{red} as a function of ionic strength for the 7-C8 copolymers (shear rate = 1.28 s^{-1}, T=25°C)

Effect of added electrolyte. It is well known that the addition of a simple salt to polyelectrolyte solutions results in electrostatic screening of the charged groups and a marked reduction in hydrodynamic volume. Analogous behaviour is observed for the 7-C6 and 7-C8 copolymers, as shown in *Figures 5* and *6*, respectively. The more hydrophobic copolymers exhibit a less marked viscosity dependence with changes in salt concentration.

Effects of surfactants. The solution properties of the water-soluble polymers can be dramatically changed by the addition of simple surfactants[30–32]. Interactions between hydrophobe-containing polyelectrolytes and surfactants are governed primarily by coulombic forces, dipole–ion interactions and the hydrophobic effect. In order to assess the effects of surfactants on the conformation of the copolymers, three surfactants differing in charge character were employed in this study.

Figure 7 illustrates the viscosity behaviour of 7-C6-7 in the presence of non-ionic (Triton X-100), anionic (sodium dodecyl sulfate (SDS)) and cationic (dodecyltrimethylammonium bromide (DTAB)) surfactants. The viscosity of the polymer solution is essentially invariant with changes in non-ionic surfactant concentration, while a continuous decrease in the viscosity of the polymer solution is observed with increasing concentration of the cationic surfactant. The latter effect may be caused by the increase in the ionic strength of the solution upon addition of the cationic surfactant[33].

The copolymer solution exhibits completely different viscosity behaviour in the presence of SDS. The viscosity increases markedly at SDS concentrations below the critical micelle concentration (CMC), reaches a maximum and then decreases rapidly at higher surfactant concentrations. This type of behaviour has been observed for several hydrophobically modified water-soluble polymers[34,35] and has been attributed to the concentration-dependent association of hydrophobic groups with the surfactant. Initial addition of SDS to the polymer solution leads to the collapse of the polymer chains, as evidenced by the slight turbidity of the solution. Upon further increasing the surfactant concentration, association of SDS and hydrophobes of the copolymer occurs, resulting in coil expansion. Eventually, mixed micelle domains develop which contain hydrophobic groups belonging to two or more distinct polymer chains. Intermolecular bridging at this critical surfactant to hydrophobe ratio results in a viscosity maximum. In the present case, this maximum occurs at a surfactant concentration equal to the hydrophobe concentration. When the surfactant concentration is above the CMC, SDS micelles are in a large excess, mixed micelles with hydrophobes from two or more chains are less prevalent and the network structure is destroyed.

It is noteworthy that for an SDS concentration well above the CMC, the viscosity of the polymer solution is lower than that in the absence of surfactant ($\eta_{app} = 2.5$ cP). These data and those from the fluorescence studies to be presented below suggest that at high surfactant concentrations, associations of SDS with the copolymer result in highly collapsed polymer coils. This might be explained in terms of an increase in the intramolecular association of hydrophobes along the polymer chain.

A change in the type of hydrophobic associations with increasing surfactant concentration is further demonstrated by the dynamic light scattering data (*Table 2*). The apparent hydrodynamic diameter of the copolymer increases in the low SDS concentration regime, at least above the stoichiometric SDS to hydrophobe ratio. It is likely that the rise in the hydrodynamic volume results from coil expansion and/or cooperative aggregation as further SDS is added. The maximum value of d_0 is observed at a lower surfactant concentration in the light-scattering studies than in the viscosity studies. This is probably because of the higher polymer concentration required in the latter measurements. Clearly, in both types of measurements, further increases in SDS concentration result in dramatic decreases in the hydrodynamic diameter. It should be noted that such a large decrease in the hydrodynamic size of the copolymer coil is not caused by the increased ionic strength of the solution with SDS addition, since addition of 0.02 M NaCl (*Table 2*) results in little additional change.

Effect of shear. Previous studies in our laboratories[13] and by other research groups[36,37] have shown that shear effects have a significant influence on time-dependent polymer conformations, particularly for hydrophobic associative copolymers. In this study, the rheological properties of the 7-C6 copolymers as a function of shear rate were first examined in dilute solutions (0.04 g dl^{-1}). Samples 7-C6-3, 7-C6-7 and 7-C6-10 exhibit exhibit shear-thickening behaviour for shear rates of 3–20 s^{-1} (*Figure 8*). The rise in the viscosity is consistent with the disruption of intramolecular hydrophobic associations, uncoiling and more complete hydration of the polymer chain. It is interesting to note that the copolymers exhibit Newtonian behaviour below and above the enhanced viscosity region. Sample 7-C6-24 exhibits little shear dependence, owing to the large quantity of hydrophobic groups; apparently, the shear

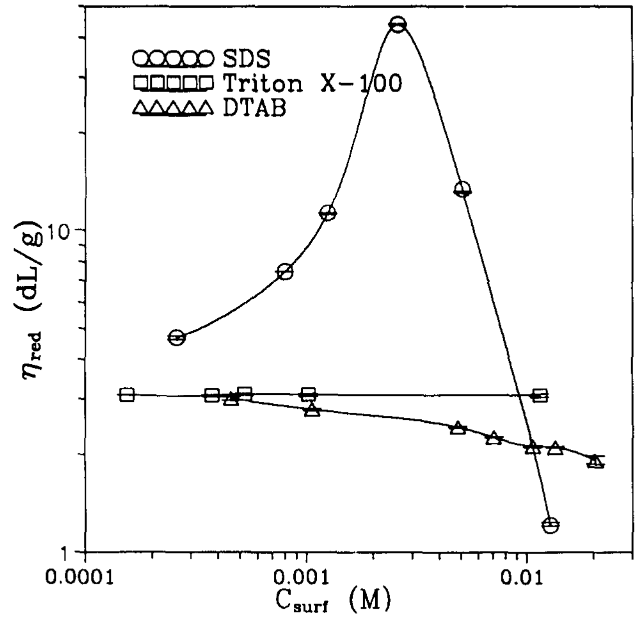


Figure 7 Effects of surfactants on η_{red} for 7-C6-7 ($C_P = 0.48$ g dl^{-1}, shear rate = 1.28 s^{-1}, $T = 25$°C)

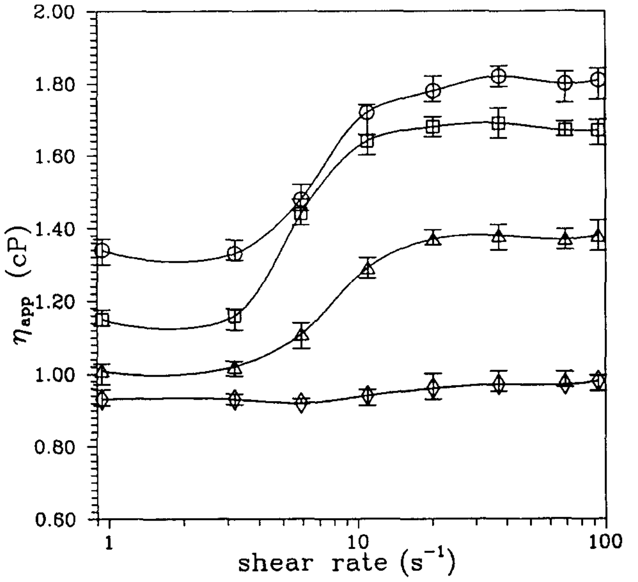


Figure 8 Effect of shear rate on η_{app} for the 7-C6 copolymers in deionized water ($C_P = 0.04$ g dl^{-1}, $T = 25$°C): (○) 7-C6-3; (□) 7-C6-7; (△) 7-C6-10; (◇) 7-C6-24

Table 2 Hydrodynamic diameter of 7-C6-7 in aqueous solution

Sample[a]	Water	0.2 mM SDS	0.8 mM SDS	2 mM SDS	20 mM SDS	20 mM NaCl
d_0 (nm)	210	340	520	130	13	189

[a] Copolymer concentration 0.05 g dl^{-1}

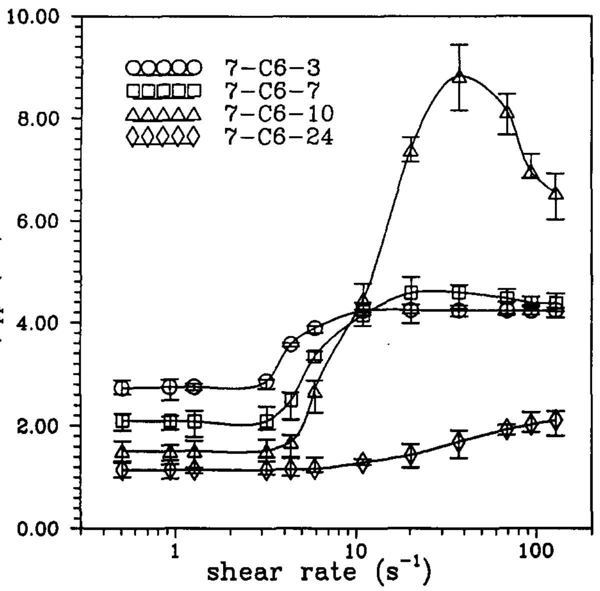


Figure 9 Effect of shear rate on η_{app} for the 7-C6 copolymers in deionized water (C_P=0.40 g dl^{-1}, T=25°C)

stress employed in this case cannot completely break up the hydrophobic associations.

A pronounced shear dependence is observed for all samples as the polymer concentrations increase from 0.04 g dl^{-1} to 0.4 g dl^{-1} (*Figure 9*). Samples 7-C6-3 and 7-C6-7 show moderate viscosity increments. A different shear response is observed for the 7-C6-10 copolymer. Increasing the shear rate from 4 to 30 s^{-1} results in a large increase in viscosity followed by a decrease at higher shear rates. Such behaviour has been reported in both aqueous[36] and hydrocarbon[37] solutions and is attributed to changes in intramolecular and intermolecular associations with shear. In the semidilute regime, intramolecular associations are disrupted above a certain shear stress and chain extension leads to an increase in the number of intermolecular associations. Further increase in the shear rate results in the disruption of intermolecular associations and the copolymer exhibits shear-thinning behaviour.

The viscosity–shear rate dependence in salt solutions was investigated with sample 7-C6-10 at a concentration of 1.248 g dl^{-1}. The copolymer solutions exhibit strong dilatant flow at a low salt concentration; shear-thickening behaviour diminishes gradually with increasing salt concentration (*Figure 10*). This is probably because of enhanced intramolecular hydrophobic associations at higher salt concentrations.

The shear response of the copolymers in the presence of SDS was examined with 7-C6-7. The viscosity can decrease, remain constant or increase with shear rate depending upon the concentration of SDS (*Figure 11*). When the concentration of SDS is below the CMC, the viscosity of the polymer solution decreases with increasing shear rate, and this is typical behaviour for intermolecular associations[13]. On the other hand, when the surfactant concentration is well above the CMC, only a slight rise in the viscosity is observed with increasing shear rate. This implies virtually no interchain aggregation and a highly collapsed conformation, as discussed earlier. Apparently, in this case, the incorporation of SDS into the polymeric micelles enhances the intramolecular hydrophobic associations and the copolymers show a less marked shear dependence.

Fluorescence studies

Fluorescence studies were conducted utilizing pyrene as a probe. The ratio of the fluorescence intensities for the first and the third emission bands (I_1/I_3) is reported to be an indicator of the polarity of the microenvironment. A lower value of I_1/I_3 can indicate a more hydrophobic environment as experienced by the probe[38].

Figure 12 depicts the concentration dependence of the I_1/I_3 values of pyrene in aqueous solutions of the 7-C6 copolymers. For PDADMAC, there are no hydrophobic side chains, and the high I_1/I_3 (about 1.7) is consistent

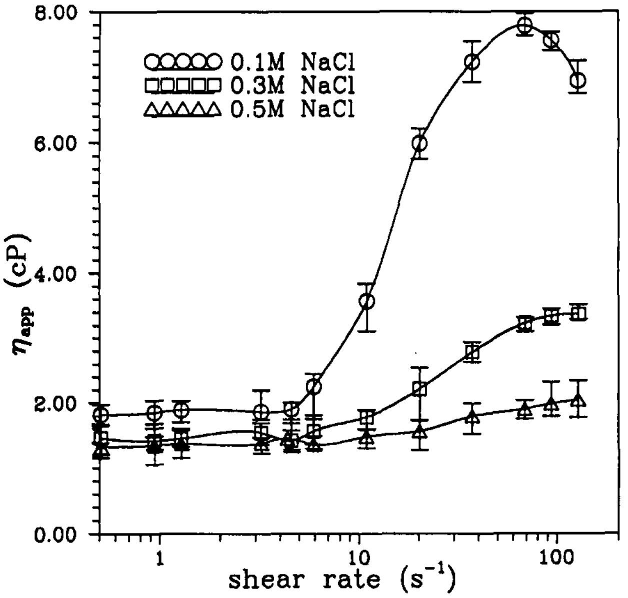


Figure 10 Effect of shear rate on η_{app} for 7-C6-10 at various salt concentrations (C_P=1.248 g dl^{-1})

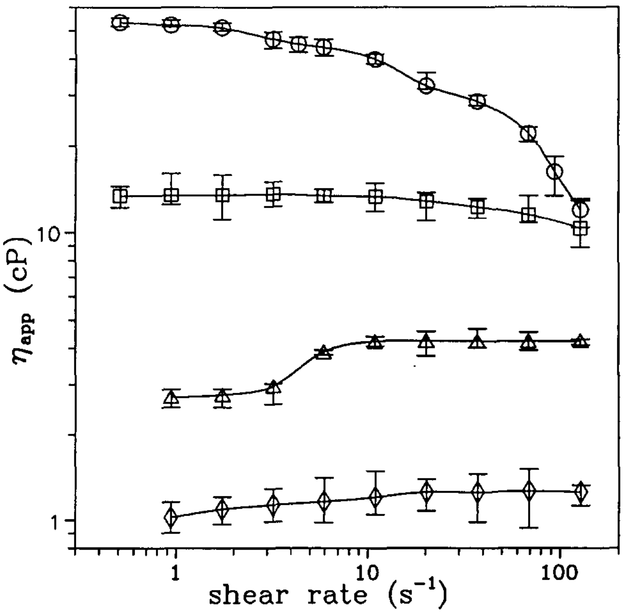


Figure 11 Effect of shear rate on η_{app} for 7-C6-7 at various concentrations (C_P=0.48 g dl^{-1}, T=25°C): (○) 2.60 × 10^{-3} M; (□) 5.08 × 10^{-3} M; (△) 0; (◇) 1.276 × 10^{-2} M

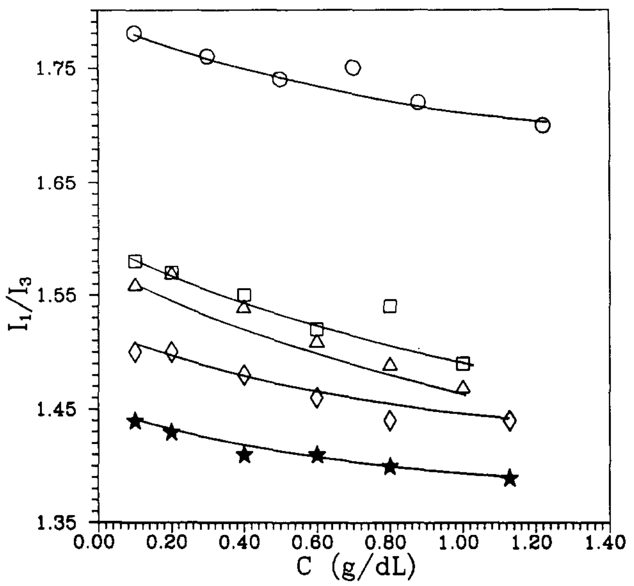


Figure 12 Effect of copolymer concentration on I_1/I_3 of the pyrene probe for the 7-C6 copolymers: (○) PDADMAC; (□) 7-C6-3; (△) 7-C6-7; (◇) 7-C6-10; (★) 7-C6-24

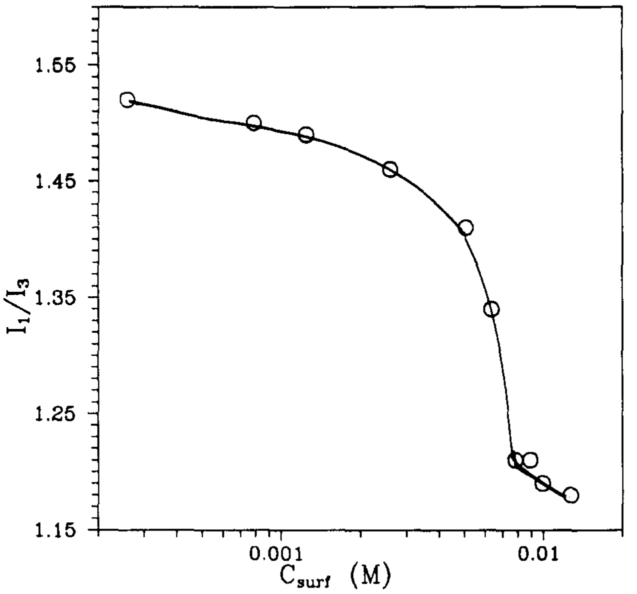


Figure 13 Effect of SDS on I_1/I_3 for 7-C6-7 (C_P=0.48 g dl^{-1}, T=25°C)

with an open, aqueous environment experienced by the probe. As the degree of incorporation of the hydrophobic groups in the copolymers increases, the I_1/I_3 value decreases, probably indicating increased shielding of the pyrene molecules from the solution. Also, the values for each copolymer are relatively insensitive to the copolymer concentration, consistent with intramolecular association. Similar results have been reported for other intramolecularly associative polymers[38,39]. It is interesting that the I_1/I_3 values for the 7-C6 copolymers are higher than those reported for small cationic surfactants[40,41] and polymeric micelles with more flexible backbones[39]. This study suggests that the hydrophobic microdomains are less compact, probably because of the rigid nature of the backbone.

The effects of SDS concentration on the I_1/I_3 value of pyrene are illustrated in *Figure 13*. Below the CMC of SDS, the I_1/I_3 values decrease slowly with increasing SDS concentration. A rapid decrease in I_1/I_3 is observed near the CMC. This implies the presence of a conformational transition from relatively open hydrophobic domains to highly collapsed ones, consistent with the viscosity studies. Note that I_1/I_3 for the compact coil is about 1.2. This value is intermediate between that for SDS micelles and that for 7-C6-7 in deionized water. Caution should be exercised in interpreting the experimental data reported here. Only a qualitative picture of associations can be gained by probe studies of this type. Partitioning of pyrene into domains which would have less organization than classical micelles formed by small molecules presents significant problems for the rigorous interpretation of photophysical data.

CONCLUSIONS

Rheological and photophysical studies of 7-C6 and 7-C8 copolymers indicate that these amphiphilic systems are capable of forming hydrophobic domains in aqueous solutions through intramolecular hydrophobic associations. The stability and hydrophobicity of these domains are related to both the concentration of the hydrophobic groups and the solvent quality. The strength of association increases with increasing either the hydrophobe content or the length of the hydrophobic group. Addition of electrolytes in moderate concentrations allows sufficient shielding of charges to result in a collapsed conformation. The effects of surfactants on the solution properties of the copolymers depend on the type of surfactant and the surfactant concentration. A viscosity maximum is observed at a critical SDS to hydrophobe ratio (near 1 in this case). Above the CMC, interactions of SDS with the copolymer result in a lower viscosity. This behaviour probably arises from intramolecular associations formed at the expense of intermolecular networks. In contrast, the addition of dodecyltrimethylammonium bromide causes only a slight decrease in the viscosity of the polymer solution, probably by increasing the ionic strength of the solution. In this case, little polymer–surfactant interaction is observed.

ACKNOWLEDGEMENTS

Supporting funds for this research by grants from the Office of Naval Research, the Defense Advanced Research Projects Agency and the Department of Energy are gratefully acknowledged. We would also like to thank Kelly Branham for assistance with the dynamic light scattering measurements.

REFERENCES

1 'Chemical Economics Handbook', Stanford Research Institute, Menlo Park, CA, 1983, pp. 581-1011I, 581-5022L, 581-1012D
2 Butler, G. B. and Ingley, F. L. *J. Am. Chem. Soc.* 1951, **73**, 895
3 Butler, G. B. and Angelo, R. J. *J. Am. Chem. Soc.* 1957, **79**, 3128
4 Butler, G. B. *Acc. Chem. Res.* 1982, **15**, 370
5 Johns, S. R., Willing, R. I., Middleton, S. and Ong, A. K. *J. Macromol. Sci., Chem. A* 1976, **10**, 875
6 Lancaster, J., Baccei, L. and Panzer, H. *J. Polym. Sci., Polym. Lett. Edn* 1976, **14**, 549
7 Ueda, T., Harada, S. and Ise, N. *Polym. J.* 1974, **6** (6), 473
8 Fendler, J. H. and Tundo, P. *Acc. Chem. Res.* 1984, **17**, 3
9 Ringsdorf, H., Schlarb, B. and Venzmer, J. *Angew. Chem, Int. Edn Engl.* 1988, **27**, 113
10 Butler, G. B. and Do, C. H. in 'Water-Soluble Polymers' (Eds S. W. Shalaby, C. L. McCormick and G. B. Butler),

ACS Symposium Series no. 467, American Chemical Society, Washington, DC, 1991, p. 151

11 Babilis, D., Dais, P., Margaritis, L. H. and Paleos, C. M. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23**, 1089

12 Babilis, D., Paleos, C. M. and Dais, P. *J. Polym. Sci., Polym. Chem. Edn* 1988, **26**, 2141

13 McCormick, C. L. and Johnson, C. B. in 'Polymers in Aqueous Media' (Ed. J. E. Glass), Advances in Chemistry Series no. 223, American Chemical Society, Washington, DC, 1989, p. 437

14 Ezzell, S. A. and McCormick, C. L. *Macromolecules* 1992, **25**, 1881

15 Ezzell, S. A. and McCormick, C. L. *Macromolecules* 1992, **25**, 1887

16 McCormick, C. L., Middleton, J. C. and Cummins, D. F. *Macromolecules* 1992, **25**, 1201

17 Chang, Y. and McCormick, C. L. *Macromolecules* in press

18 Valint Jr, P. L., Bock, J. and Schulz, D. N. in 'Polymers in Aqueous Media' (Ed. J. E. Glass), Advances in Chemistry Series no. 223, American Chemical Society, Washington, DC, 1989, p. 399

19 McCormick, C. L., Middleton, J. C. and Grady, C. E. *Polymer* 1992, **33**, 4184

20 Harada, S. and Arai, K. *Makromol. Chem.* 1967, **107**, 78

21 Corey, E. J., Kim, C. U. and Takeda, M. *Tetrahedron Lett.* 1972, **42**, 4339

22 Haruta, M., Kageno, K. and Harada, S. *Makromol. Chem.* 1973, **167**, 95

23 Ueda, T. and Harada, S. *Polym. J.* 1974, **6**, 473

24 Boothe, J. E., Flock, H. G. and Hoover, M. F. *J. Macromol. Sci., Chem. A* 1970, **4** (6), 1419

25 Biggs, S., Hill, A., Selb, J. and Candau, F. *J. Phys. Chem.* 1992, **96**, 1505

26 Fuoss, R. M. and Cathers, G. I. *J. Polym. Sci.* 1949, **4**, 96

27 Strauss, U. P. and Gershfeld, N. L. *J. Phys. Chem.* 1954, **58**, 747

28 Strauss, U. P., Gershfeld, N. L. and Crook, E. H. *J. Phys. Chem.* 1956, **60**, 577

29 Ghesquiere, D., Chachaty, C., Ban, B. and Loucheux, C. *Makromol. Chem.* 1976, **177**, 1601

30 Glass, J. E. (Ed.) 'Polymers in Aqueous Media', Advances in Chemistry Series no. 223, American Chemical Society, Washington, DC, 1989

31 Goddard, E. D. *Colloids Surf.* 1986, **19**, 255

32 Goddard, E. D. *Colloids Surf.* 1986, **19**, 301

33 Wennerstrom, H. and Lindman, B. *Phys. Rep.* 1979, **52**, 1

34 Iliopoulos, I., Wang, T. K. and Audebert, R. *Langmuir* 1991, **7**, 617

35 Goddard, E. D. and Leung, P. S. *Colloids Surf.* 1985, **13**, 47

36 Bock, J., Siano, D. B., Valint Jr, P. L. and Pace, S. L. in 'Polymers in Aqueous Media' (Ed. J. E. Glass), Advances in Chemistry series no. 223, American Chemical Society, Washington, DC, 1989, p. 411

37 Lundberg, R. D. and Duvdevani, I. in 'Polymers as Rheology Modifiers' (Eds D. N. and J. E. Glass), ACS Symposium Series no. 462, American Chemical Society, Washington, DC, 1991, p. 155

38 McCormick, C. L., Hoyle, C. E. and Clark, M. D. *Polymer* 1992, **33**, 243

39 Laschewsky, A. and Zerbe, I. *Polymer* 1991, **32**, 2081

40 Kalyanasundaram, K. and Thomas, J. K. *J. Am. Chem. Soc.* 1977, **99**, 2039

41 Kalyanasundaram, K. *Langmuir* 1988, **4**, 842

42 Jaeger, W., Hang, L. T., Phillip, B., Reinisch, G. and Wandrey, C. in 'Polymeric Amines and Ammonium Salts' (Ed. E. J. Goethals), Pergamon Press, Oxford, 1980, p. 155