

Effect of Hydrophobic Modification on the Rheological Properties of Poly(*N*-vinyl pyrrolidone-*co*-dimethylaminopropylmethacrylamide)

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ABSTRACT: The viscoelastic properties of poly(*N*-vinyl pyrrolidone-*co*-dimethylaminopropylmethacrylamide) (copolymer **I**) and its hydrophobically modified analogue, poly(*N*-vinyl pyrrolidone-dimethylaminopropylmethacrylamide-dimethylaminopropylmethacrylamide⁺-C₁₂H₂₅Cl⁻) (copolymer **II**), were compared in the concentration range from 1 to 20% with dynamic and Brookfield rheometers. In addition, gel permeation chromatography/multi-angle laser light scattering data were obtained to characterize the molecular weights and radii of gyration for the polymer samples. In general, the hydrophobically modified polymer copolymer **II** was characterized by a chain configuration that was more compact and a viscosity that was an order of magnitude lower than that of its unmodified counterpart, copolymer **I** (both polymers were characterized by similar molecular weights), in dilute (1% w/w) and semiconcentrated solutions (<5% w/w). The difference in the chain configurations resulted in significant differences in the measured viscosities of the polymer solutions as a function of polymer concentration and in the presence of added electrolyte. On the basis of dynamic rheological measurements for more concen-

trated solutions in the range of 5–10% for copolymer **I** and 5–20% for copolymer **II**, the viscous modulus predominated (loss modulus > storage modulus), with crossover points occurring at 10% (w/w) and 10 Hz for copolymer **I** and 20% (w/w) and 20 Hz for copolymer **II**. The mixtures of copolymer **II** with anionic surfactants, such as sodium dodecyl sulfate and polyoxyethylene (2) dodecyl ether sulfate (sodium laureth-2-sulfate), showed strong interactions by exhibiting viscosity maxima and flocculation points corresponding to the surfactant/polymer alkyl group and surfactant/polymer charge concentration ratios in the range of 1–2. Copolymer **II** showed network formation by significant viscosity buildup in combination with two nonionic surfactants, which included C_{14–15} Pareth-7 and C_{12–13} Pareth-3. On the basis of viscosity measurements, copolymer **I** was found not to interact with anionic and nonionic surfactants. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 190–200, 2007

Key words: water-soluble polymers; viscoelastic properties; PEG-150-poly(ethylene glycol)-150 SMDI-dicyclohexylmethane-4,4'-diisocyanate

INTRODUCTION

Hydrophobic substitution is frequently used in cosmetic industrial practice for the modification of the rheological properties of polymers. Specific materials and their structures are reviewed in the *International Cosmetic Ingredient Dictionary and Handbook*.¹ Anionic and nonionic polymers, such as hydrophobically modified, alkali-soluble emulsion polymers, have been primarily designed as thickeners in which alkyl side chains provide a means for physical crosslinking in aqueous solutions. There are a significant number of commercially available examples within this class of materials, which include poly(acrylic acid/C_{10–30} alkyl acrylate/allyl ether of pentaerythritol or allyl ether of sucrose),² poly(steareth-20 itaconate/acrylic acid/methacrylic acid/alkyl acrylate/alkyl methacrylate),³ poly(alkyl acrylate/

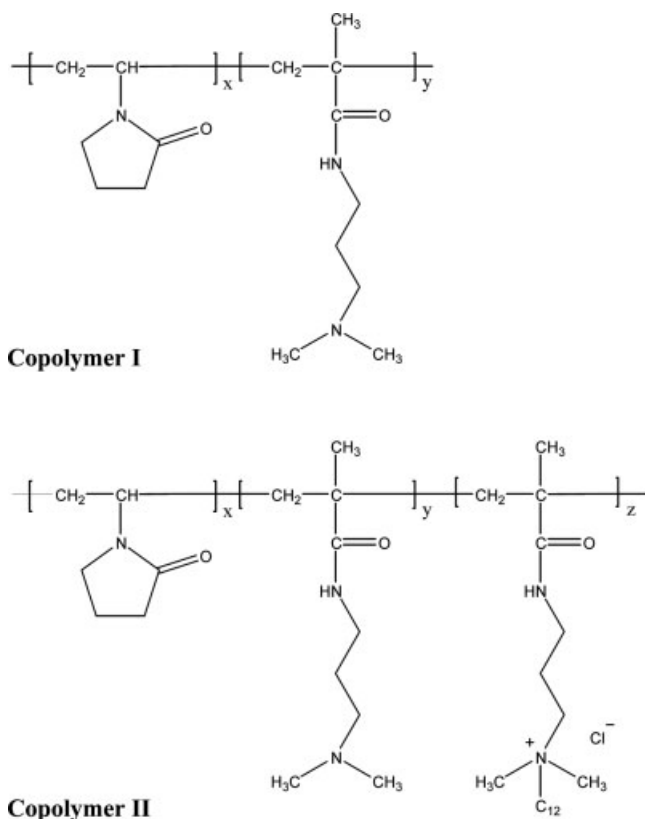
methacrylic acid/steareth-20 methacrylate),⁴ hydrophobically modified ethylene oxide urethane polymers such as poly(PEG-150/stearyl alcohol/SMDI),⁵ and alkylated cellulose polymers such as ethyl hydroxyethyl cellulose¹ and C_{12–16} alkyl hydroxyethyl ethylcellulose.¹ An example of a hydrophobically modified cationic polymer is hydroxyethylcellulose glycidyl lauryl dimethyl ammonium chloride,⁶ which was introduced as a hair-conditioning and foam-enhancing agent. Hydrophobic groups can also be used to ensure viscoelastic stability in the presence of electrolytes or in solutions with extreme pH values and for synergistic interaction with surfactants.⁷ The last aspect of the properties of hydrophobically modified polymers is important because they are frequently used in combination with surfactants in aqueous solutions. The interactions between hydrophobically modified polymers and surfactants can lead to network formation and noteworthy rheological properties, which often include a significant increase in the solution viscosity.

Although the rheology of hydrophobically modified nonionic polymers^{8–11} and anionic polymers^{12–14} has been described in the literature in detail, the visco-

This article is dedicated to the memory of Professor Marian Kryszewski.

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Scheme 1

elastic properties of cationic and hydrophobically modified cationic polymers are less known.

In this study, we compared the rheological behavior of a cationic copolymer recently introduced to the cosmetic industry, poly(*N*-vinyl pyrrolidone-*co*-dimethylaminopropylmethacrylamide) (copolymer I),¹⁵ with its hydrophobically modified analogue, poly(*N*-vinyl pyrrolidone-dimethylaminopropylmethacrylamide-dimethylaminopropylmethacrylamide⁺-C₁₂H₂₅Cl[−]) (copolymer II).¹⁶

EXPERIMENTAL

Rheological analysis was carried out for 1–20% (w/w) solutions of copolymer I and for its hydrophobically modified analogue, copolymer II. The structures for these materials are provided in Scheme 1. Both materials were prepared by free-radical copolymerization of constituent monomers in a process similar to that described for copolymer II in a previous communication.¹⁷

Preparation of lauryl dimethyl methacrylamidopropyl ammonium chloride (DMAPMA⁺-C₁₂H₂₅Cl[−])

A mixture of 350 g of dimethylaminopropylmethacrylamide (DMAPMA) and 280 g of dodecyl chloride (1.5 : 1) was stirred with 111.2 g of water (15%) and six drops of concentrated sulfuric acid. The reaction mixture was heated up to 95°C, and air was bubbled

through it. The progress of the reaction was monitored by gas chromatography. After 24 h and the quantitative conversion of dodecyl chloride, the reaction mixture was cooled off, and the product was used in polymerization without further purification.

Preparation of copolymer II

N-Vinylpyrrolidone (VP; 280 g) and deionized water (1400 g) were charged into a 2-L resin pot equipped with a gas inlet, liquid inlet, a thermometer, and a condenser. The pH of the solution was adjusted to about 7.5 with KOH, and a stream of nitrogen was introduced, which bubbled through the solution during the reaction. Then, DMAPMA (17.5 g) and DMAPMA⁺-C₁₂H₂₅Cl[−] (52.5 g) were added continuously and uniformly into the pot with vigorous stirring over a period of 4 h so that the relative monomer concentrations of VP, DMAPMA, and quat remained constant throughout the reaction at predetermined levels.

As soon as DMAPMA and DMAPMA⁺-C₁₂H₂₅Cl[−] were introduced into the pot, the catalyst, Vazo 67 [2,2-azobis(2-methylbutyronitrile)], was gradually added over a period of 5 h. After the addition of the initiator was complete, the solution temperature was held constant for an additional 3 h at 78°C. The product was an aqueous solution of a homogeneous terpolymer of VP, DMAPMA, and DMAPMA⁺-C₁₂H₂₅Cl[−]. It had a predetermined composition indicative of the relative amounts of each monomer used in the process and was substantially free of any residual homopolymer or copolymer. The yield of the terpolymer product was substantially quantitative.

Copolymer I was prepared with essentially the same polymerization procedure.

The content of DMAPMA in copolymer I was 20% (w/w), which corresponded to 14% mol/mol. The composition of copolymer II was 84.8% mol/mol VP, 11.2% mol/mol DMAPMA, and 4.0% mol/mol DMAPMA⁺-C₁₂H₂₅Cl[−]. The concentrated solutions of copolymer I and copolymer II were characterized by pH values of 6.0–8.0 and 3.5–4.0, respectively. After dilution with deionized water, the solutions had pH values in the ranges 5–6 and 4–5 for copolymer I and copolymer II, respectively, and were used in the measurements without pH adjustments.

The interactions with the surfactants were studied with anionic surfactants, which included sodium dodecyl sulfate (SDS; Aldrich) and sodium laureth-2 sulfate [C₁₂(OCH₂CH₂)₂OSO₃Na or SLES-2; Stepan Chemical Co. Northfield, IL]. Mixtures of the polymers with nonionic surfactants were studied for C_{14–15} Pareth-7 [C_{14–15}O(CH₂CH₂O)₇H] and C_{12–13} Pareth-3 [C_{12–13}O(CH₂CH₂O)₃H], which were obtained from Shell Chemical Co. (Houston, TX) under the commercial names Neodol 45-7 and Neodol 23-3, respectively. The effect of the salt concentration on the rheological

TABLE I
Characterization of Copolymers I and II by Light Scattering (GPC–MALLS) and Viscosity Measurements

Copolymer	M_w (g/mol)	R_g (nm)	Brookfield viscosity (cPs) ^a	Dynamic viscosity (cPs) ^b
I-1	2,960,000	92	41,000 at 10% (w/w)	2935
I-2	3,010,000	90	—	—
I-3	4,340,000	115	—	—
II-1	2,780,000	80	59,800	185
II-2	2,880,000	77	66,000	194
II-3	3,440,000	87	79,800	226
II-4	3,510,000	85	71,000	186
II-5	3,940,000	90	99,600	297

^a At 10 rpm and 20% (w/w).

^b At 5% (w/w).

properties of both of these materials was investigated with NaCl (Aldrich).

For the copolymer characterization, multi-angle laser light scattering (MALLS) was carried out with a Wyatt Dawn laser photometer (Wyatt Technology Corp., Santa Barbara, CA) operating in conjunction with a Shodex OHPAK KB-80M linear gel permeation chromatography (GPC) column (Showa Deuko America, Inc., New York, NY). The GPC–MALLS setup consisted of a solvent pump, a sample introduction port, a size exclusion column, a light scattering detector, and finally a refractive-index (concentration) detector. The absolute weight-average molecular weight (M_w) was obtained from the intensity of the excess Rayleigh scattered light, whereas the radius of gyration (R_g) was obtained from the angular dependence of the Rayleigh scattering. Polymers fractionated on a GPC column were detected by the light scattering and differential refractive-index (concentration) detectors, and their molecular weights and size distributions were generated. For this work, a Shodex KB-80M column was employed as the GPC column with a mobile phase of 50/50 (v/v) water/methanol, which was made 0.2M with lithium nitrate and 0.1M with Tris and adjusted to pH 9.0 with nitric acid. A flow rate of 0.5 mL/min was maintained, and the experimental temperature was 30°C. The sample concentration was 0.15% (w/v), and the injection volume was 100 μ L. Essential to obtaining absolute molecular weights from light scattering measurements is the change in the polymer refractive index with the sample concentration, which is otherwise known as the specific refractive-index increment (dn/dc). For this work, a dn/dc value of 0.140 mL/g was used, as back-calculated with Wyatt Astra software (version 4.50), assuming complete sample recovery from the GPC column.

The apparent viscosity was measured at 25°C with a Brookfield model LVDV-I digital viscometer (Brookfield Engineering Laboratories, Middleboro, MA). Spindles LV1–LV4 were used in the analysis for most of the solutions. However, the UL adapter and spindle

were used for very dilute solutions. The data were collected for spindle rotation rates in the range of 8.33×10^{-3} to 1.67 Hz. The solutions were typically stored for 24 h in a temperature bath (25°C) before viscosity measurements were obtained.

Dynamic rheological studies were carried out by with a Carri-Med CSL 100 controlled-stress rheometer for stress-controlled experiments and a TA Instruments ARES rheometer (Wilmington, DE) for strain-controlled experiments. The stress-controlled instrument was operated in the oscillation mode with the cone and plate method, in which controlled oscillation stress from 1 to 100 dyn/cm² was applied. Similarly, the strain-controlled instrument was operated with the cone and plate method at various strains. All dynamic measurements were carried out at 25°C.

RESULTS AND DISCUSSION

Copolymer solutions

The characterization of the copolymers was carried out through light scattering measurements of several samples of copolymers **I** and **II**. The results yielded M_w and R_g values, which are shown in Table I and Figure 1.

The values of R_g for copolymer **I** fall in the range of 90–115 nm and are greater than the corresponding R_g values for hydrophobically modified copolymer **II**, which range from 77 to 90 nm. The data suggest that copolymer **II** assumes a more compact configuration in dilute solutions as a result of hydrophobic interactions in comparison with its unmodified analogue, copolymer **I**. This is further supported by dynamic viscosity data for both polymers, which were obtained for 5% (w/w) solutions with a stress-controlled rheometer. Although the dynamic viscosities of copolymer **II** vary from 185 to 297 cPs, the corresponding viscosities of copolymer **I** are an order of magnitude greater (\sim 2935 cPs). In further rheological studies, copolymer samples **II-1** and **I-1**, characterized by molecular weights of 2,780,000 and 2,960,000, respectively, were used.

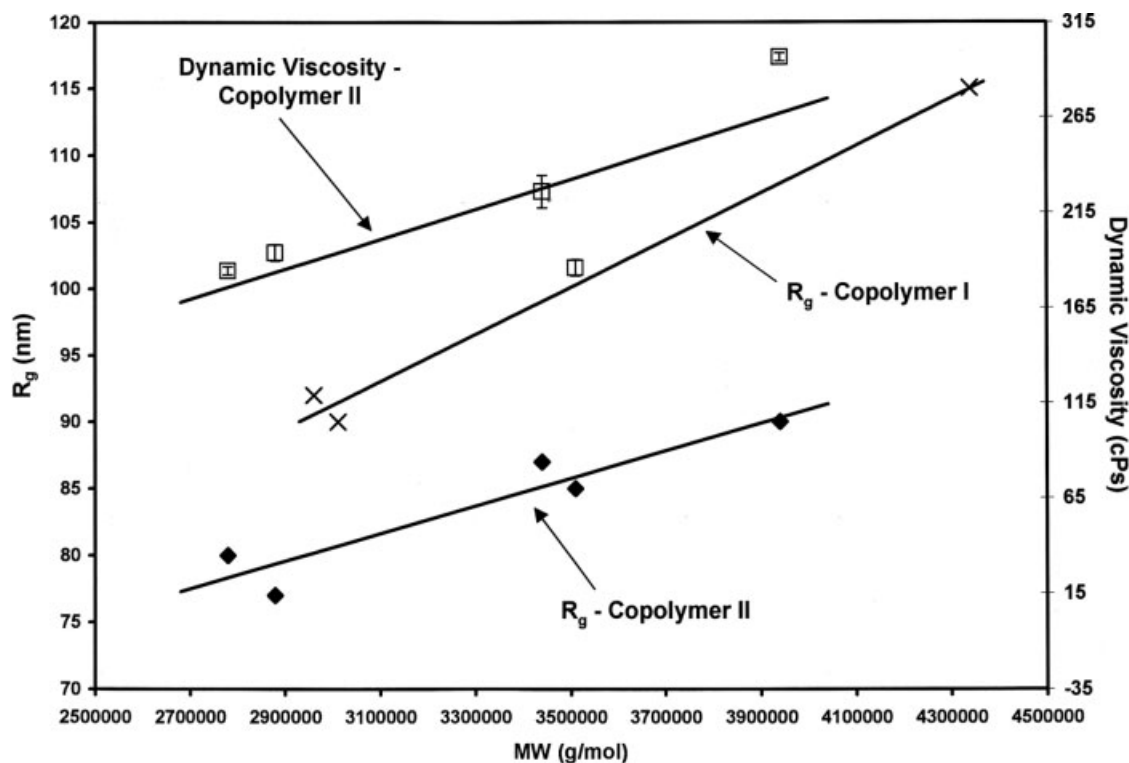


Figure 1 R_g and dynamic viscosity data as functions of M_w for copolymers I and II.

Figure 2 presents a plot of the apparent viscosity as a function of the shear rate (the rate of spindle rotation) for 1, 5, and 10% (w/w) solutions of both copolymers. The data indicate a higher viscosity for copolymer I by more than an order of magnitude, shear-thinning rheological behavior for the solutions of copolymer I, and Newtonian character (no dependence on the shear rate) for the solutions of copolymer II. Such results suggest that the stress accompanying the flow of copolymer solutions is capable of disrupting or disentangling the chains of copolymer I, which is reflected in diminished viscosity values at higher shear rates. In contrast to this, the strength and stability of intramolecular junctions in solutions of copolymer II, combined with the lack of interchain association, lead to the Newtonian behavior of 1–10% (w/w) solutions. Similar relative patterns of rheological behavior were observed for all 1–10% solutions of both copolymers.

Figure 3 shows the apparent viscosity as a function of the concentration in aqueous solutions for both copolymers. For copolymer I, a dramatic increase in the viscosity occurs at concentrations higher than 4–5% (w/w), presumably because of chain entanglement. A corresponding increase in the viscosity of copolymer II is evident at concentrations above 15% (w/w). It should be stressed again that in dilute solutions (0–2% w/w), the viscosity of I is also significantly higher than that of II, presumably because of the presence of hydrophobic side chains interacting to form associa-

tive intramolecular junctions and leading to a more compact polymer chain configuration in solution.

In dilute solutions, the polymer coils are separated from one another by the solvent, and the measured viscosity is related to the size of the individual coils. The chains begin to interpenetrate at a critical entanglement concentration (given by the reciprocal of the intrinsic viscosity), and they form an intertwined network in concentrated solutions. These processes are schematically visualized in Scheme 2. The data obtained for copolymers I and II suggest that the process of polymer chain entanglement and the formation of fully interpenetrated network occur at a higher solution concentration for copolymer II, probably because of the contracted configuration of chains as a result of intramolecular hydrophobic interactions. Contracted chains form denser intramolecular networks, which do not readily permeate one another at lower concentrations. The viscosity measurements indicate that only above 10–15% (w/w) does a conversion of intramolecular association to intermolecular association occur with the formation of a larger network. In comparison, the formation of an extended network or entangled chains begins at 4–5% for unmodified copolymer I.

We have also examined the effect of a salt (NaCl) on the apparent viscosity of 1, 5, and 10% (w/w) copolymer solutions (Fig. 4). At 1% NaCl, both copolymers experience a decrease in the viscosity as a function of the salt concentration; this is typical polyelectrolyte

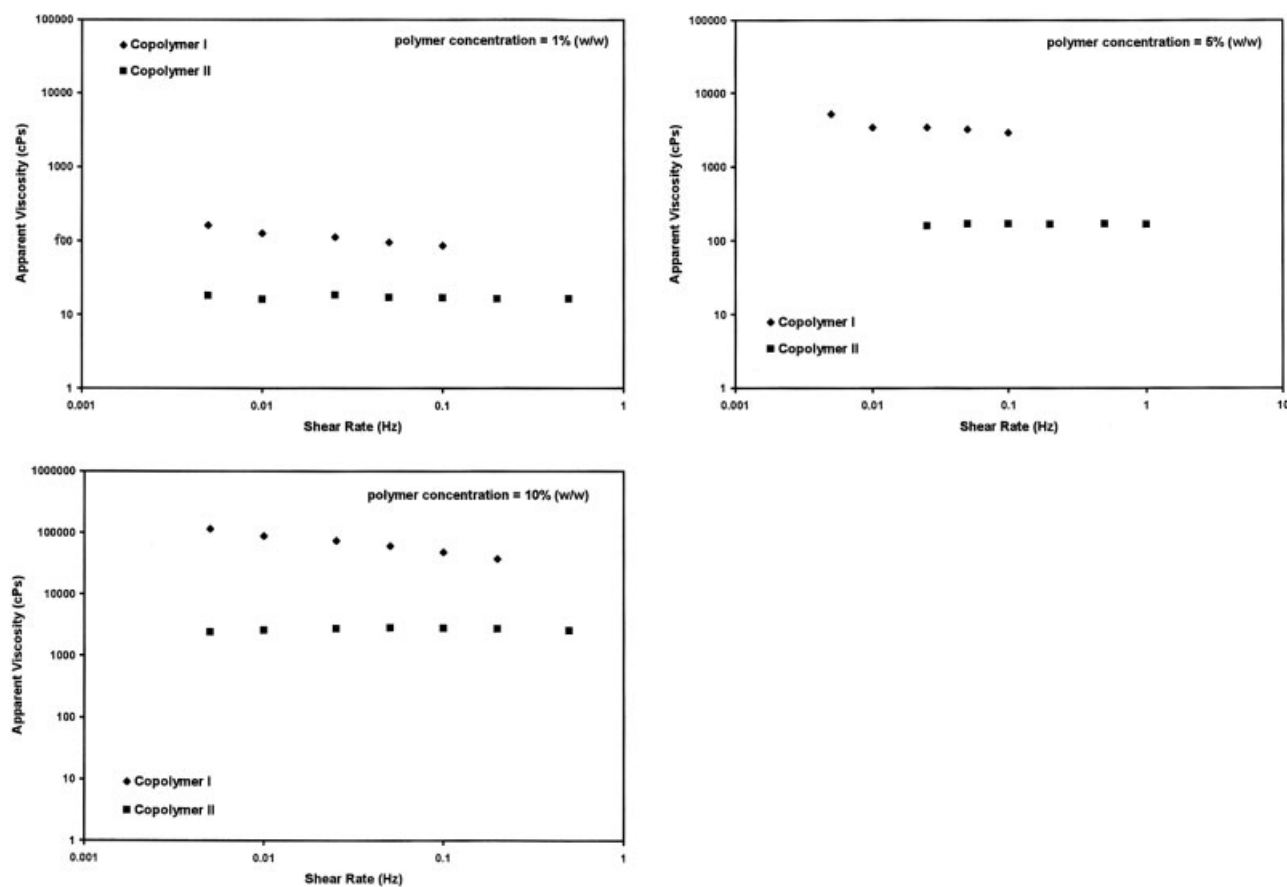


Figure 2 Brookfield viscosity as a function of the shear rate for copolymers I and II.

behavior and is caused by the screening electrostatic repulsion of cationic sites on the polymer chains. However, the decrease in the viscosity for copolymer II (from 17 to 5 cPs) is much smaller than that observed for copolymer I (from 86 to 18 cPs). This could be a reflection of the fact that copolymer II already exists in a compressed configuration, and further collapse and reduction in the coil dimensions are limited. At polymer concentrations of 5 and 10%

(w/w), copolymer I displays a decrease in the viscosity, whereas copolymer II shows a small increase in the viscosity. This is probably related to either (1) the reorganization of intramolecular associative junctions and the dimensional expansion of polymer coils or (2) the increased probability of the formation of intermolecular aggregates stabilized by hydrophobic interactions, as visualized in Scheme 3.

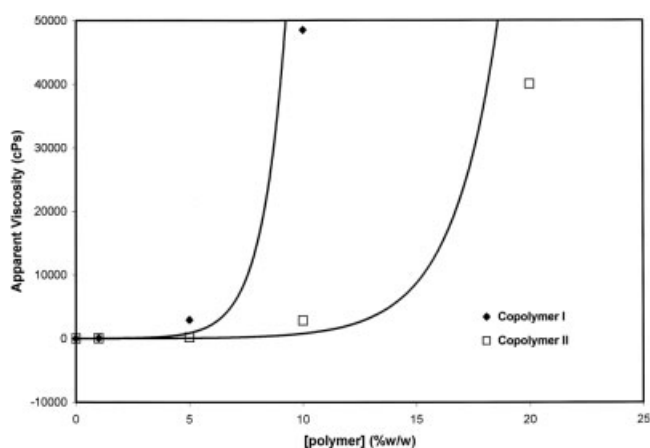
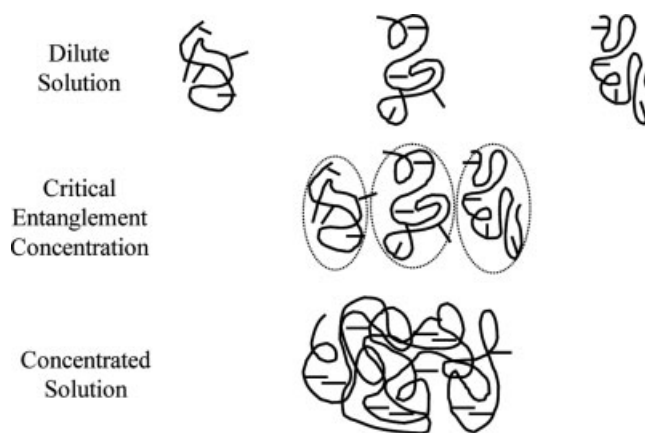


Figure 3 Apparent viscosity as a function of the polymer concentration for copolymers I and II.



Scheme 2 Schematic representation of the transition from a dilute polymer solution to a semidilute polymer solution to a concentrated polymer solution for a hydrophobically modified copolymer.

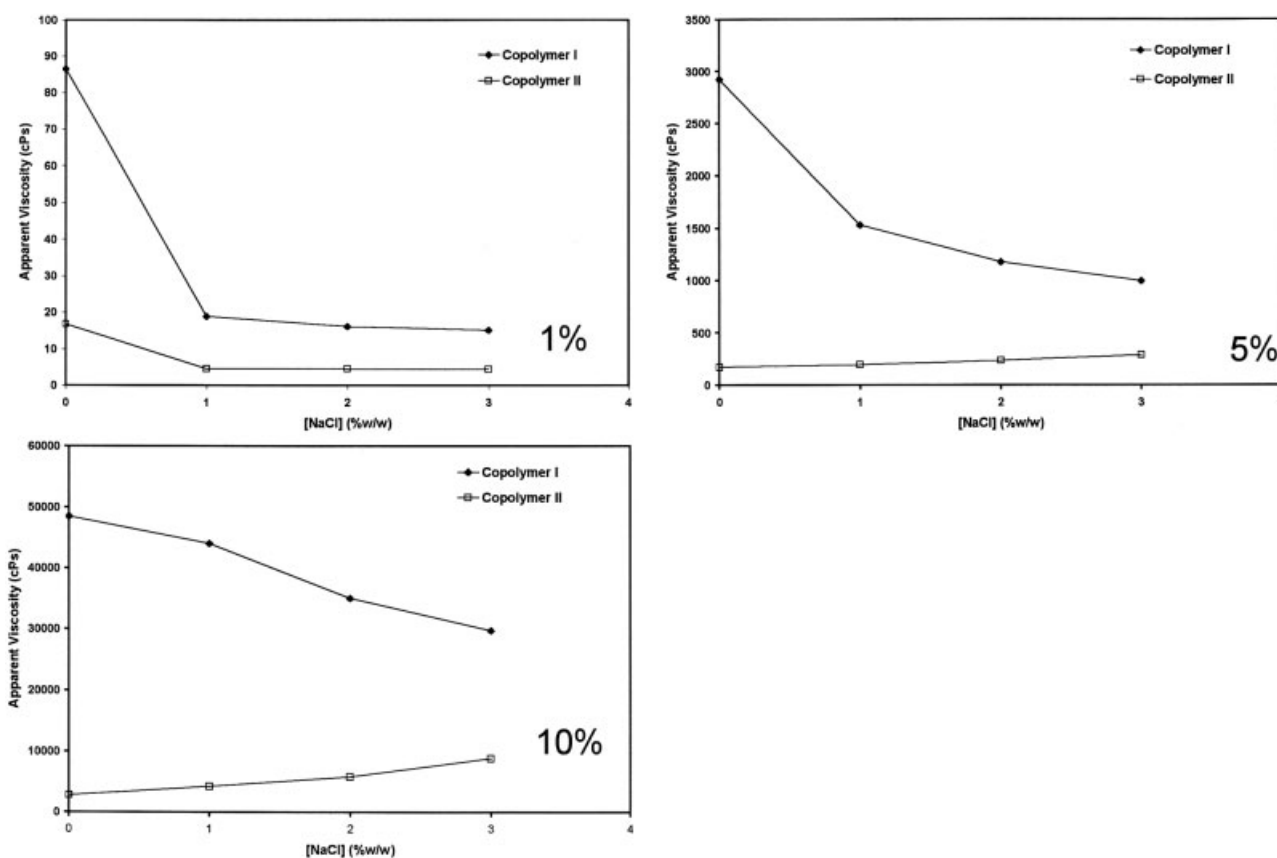
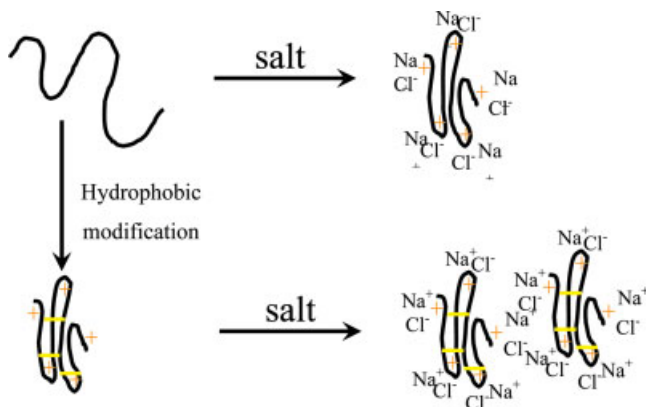


Figure 4 Apparent viscosity as a function of the NaCl concentration for 1, 5, and 10% (w/w) solutions of copolymers I and II. The viscosity was measured at 0.17 Hz.

The dynamic rheological behavior of both copolymers was determined at various concentrations (5, 10, and 20%) with stress-control and strain-control rheometers. We monitored the elastic component of the shear modulus [i.e., the storage modulus (G')], the viscous component of the shear modulus [i.e., the loss modulus (G'')], and the complex viscosity (η^*) for both



Scheme 3 Schematic representation of the chain transition for unmodified and hydrophobically modified copolymers after the addition of an electrolyte to the solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymers (Figs. 5 and 6). Figure 5 contains plots of all three rheological parameters as a function of the oscillation stress for 5 and 10% solutions of copolymer I at a low frequency of 0.32 Hz. At both concentrations, G'' is greater than G' ; therefore, the viscous character of the solution predominates. η^* decreases as a function of the oscillation stress, which is particularly pronounced for solutions at 5% (w/w). This result confirms an observation based on the measurements of the apparent viscosity as a function of the strain rate, which pointed to weak shear-thinning characteristics of the solutions of copolymer I. In the case of copolymer II (Fig. 6), G'' is also greater than G' (the viscous character predominating) at 5, 10, and 20%, although an increase in the polymer concentration leads to higher relative values of G' . In practice, this means that progressively more concentrated solutions of both copolymers acquire a stringy feel and rubberlike response to deformation, which is evident at a higher deformation stress.

η^* of copolymer II shows little change with an increase in the oscillation stress, demonstrating the Newtonian characteristics of the solution of this copolymer.

On the basis of the plots of G' and G'' as functions of the oscillation stress (and corresponding strain values), we can determine the linear (elastic) region for a

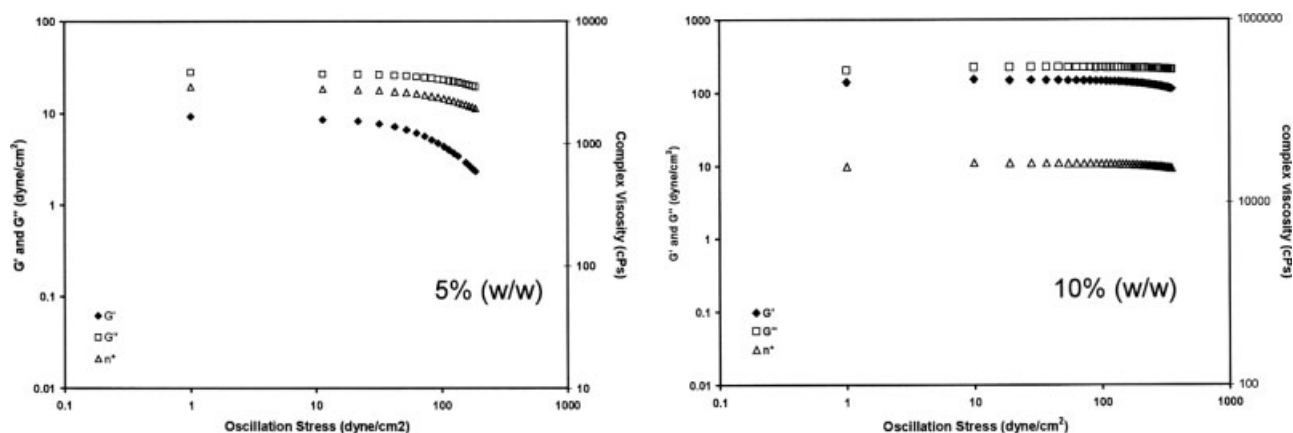


Figure 5 G'' , G' , and η^* as functions of the oscillation stress for 5 and 10% (w/w) solutions of copolymer I. The measurements were performed at a frequency of 0.32 Hz.

given material in which the stress-strain cycle is reversible and no damage occurs to the microstructure of the sample. In the case of a strain-control rheometer, the determination of the linear range is accomplished with a strain sweep (G' as a function of the strain percentage). On the basis of these data, and with a strain value within the linear range, the de-

pendence of G' and G'' as a function of the deformation frequency has been determined, as shown in Figure 7, for solutions of copolymer I with both stress- and strain-controlled rheometers. Both G' and G'' increase as functions of the frequency with a crossover point, at which the elastic modulus becomes greater than G'' (at 10 Hz for the 10% solution). Similar data

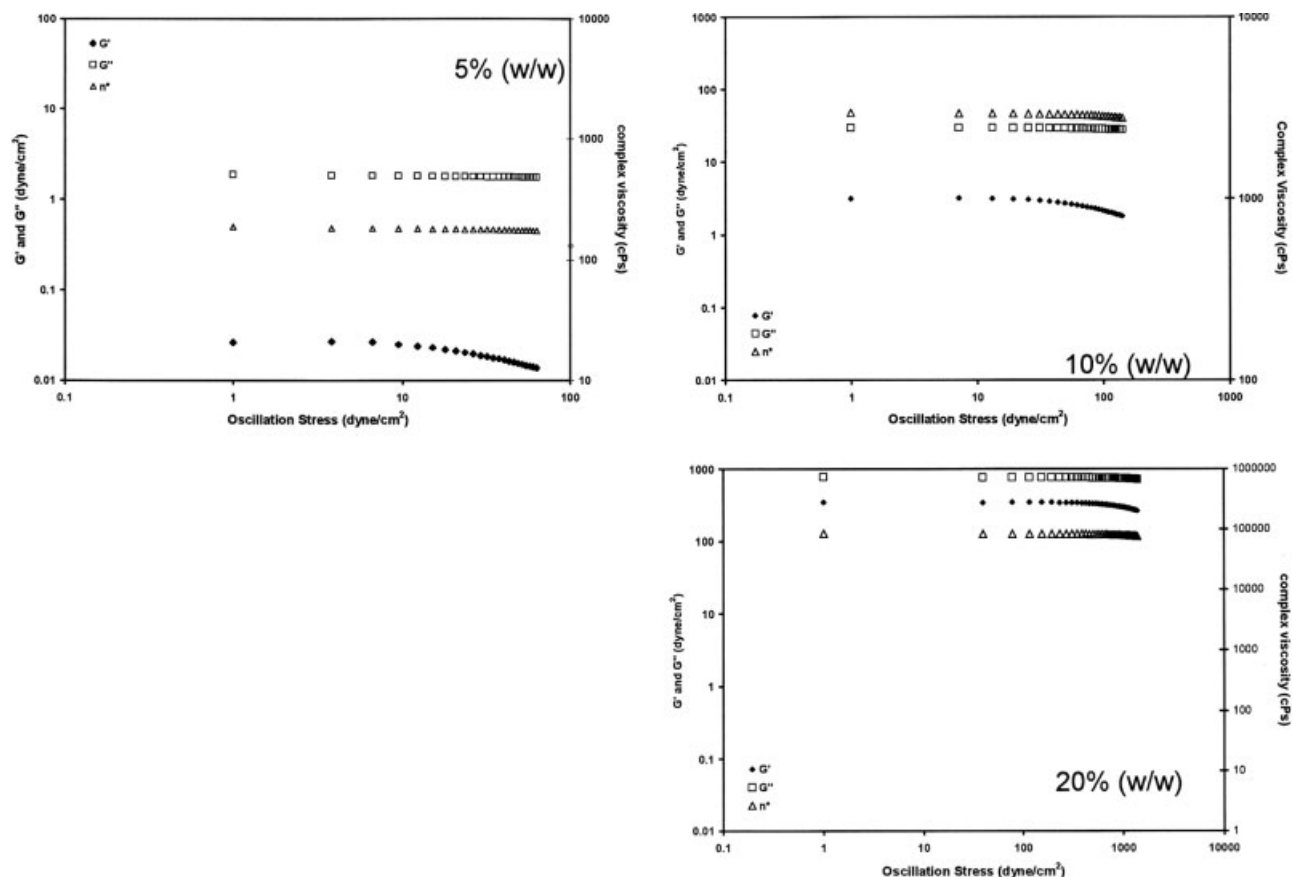


Figure 6 G'' , G' , and η^* as functions of the oscillation stress for 5, 10, and 20% (w/w) solutions of copolymer II. The measurements were performed at a frequency of 0.32 Hz.

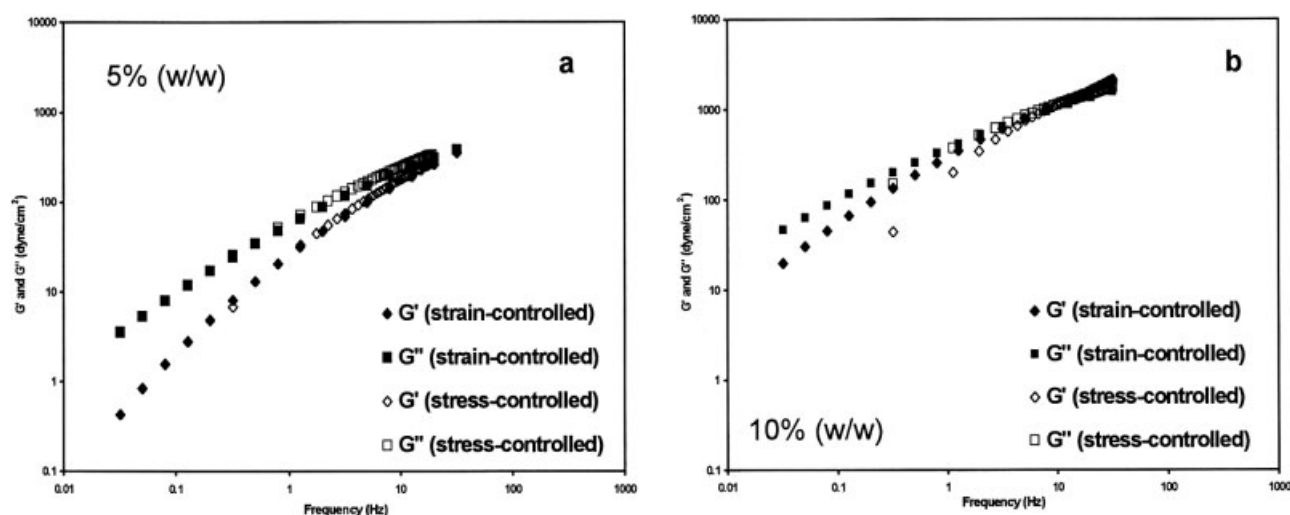


Figure 7 G'' and G' as functions of the frequency for (a) 5 and (b) 10% (w/w) solutions of copolymer I. The measurements were performed at constant strains of (a) 40 and (b) 10%.

obtained for copolymer II show a crossover point at 20 Hz for a 20% copolymer solution (Fig. 8). In addition to this, η^* plotted as a function of the frequency

shows a small decrease as a function of the frequency for copolymers I and II, which may indicate weak shear-thinning behavior of both materials.

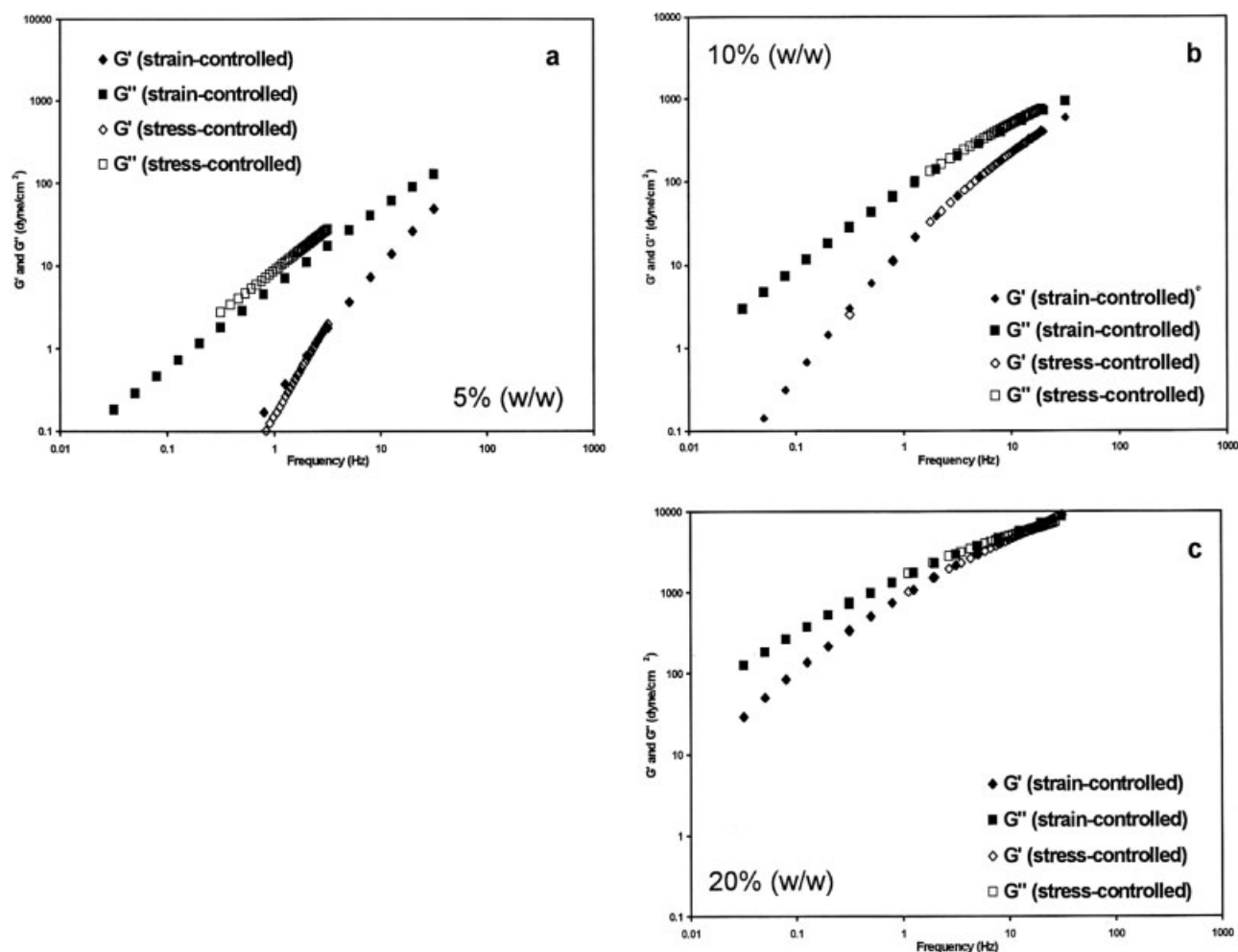


Figure 8 G'' and G' as functions of the frequency for (a) 5, (b) 10, and (c) 20% (w/w) solutions of copolymer II. The measurements were performed at constant strains of (a) 40, (b) 40, and (c) 10%.

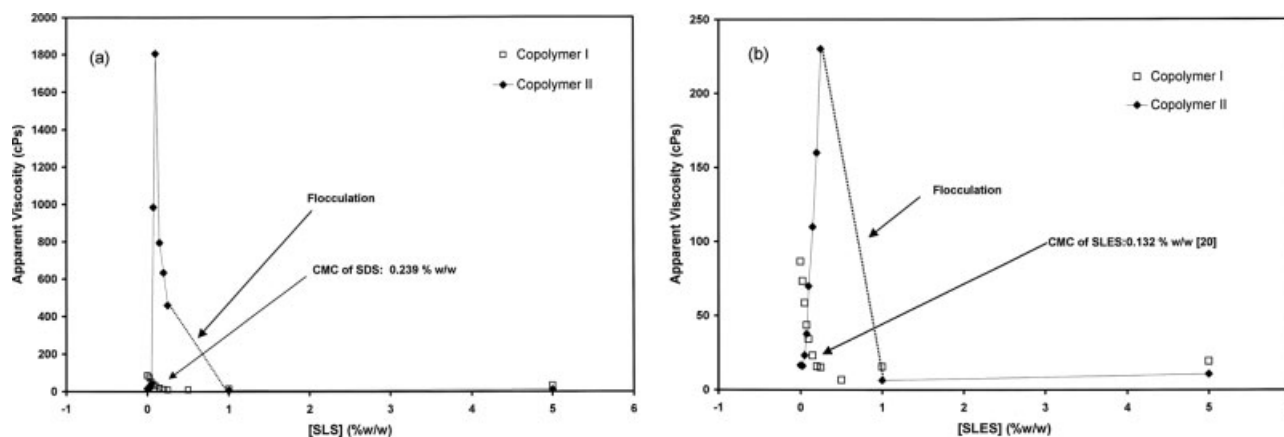


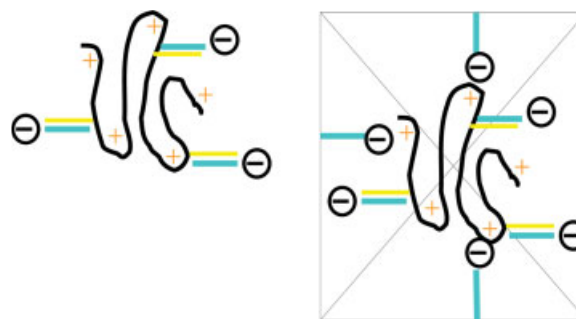
Figure 9 Apparent viscosity as a function of the concentration of (a) SLS and (b) SLES-2 for copolymers I and II at 1% (w/w).²⁰ The viscosity was measured at 0.17 Hz.

Copolymer solutions in the presence of surfactants

Copolymers I and II are frequently employed in combination with a variety of different surfactants in cosmetic and industrial formulations such as shampoos, hair conditioners, hair dyes, and cleaners. It is thus interesting to examine the rheological properties of mixtures of the copolymers with various types of surfactants employed in commercial systems. The most common are blends of polymers with anionic surfactants, such as SDS and SLES-2. Figure 9 illustrates changes in the viscosity of 1% solutions of copolymers I and II as a result of the addition of SDS in the concentration range of 0–5% (w/w). The viscosity dependence obtained for copolymer I does not suggest any interactions that would lead to a change in the rheological behavior of the polymer solution. A monotonous decrease in the viscosity from an initial value of about 90 cPs, obtained in the absence of a surfactant, to about 10 cPs at 0.5% SDS can be observed. Such a decrease is probably related to an electrolytic effect of SDS, which is capable of screening the intramolecular electrostatic repulsion of cationic charges, resulting in the shrinkage of the polymer chain dimensions. In contrast to this, the viscosity curve obtained for copolymer II shows an increase from about 18 cPs at 0% SLS to about 1800 cPs at 0.1% sodium dodecyl sulfate (SDS), followed by a decrease in the viscosity at higher SDS concentrations. The maximum in the viscosity curve corresponds to the SDS/copolymer alkyl group concentration ratio of 1.1, that is, close to 1:1 binding of the surfactant by the copolymer alkyl groups (Scheme 4, model on the left).¹⁸ This is also termed the *critical complexation concentration*, as indicated by Deo et al.,¹⁴ for the poly (maleic acid/octyl vinyl ether)–SDS system. Flocculation, as detected by the appearance of haziness, occurs at 0.5% SDS, which corresponds to the SDS/cationic polymer group concentration ratio of 1.5. The precipitation of the polymer from the solution can be expected to occur as a

result of complete neutralization of cationic sites by the anion of SDS (Scheme 4, model on the right). The concentration of cationic groups has been calculated under the assumption of 100% neutralization of the tertiary amino groups of DMAPMA, which probably overestimates the number of cationic sites. Moreover, the maximum viscosity (0.1%) and flocculation (0.5%) occur close to the critical micelle concentration (cmc) of SDS, which has been reported to be equal to 8.2×10^{-3} mol/L (0.239%).¹⁹

Similar results have been obtained for aqueous solutions of copolymers I and II with SLES-2, as shown in Figure 9(b). The surfactant, SLES-2, is more hydrophilic than SLS and, because of a different molecular geometry, can form larger micelles. For copolymer I, a monotonous decrease in the solution viscosity from 90 to about 10 cPs can be observed as the concentration of the surfactant increases from 0 to 0.5% (w/w). At higher surfactant concentrations, there is a small increase in the viscosity, probably due to the contribution of the viscosity of the surfactant itself. In the case of copolymer II, there is an increase in the viscosity up to 0.25% (w/w) SLES-2, with the maximum corre-



Scheme 4 Schematic representation of the species involved in the formation of complexes between a hydrophobically modified copolymer and a negatively charged surfactant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

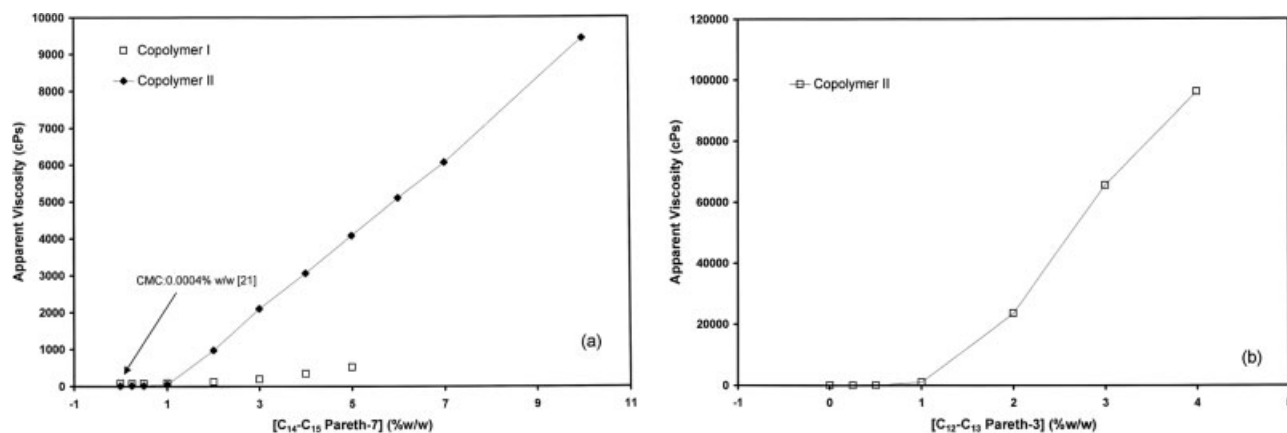


Figure 10 Apparent viscosity as a function of the concentration of (a) C₁₄₋₁₅ Pareth-7 and (b) C₁₂₋₁₃ Pareth-3 for copolymers I and II at 1% (w/w). The viscosity was measured at 0.17 Hz.

sponding to an SLES-2/copolymer alkyl group concentration ratio of 2.1, followed by flocculation at 0.5% SLES-2 with an SLES-2/copolymer cationic group concentration ratio of 1.1.

We have also investigated the viscosity of solutions containing 1.0% copolymer I or copolymer II in combination with a water-soluble nonionic surfactant, C₁₄₋₁₅Pareth-7, which is characterized by a high HLB of 11.6 [Fig. 10(a)]. For copolymer I, the viscosity increases only slightly in the presence of 0–5% surfactant, whereas for copolymer II, a much more substantial increase (to ca. 9500 cPs) can be observed in the surfactant concentration range from 0 to 10% (w/w). The onset of the viscosity increase occurs at a concentration of 1% C₁₄₋₁₅Pareth-7, which corresponds to a C₁₄₋₁₅Pareth-7/copolymer alkyl group concentration ratio equal to 7.0, which is well above the cmc of C₁₄₋₁₅Pareth-7 (0.0004% w/w).²¹ Thus, the formation of a network requires a large excess of the surfactant. For a water-dispersible, low-HLB surfactant, C₁₂₋₁₃Pareth-3 (HLB = 7.9), in combination with copolymer II, the increase in the viscosity is much more significant, the viscosity reaching about 95,000 cPs at a 4% surfactant concentration [Fig. 10(b)].

In addition to anionic and nonionic surfactants, we have also analyzed the viscosity of solutions of copolymer II in the presence of a cationic surfactant, cetyl trimethyl ammonium chloride, and in the presence of an amphoteric surfactant, cocamidopropyl betaine. In both cases, copolymer II shows only a polyelectrolyte salt effect, that is, a decrease in the viscosity as a function of the surfactant concentration.

CONCLUSIONS

Hydrophobically modified copolymer II is characterized by a more compact chain configuration in aqueous solutions than its unmodified analogue, copolymer I. This is the result of intramolecular hydrophobic interactions and is evident for dilute and

semiconcentrated solutions (<5% w/w). It also affects the dependence of the viscosity as a function of the polymer concentration and results in completely disparate effects of electrolyte (NaCl) on the viscosities of the copolymer solutions. For both copolymers I and II, G'' is higher than G' in 5–10 and 5–20% concentration ranges, respectively. For copolymer I, a transition from a viscous-dominated response ($G'' > G'$) to an elastic-dominated response ($G'' < G'$) occurs at 10% (w/w) and a frequency of 10 Hz. A similar crossover point has been observed for copolymer II at 20% (w/w) and a frequency of 20 Hz.

Copolymer II exhibits strong interactions with the surfactants SDS and SLES-2, showing viscosity maxima at surfactant/polymer alkyl concentration ratios of 1.1 and 2.1, respectively, and flocculation at surfactant/polymer charge concentration ratios equal to 1.5 and 1.1, respectively. Copolymer I does not interact with these surfactants according to the viscosity measurements.

The nonionic surfactants C₁₄₋₁₅Pareth-7 and C₁₂₋₁₃Pareth-3 interact with copolymer II, resulting in a monotonous viscosity increase in the concentration ranges of 1–10 and 1–4% (w/w), respectively, as a result of polymer–surfactant network formation.

This article is dedicated to the memory of Professor Marian Kryszewski, who was a teacher, mentor, and friend to J. Jachowicz.

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