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Water-Soluble Copolymers. 49. Effect of the Distribution of the Hydrophobic Cationic Monomer Dimethyldodecyl(2-acrylamidoethyl)ammonium Bromide on the Solution Behavior of Associating Acrylamide Copolymers

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ABSTRACT: A novel water-soluble monomer, dimethyldodecyl(2-acrylamidoethyl)ammonium bromide (DAMAB), was synthesized. This monomer possesses a critical micelle concentration of 4.9×10^{-3} M. A series of copolymers of DAMAB with acrylamide (AM) have been prepared by radical copolymerization by micellar and solution techniques. The rheological properties of the copolymers were strongly affected by their microstructures. A random copolymer with 5 mol % of DAMAB obtained by solution polymerization in *tert*-butyl alcohol showed a tendency for intramolecular hydrophobic association, while microheterogeneous copolymerization of AM with 5 and 10 mol % of DAMAB in water yielded microblocky structures which promoted intermolecular association of hydrophobes. The intermolecular association was enhanced by increasing the length of the hydrophobic block and/or the number of blocks in the polymer chain. Evidence of hydrophobic microdomains was obtained utilizing pyrene probe fluorescence.

Introduction

Hydrophobically modified polymers have been the subject of considerable research beginning with the classical studies of Strauss.[1] These amphipathic polymers exhibit unusual aqueous solution behavior, arising from hydrophobic assocations that occur in order to minimize water–hydrophobe contact.[2–6] Such associations determine the macromolecular conformation, which, in turn, controls the rheological properties of aqueous fluids. These polymers have potential applications in such diverse fields as enhanced oil recovery, fluid modification, controlled drug release, personal care formulation, and frictional drag reduction.[7,8]

Certain hydrophobically modified polymer systems exhibit intermolecular association in aqueous solution[2,3] while others show a preference for intramolecular association.[1,4] The number of hydrophobic groups incorporated within the amphipathic polymers has been suggested to play an important role in determining the polymer conformation adopted in aqueous solution. Several polymer systems containing either hydrocarbon[9] or fluorocarbon[10] pendent chains show viscosity maxima with increasing hydrophobic group content, implying a transition from intermolecular to intramolecular association. Recent studies in our laboratory have indicated that the distribution of the hydrophobic groups along the polymer chain also significantly affects the conformation of such copolymers.[11,12] When the hydrophobic groups in pyrene-labeled acrylamido copolymer systems are arranged in a blocklike fashion with long intervening hydrophilic sequences, the hydrophobic interactions promote intermolecular association. Polymers with a random distribution of the same units, on the other hand, exhibit intramolecular associative behavior.

Although many hydrophobically modified polymer systems have been reported, much less attention has been focused on the control of the type of association by altering the polymerization process. As well, structure–property relationships for amphipathic copolymers in aqueous solution are not well established. This paper describes the synthesis and solution properties of copolymers of acrylamide and dimethyldodecyl(2-acrylamidoethyl)ammonium bromide. The blockiness of the hydrophobic sequences can be controlled utilizing mixed micelle polymerization. Introduction of cationic groups into the polymers increases water solubility and allows arrangement of hydrophobes in blocklike structures using simple solution polymerization techniques. The length of hydrophobic blocks can be controlled under selected conditions. For comparison, a copolymer of identical composition but random hydrophobe distribution was prepared by solution polymerization in *tert*-butyl alcohol. The effect of random hydrophobe incorporation versus block hydrophobe incorporation on solution behavior was investigated. Changes in the run number of blocks were also examined. These data are interpreted in terms of inter- versus intramolecular associations.

Experimental Section

Materials. Acrylamide was recrystallized twice from acetone prior to use. Water was deionized to a conductivity of 1×10^{-17} mho/cm. Other materials were used as received.

Monomer Synthesis. Scheme I illustrates the synthesis of the hydrophobically modified acrylamido monomer dimethyldodecyl(2-acrylamidoethyl)ammonium bromide. Into a 250-mL three-necked round-bottom flask were added methylene chloride (82 mL), *N,N*-dimethylethylenediamine (8.82 g, 0.100 mol), and 6 N sodium hydroxide (25 mL). The mixture was placed in an ice bath and agitated by a magnetic stirrer under a nitrogen atmosphere. When the temperature dropped below 5 °C, acryloyl chloride (9.36 g, 0.104 mol) in 20 mL of methylene chloride was added slowly from an addition funnel such that the temperature was maintained below 10 °C. The mixture was stirred for an additional 30 min after complete addition of acryloyl chloride. The organic layer was then separated, washed twice with water and once with concentrated NaCl solution, and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator to yield a slightly yellow oil (11.67 g, 80% yield). The crude product was purified by vacuum distillation in the presence of a small amount of phenothiazine as an inhibitor. A colorless oil was collected at 88–90 °C under vacuum of 0.5 mmHg. IR (KBr) 3284 (N–H), 1655 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.23 (s, 6 H), 2.46 (t, 2 H), 3.42 (m, 2 H), 5.55–5.60 (m, 2H), 6.25–6.27

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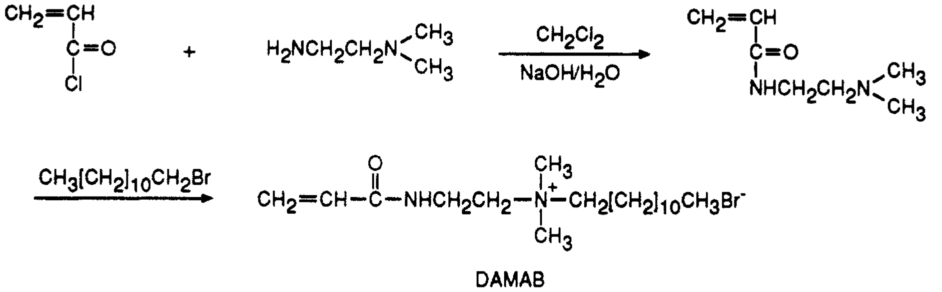
Scheme I. Synthesis of DAMAB Monomer



(m, 4 H), 7.53 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 36.45, 44.43, 57.29, 124.61, 130.59, 165.05.

Freshly distilled *N*-[(dimethylamino)ethyl]acrylamide (5.0 g, 0.035 mol) was then treated with dodecyl bromide (13 g, 0.052 mol) under nitrogen at room temperature for 48 h. Excess dodecyl bromide was decanted and the transparent gel precipitated into a white solid on cooling. The resulting material was washed with two portions of ether and dried under vacuum. Further purification of the final product was accomplished by recrystallization from a 1:1 mixture of acetone and ether. Yield 13.26 g (96%); mp 70.5–72 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.25–1.34 (br m, 20 H), 1.76 (m, 2 H), 3.42 (s, 6 H), 3.82 (m, 4 H), 5.63–5.74 (m, 1 H), 6.28–6.48 (m, 2 H), 8.79 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.18, 21.71, 21.97, 25.36, 28.36, 28.55, 28.65, 30.94, 33.18, 50.89, 51.18, 64.39, 165.56.

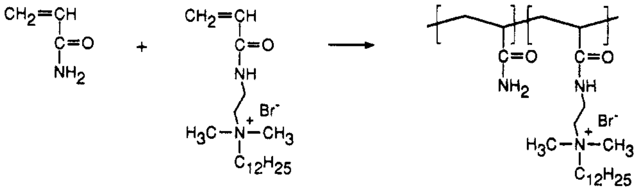
Copolymerization in the Absence of External Surfactant. To a 1000-mL three-necked round-bottom flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet were added acrylamide (AM) and dimethyldodecyl(2-acrylamidoethyl)ammonium bromide (DAMAB) in the desired ratio and 500 mL of deionized water. The total concentration of the comonomers was kept constant at 0.21 M. The solution was heated to 50 °C in a water bath with a small nitrogen stream passing through the system. Polymerization was then initiated by addition of $K_2S_2O_8$ (0.0262 g, 9.71×10^{-5} mol in 3 mL of deionized water) via a syringe. Polymerization was conducted continuously at 50 °C for 6 h, and then the reaction stopped by precipitating the polymer in 800 mL of acetone. The precipitated polymer was washed twice with acetone and vacuum-dried. Conversion was 60–72%. Further purification was accomplished by redissolving the polymer in water and dialyzing for a week against water using a 12000–14000 molecular weight cutoff dialysis tubing. The polymer was recovered by freeze-drying.

Copolymerization in the Presence of External Surfactant. Equimolar amounts of cetyltrimethylammonium bromide and DAMAB monomer were added with acrylamide to the polymerization system. The same procedure as in the previous case was followed for polymerization and polymer purification.

Solution Polymerization. A copolymer containing 5 mol % DAMAB in the feed was prepared via homogeneous solution polymerization. AM (23.3 g, 0.328 mol) and DAMAB (6.79 g, 0.0173 mol) were dissolved in 300 mL of *tert*-butyl alcohol. The solution was purged with nitrogen for 30 min at 50 °C. AIBN (0.056 g, 3.4×10^{-4} mol) was then added to initiate the polymerization. Polymerization was conducted for 10 h. In this case, the copolymer precipitated from solution as polymerization continued. The purification procedure was as described for the polymerization in water. A quantitative yield was obtained.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AC-300. A Mattson 2020 Galaxy Series FTIR was used to obtain infrared spectra. The critical micelle concentration of DAMAB was determined by surface tension measurements with a Kruss processor–tensiometer K12 instrument using the DeNouy ring method at 25 °C. Viscosity measurements were conducted with a Contraves LS-30 low-shear rheometer at a constant shear rate of 6 s^{-1} at 25 °C. Classical light scattering studies were performed on 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 refractometer. Steady-state fluorescence measurements were made with a Spex Fluorolog-2 fluorescence spectrometer. Elemental analyses to determine bromine content were conducted by MHW Laboratories of Phoenix, AZ.

Scheme II. Copoymerization of AM and DAMAB



Results and Discussion

Monomer Structure and Micellar Formation. In devising synthetic strategies for ionic monomers, it is generally better to generate the ionic structure in the last synthetic step to minimize any isolation and purification problems.[13] In our DAMAB monomer synthesis, the polymerizable group was first attached to the organic framework, followed by a single reaction which connected the hydrophobic group to the monomer and simultaneously generated the ionic structure. This two-step process proved to be very convenient, and the yield and purity of the product are quite satisfactory. The DAMAB monomer provides a quaternary ammonium group for enhanced solubility as well as the dodecyl group for hydrophobic association. The acrylamido functionality of the monomer provides a competitive copolymerization rate with acrylamide. Furthermore, this monomer has an amphipathic structure analogous to cationic surfactants; hence it will form micelles at concentrations above the critical micelle concentration (cmc). The cmc of this monomer was measured to be 4.9×10^{-3} M. Negligible change in the cmc was observed on addition of 0.21 M acrylamide. Kinetic studies have demonstrated that monomers of this type possess much higher polymerization rates due to aggregation of the monomers in water.[12] In our case, formation of micelles provides a high concentration of the reactive acrylamido groups near the micelle–water interface, facilitating the formation of the blocklike structures during the copolymerization with acrylamide.

Copolymer Synthesis. DAMAB and AM monomers were copolymerized successfully in water and in the presence of external surfactant (Scheme II). Incorporation of cetyltrimethylammonium bromide as the cationic cosurfactant should dilute the number of DAMAB molecules in each micelle; therefore, the blocks or "runs" of hydrophobic monomer units in the copolymer are expected to be shortened.

The solution polymerization was designed to yield a random copolymer. Copolymerization studies of AM (M_1) and DAMAB (M_2) in *tert*-butyl alcohol indicate that two monomers tend to undergo random, nearly ideal, copolymerization with $r_1 = 1.14 \pm 0.06$ and $r_2 = 0.88 \pm 0.04$. The degree of DAMAB incorporation in each of the copolymers was determined by elemental analysis for

Table I. Structural Parameters of the Copolymers

copolymer	DAMAB content (mol %)	$M_w \times 10^{-6}$
PAM	0	1.12[a]
R-C12-1	0.32	0.74[a]
BS-C12-4.3	4.3	0.95[b]
B-C12-4.7	4.7	1.04[b]
R-C12-5.1	5.1	0.46[b]
B-C12-10.5	10.5	1.12[b]

[a] Measurement was taken in deionized water. [b] Measurement was taken in MeOH/H_2O mixture (50/50 by volume).

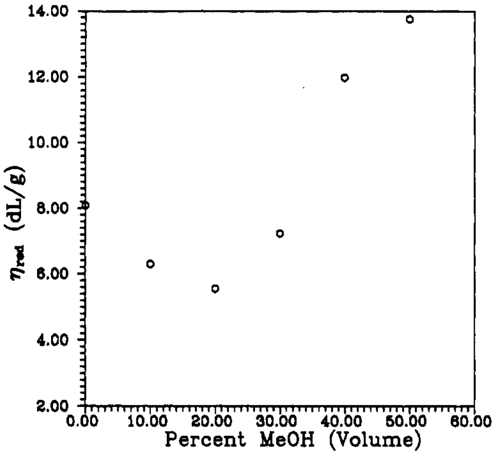


Figure 1. Effect of solvent on the η_{red} of R-C12-5.1 copolymer. The copolymer concentration is 0.127 g/dL.

bromine content. The resulting compositions are summarized in Table I.

The copolymers are named according to their microstructures. The random and microblocky copolymers are distinguished by having R for "random" and B for "blocky" at the beginning of their names. C12 indicates that hydrophobes involved in the copolymers are dodecyl groups. The concentration of the hydrophobic groups in the copolymers are identified by the last number. For instance, R-C12-5.1 is a random copolymer containing 5.1 mol % dodecyl groups, and SB-C12-4.3 is a microblocky copolymer which was prepared in the presence of external surfactant and contains 4.3 mol % dodecyl groups.

Light Scattering Studies. For hydrophobically associating copolymers (BS-C12-4.3, B-C12-4.7, R-C12-5.1, and B-C12-10.5), methanol was used as a cosolvent in the light scattering measurement to disrupt hydrophobic associations and to keep the copolymers from interacting with the filter. As shown in Figure 1, for example, R-C12-5.1 in the methanol/water mixture (50/50 by volume) shows a higher viscosity than in deionized water. This is believed to be a result of breakage of intramolecular hydrophobic associations. Lack of hydrophobic associations for the copolymers in the mixed solvent is further demonstrated by studying the response of viscosity of the copolymer solution to changes in shear rate. As shown in Figure 2, a region in which the viscosity of R-C12-5.1 in water increases with increasing shear rate is observed. Below and above this region, the copolymer exhibits Newtonian flow. This shear thickening behavior has been reported by other researchers[3] and can be explained by changes in intra- and intermolecular associations. The intramolecular associations are disrupted above a certain shear stress, and chain extension results in an increase in the number of intermolecular associations. The viscosity of the same polymer in the methanol/water mixture only increases slightly with increasing shear rate, indicating a much less intramolecular hydrophobic association.

The weight-average molecular weight data for the copolymers are presented in Table I. The copolymer synthesized in *tert*-butyl alcohol has a substantially lower molecular weight than those prepared in water. However, the difference in the molecular weight for the two types of copolymers should not be taken alone as the reason for their different association behaviors.

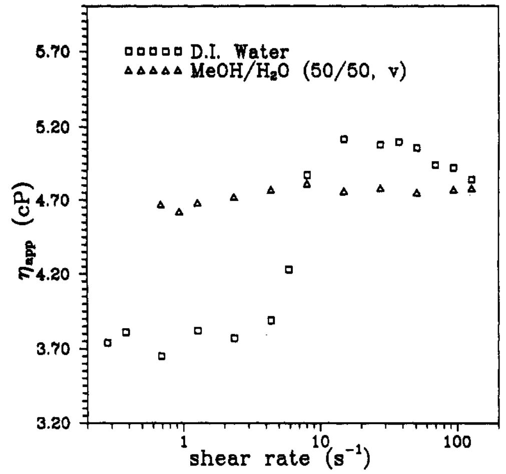


Figure 2. Effect of the shear rate on the viscosity of R-C12-5.1 at 0.484 g/dL.

Copolymer Solubility. Copolymers formed in the absence and presence of the cationic cosurfactant exhibit different solubilities. DAMAB monomer concentrations of 1, 5, and 20 mol % in the feed, respectively, result in complete water solubility. The copolymer with 25 mol % DAMAB monomer is only partially soluble, probably because of multiple associations. The effect is more pronounced for the copolymer containing a higher level of hydrophobe. Increasing DAMAB monomer concentration to 40 mol % results in total insolubility.

Dilute Solution Properties. Viscometry is a convenient and reliable method for determining associative properties of amphipathic copolymers in aqueous solution. A typical intramolecular associating polymer in aqueous solution is characterized by a lower viscosity compared to its parent polymer containing no hydrophobic groups. The viscosity will increase gradually with polymer concentration due to an increase in the hydrodynamic volume occupied by the macromolecule. If a rapid increase in apparent viscosity occurs at a critical concentration, C^*, the polymer is then described as intermolecularly associative in nature.

Associating properties of the copolymers can also be investigated by fluorescence spectroscopy using pyrene as a probe. The ratio of the pyrene fluorescence intensities of band I to band III (I_1/I_3) serves as an indicator of the polarity of the microenvironment. A lower value of I_1/I_3 indicates a more hydrophobic environment as experienced by the probe.[14]

Effect of Copolymer Composition. Before discussing the viscosity properties of the copolymers as a function of the copolymer composition, it is necessary to emphasize that since the copolymers are made at relatively high conversions, they are expected to have somewhat broad molecular weight distributions and copolymer compositions. Studies in Candau's group have shown that in the micellar copolymerizations both the molecular weight and hydrophobic content in the copolymers decrease as copolymerization runs to higher conversion.[15] In our experiments, the copolymerizations were terminated at 60–72% conversion and the DAMAB concentration remains above its cmc even at the highest conversion. Therefore, the number of the hydrophobic blocks in the copolymers may decrease as the copolymerization pro-

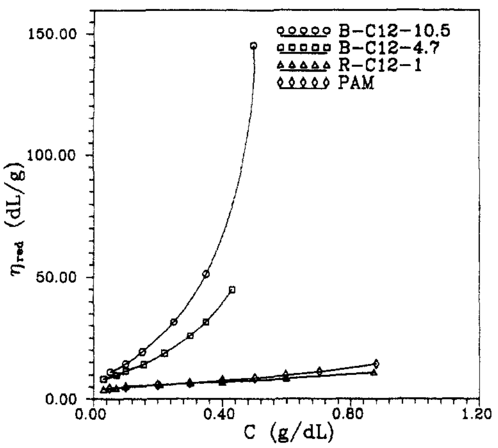


Figure 3. Effect of concentration on η_{red} for copolymers with various hydrophobic group contents in deionized water.

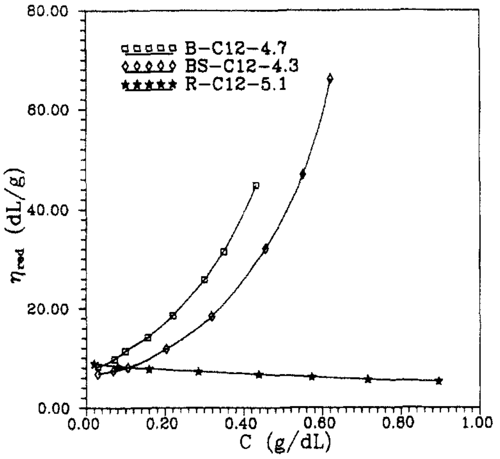


Figure 4. Effect of polymer concentration on η_{red} for copolymers containing various hydrophobic sequence lengths in deionized water.

ceeds, but the sequence length of the blocks should remain relatively constant.

Figure 3 illustrates the effect of polymer composition on solution properties. Viscosity increases with increasing DAMAB content. The copolymer containing 0.32 mol % of DAMAB (R-C12-1) displays viscosity behavior similar to that of polyacrylamide prepared under the same conditions; there are no significant hydrophobic associations in the concentration range investigated. Copolymers with higher DAMAB content show a significantly greater dependence of the viscosity on concentration, similar to the previously reported behavior of AM and *n*-alkylacrylamide copolymer systems.[2] The copolymer with 10.5 mol % DAMAB (B-C12-10.5) possesses a lower C^* and a steeper slope beyond C^* than the copolymer with 4.7 mol % DAMAB (B-C12-4.7). This is attributed to stronger intermolecular associations in the former. The C^* values of AM–DAMAB copolymers are generally higher than that of an AM and dodecylacrylamide copolymer containing 0.25 mol % dodecyl groups. This may be attributed to the presence of charged groups in the polymer chain. It is noteworthy, however, that no polyelectrolyte effect is observed for these systems in the dilute regime due to the low DAMAB concentration.

Addition of a cationic surfactant to the polymerization system containing 5 mol % DAMAB results in a lower slope gradient in the viscosity profile of the resulting polymer (BS-C12-4.3) relative to the one without external surfactant (B-C12-4.7) (Figure 4). This is consistent with formation of shorter blocks and/or a more random distribution of DAMAB units, decreasing the tendency of intermolecular association.

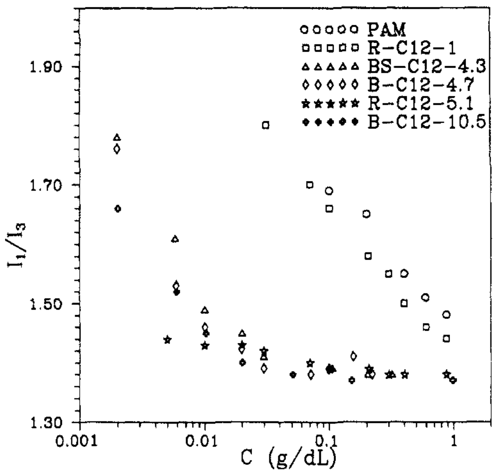


Figure 5. I_1/I_3 as a function of polymer concentration for various copolymers in deionized water.

A completely different viscosity profile for the copolymer with 5.1 mol % DAMAB prepared by solution polymerization (R-C12-5.1) is observed (Figure 4). The reduced viscosity decreases with increasing polymer concentration, indicating that hydrophobic associations are largely intramolecular in nature. This point will be addressed further in the discussion of fluorescence data and solvent effects.

Fluorescence Studies. Figure 5 depicts the dependence of I_1/I_3 values of pyrene steady-state fluorescence spectra on polymer concentration in aqueous solutions of the copolymers. I_1/I_3 values for BS-C12-4.3, B-C12-4.7, and B-C12-10.5 copolymers remain almost constant at 1.36–1.38 in the concentrations above 0.05 g/dL upon dilution. Further decreases in the copolymer concentrations result in rapid increases in I_1/I_3 values. The data suggest that pyrene molecules initially reside inside the hydrophobic microdomains formed through association of the hydrophobic groups. These hydrophobic microdomains vanish as polymer molecules are diluted to concentrations below 0.05 g/dL such that pyrene probes are exposed to a more aqueous environment. This behavior is consistent with intermolecular hydrophobic association. Furthermore, increase in I_1/I_3 occurs at concentrations well below C^*. This implies that hydrophobic interactions at the microscopic level take place at much lower concentration than reflected by macroscopic properties.

Pyrene fluorescence spectra for the R-C12-5.1 copolymer are consistent with classical water-soluble polymeric surfactant behavior[16] (Figure 5). A low I_1/I_3 value of pyrene throughout the copolymer concentration range is observed. This indicates that the R-C12-5.1 copolymer provides hydrophobic microdomains and acts as a host. The presence of hydrophobic microdomains is independent of copolymer concentration, consistent with intramolecular association.

I_1/I_3 values in the R-C12-1 copolymer solution decrease continuously with increasing polymer concentration (Figure 5). A similar behavior is observed in polyacrylamide solutions. There is no well-defined transition point in the I_1/I_3 vs copolymer concentration curve, suggesting the absence of hydrophobic interactions between long alkyl chains capable of sequestering a pyrene probe from the aqueous environment. This information agrees favorably with that obtained from viscosity studies.

Effect of Solvent. Hydrophobic associations are induced by the water-structuring effect. Change in the

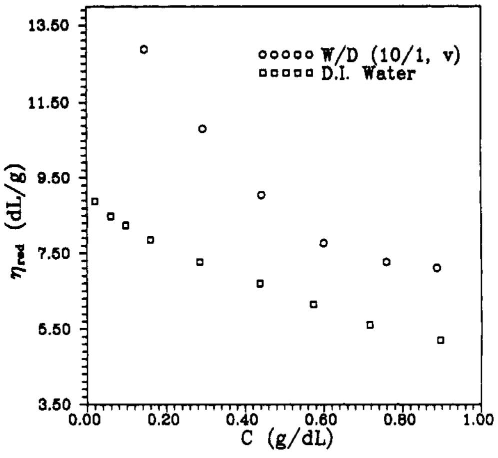


Figure 6. Effect of solvent on η_{red} of R-C12-5.1 copolymer.

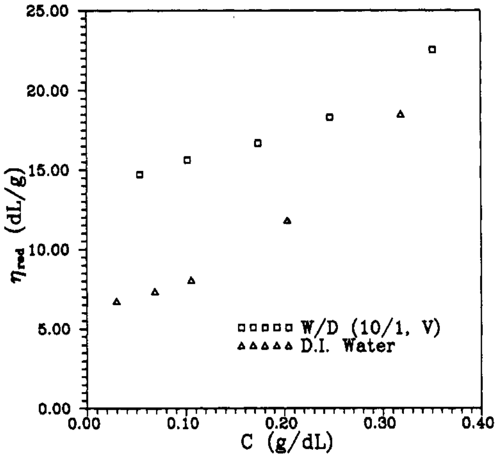


Figure 7. Effect of solvent on η_{red} of BS-C12-4.3 copolymer.

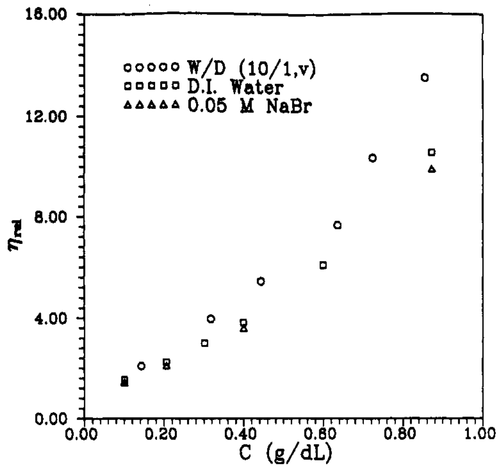


Figure 8. Effect of solvent on η_{rel} of R-C12-1 copolymer.

water structure by addition of additives or cosolvents can either enhance or reduce hydrophobic interactions, depending on the nature of the additive. Controlled studies of changes in the rheological properties of polymer solutions in different aqueous media provide information on polymer conformation. In this work, NaBr is used as a water-structure-forming agent[17] and 1,4-dioxane as a water-structure-breaking agent.[18] The R-C12-1 copolymer is soluble in both 0.05 M NaBr aqueous solution and a water/dioxane mixture in a ratio of 10 to 1 by volume. However, solubility of the copolymers with higher hydrophobe content is affected significantly by added external electrolyte. Addition of NaBr results in precipitation from solution due to a "salting out" effect.[17] The copolymers are soluble in the water/dioxane mixture.

Figure 6 shows the effect of solvent on the viscosity of the R-C12-5.1 copolymer. The reduced viscosity increases upon addition of 10% dioxane. This is attributed to the decrease in the extent of intramolecular association resulting in the expansion of the polymer coil. Intermolecular association is also disrupted as dioxane is introduced into BS-C12-4.3 and B-C12-4.7 copolymer solutions. The viscosity of the BS-C12-4.3 copolymer shows less concentration dependence due to reduced intermolecular association tendency (Figure 7). It is interesting to note that this copolymer possesses a higher reduced viscosity in the lower concentration range in the water/dioxane mixture than in deionized water. A similar behavior is also observed for the B-C12-4.7 copolymer. A possible explanation is that there are some intramolecular associations of hydrophobic groups in the low-concentration regime which are disrupted upon addition of dioxane. This indicates that hydrophobic associations undergo a transition from intermolecular to intramolecular when the solution is diluted. A similar observation was reported by Siano et al.[19] in a study of acrylamide and *n*-octylacrylamide copolymers using 8-anilino-1-naphthalenesulfonic acid as a fluoresence probe. Schulz et al.[20] also observed such a transition for the copolymer of acrylamide and a nonionic surfactant monomer. However, such an intramolecular association at low concentration was not seen in pyrene probe studies. This suggests that while polymer solution properties may be influenced considerably by the presence of hydrophobic interactions, aggregates may not be of sufficient size to protect pyrene molecules from the bulk aqueous solution. I_1/I_3 values of pyrene fluorescence in such cases fail to "report" the presence of hydrophobic interactions.[21] The viscosity profile of the R-C12-1 copolymer is essentially invariant with addition of NaBr or dioxane, again indicating the lack of hydrophobic interactions in this system (Figure 8).

Conclusions

Rheological and fluorescence studies of amphipathic copolymers of AM and DAMAB have demonstrated that the associating behavior of the copolymers is governed by the arrangement of DAMAB units along the polymer chains. A random copolymer with 5 mol % of DAMAB shows a tendency for intramolecular hydrophobic association, while a microblocky copolymer of identical composition results in intermolecular association of hydrophobes. The intermolecular hydrophobic associations are enhanced by increasing the length of the hydrophobic block and/or the number of blocks in the polymer chain.

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