

Rheological Behavior of Solutions of Amphiphilic Acrylic Copolymers in Mixed Solvents

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SYNOPSIS

A descriptive model was developed, using viscometry and light scattering, that explains the anomalous rheological behavior of solutions of amphiphilic acrylic copolymers upon the addition of water. The rheological behavior can be explained by considering the relative magnitudes of three interactions: the intra- and intermolecular electrostatic interactions between the ionizable acid groups in the copolymer, the intramolecular hydrophobic interactions, and the intermolecular hydrophobic interactions. The initial addition of water enhances the ionization of the acid groups, causing the electrostatic interactions between the acid groups to dominate the other two interactions. This leads to expansion of the polymer molecules and, consequently, to a relatively constant viscosity during dilution with water. Upon attaining the maximum ionization of the acid groups on the chain, the intramolecular hydrophobic interactions dominate the electrostatic repulsion, and the chains start to contract. Further addition of water leads to aggregation of the polymer chains into large polymolecular domains, resulting in a sharp decrease in the viscosity. Intermolecular hydrophobic interactions dominate the rheological behavior in this stage of water dilution.

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INTRODUCTION

An environmentally preferable alternative to solvent-borne coatings, water-reducible coatings are based on amphiphilic polymers of intermediate water solubility. These polymers are primarily random copolymers of carboxylic acid with (meth)acrylates or polyesters which are made and packaged as solutions in water-miscible solvents, referred to as cosolvents. Following the addition of an amine to solubilize the copolymer, the solutions are diluted with water and crosslinked to produce coatings that offer improved film formation and appearance compared to latex coatings.¹ To achieve acceptable viscosity characteristics, water-reducible coatings are formulated with relatively high concentrations of the cosolvent.² The resulting large volatile organic content (VOC) provides a strong incentive for developing water-reducible coatings that contain less co-

solvent but still provide acceptable rheological characteristics.

Developing lower-VOC water-reducible coatings with acceptable rheological behavior is not straightforward. The viscosity variation of water-reducible polymer solutions upon water dilution, known as a "reduction curve," is anomalous as compared to the dilution of true polymer solutions or latex dispersions.³ A reduction curve for a typical water-reducible acrylic copolymer solution is shown in Figure 1. Upon the addition of water, the viscosity of the polymer solution initially decreases, then remains approximately constant, and, finally, decreases very sharply; in contrast, upon the addition of cosolvent, the viscosity of the same polymer solution decreases monotonically and nearly linearly. Efforts made in reducing the VOC have been impeded by an incomplete understanding of the mechanisms that are responsible for this observed rheological behavior. Reducing the VOC of these systems by simply decreasing the amount of cosolvent or modifying the polymer structure imparts undesirable features to this already anomalous rheological behavior.⁴

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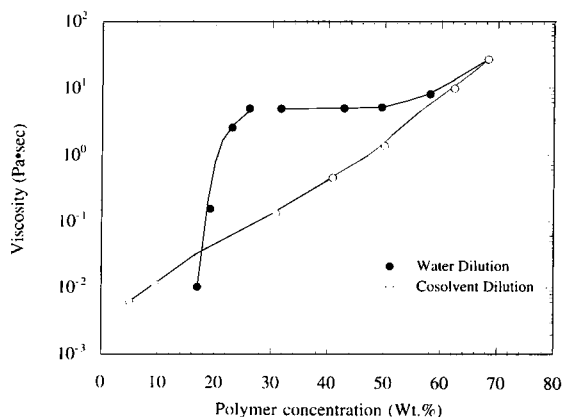


Figure 1 Comparison of the water reduction and solvent (EB) dilution curves for a water-reducible acrylic copolymer solution, showing the viscosity as a function of polymer concentration. The polymer is WRAC at 75% initial polymer concentration by weight (see the Experimental section for a description).

A qualitative model has been proposed that explains the main features of the reduction curve of amphiphilic water-reducible polymers.^{2,4} The presence of a viscosity plateau or an increase in viscosity is attributed to the formation of polymer aggregates due to the incompatibility of the hydrophobic segments of the copolymer with the increasingly hydrophilic medium. These hydrophobic segments, along with some entrapped carboxylic groups, remain predominantly in the interior of the aggregate, and the majority of segments containing the polar carboxylic acid salt groups locate on the exterior of the aggregate, hence stabilizing the aggregate. The viscosity decreases only when there is a reduction in the crowding of the polymer aggregates; it is this crowding that is hypothesized to lead to the relatively large viscosities, prior to the sharp decrease in viscosity, at lower polymer concentrations. While this qualitative model can explain some of the rheological features, a quantitative understanding of the microscopic behavior underlying these features does not exist. Such an understanding would not only further knowledge of the behavior of amphiphilic copolymers in mixed solvents, but also aid in addressing problems encountered in reducing VOC below present levels.

The aggregation of water-reducible copolymers can be compared to the micellization of block copolymers in selective solvents. Similar to the aggregation of water-reducible copolymers upon increasing the relative water concentration in the medium, amphiphilic block or graft copolymers form uni- or polymolecular micelles when the solvency for one of

the blocks decreases.⁵ However, there are also differences between the aggregation of water-reducible copolymers upon water dilution and the micellization of block copolymers in selective solvents. Water-reducible polymers are generally random copolymers with molecular weights of 5000–10,000, nearly an order of magnitude smaller than those of micellizing block copolymers. Since both the structure and the molecular weight of polymers can significantly affect their conformation, we expect some differences between the aggregation processes of water-reducible and block copolymers. In addition, electrostatic repulsion between the ionic groups of the water-reducible copolymer competes with the hydrophobic attractions between the nonpolar segments, with this competition controlling the conformational changes of the copolymer upon water dilution.^{6,7} Finally, the viscosity of water-reducible polymer solutions initially increases upon the addition of water,⁴ in contrast to the decrease observed upon micellization of block copolymers in selective solvents.⁵

In this article, we propose a more detailed model for the aggregation behavior of water-reducible copolymers that is responsible for the observed reduction behavior. To analyze the aggregation of water-reducible copolymers, we employed methods often used for micellizing block copolymer solutions, such as light-scattering and intrinsic viscosity measurements. This model differs from previous models^{2,4} in that aggregation is found not to be significant until very near the sharp drop in viscosity; instead, most of the viscosity plateau noted upon increasing the water concentration can be attributed to the expansion of the copolymer chains. We also address the differences between the aggregation behavior of water-reducible and block copolymers.

EXPERIMENTAL

Materials

Model amphiphilic acrylic copolymers were synthesized whose reduction behavior resembled that of representative commercial water-reducible copolymers. The commercial water-reducible acrylic polymers used for comparison were "Acryloid" WR-97 (Rohm and Haas) and "Chempol" 10-1706 (Freeman Polymers). The model acrylic copolymer, designated "WRAC," had a monomer composition of methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), and 2-hydroxyethyl acrylate (2HEA) in a weight ratio of 41.2/42.3/5.1/11.4 and a mol ratio

of 45.2/36.2/7.8/10.8, respectively. This monomer ratio was selected to yield a theoretical glass transition temperature (T_g) of 5°C as calculated by the Fox equation. Ethylene glycol *n*-butyl ether (EB), also referred to as 2-*n*-butoxyethanol, was used as the polymerization solvent and, hence, cosolvent. The monomers were obtained from Rohm & Haas and were used without removal of inhibitors. The initiator azobisisobutyronitrile (AIBN) was purchased from Polysciences, and the cosolvent EB (99% grade) and the neutralizing amine *N,N*-dimethylethanolamine (DMAE) were purchased from Aldrich Chemicals.

Polymerization was effected under monomer-starved conditions intended to provide a nominally random composition. Forty grams of EB were placed in a 500 mL flask equipped with a mechanical stirrer, a dropping funnel, a thermometer, a condenser, a gas inlet, and a heating mantle. The flask was then flushed with nitrogen and the solvent heated to 98°C. A solution of 82.4 g (0.824 mol) of MMA, 84.6 g (0.660 mol) of BA, 10.2 g (0.142 mol) of AA, 22.8 g (0.196 mol) of 2HEA, and 3.8 g (0.023 mol) of AIBN in 80 g of EB was added continuously during a 3 h period with stirring under a N_2 atmosphere at about 100°C. The solution was then stirred at 100°C for 3 more hours with addition of a 0.1 g portion of AIBN at the end of the first and the second hours, resulting in a colorless polymer solution. The number-average molecular weight of the copolymer varied from 5800 to 6600 in several batches, and the polymer solution was used in rheological experiments without purification.

The physical and chemical properties of the commercial and "model" water-reducible copolymers are given in Table I. These properties include the acid number (AN), nonvolatile weight percent (NVW%), and number- and weight-average molecular weights (M_n and M_w , respectively). The acid numbers were measured according to ASTM D1639-83 by titration with KOH to the phenolphthalin end point.⁸ The

molecular weights, M_n and M_w , were estimated by gel permeation chromatography (GPC) in tetrahydrofuran solvent at 0.9 mL/min using a Waters Model 510 pump, a Model R401 differential refractometer detector, and 10 μ m PLgel columns rated at 10^5 , 10^3 , and 10^2 Å; polystyrene standards were used for calibration. Nonvolatile weight percent was measured according to ASTM D2369-87 by heating a known weight of resin to approximately 110°C, followed by monitoring of the dried resin weight.

The solvent EB is left with the resin as the cosolvent due to its simultaneous good solvency for the copolymer and miscibility with water. Although the T_g of WRAC is at the low end of the T_g range for commercial resins (with the upper end being slightly lower than room temperature), the rheological behavior and film-forming characteristics of the resin were found to be similar to those of representative commercial water-reducible acrylic resins.

For the water-dilution experiments, 70 mol % of the acid groups on the copolymer were neutralized with dimethylaminoethanol (DMAE), giving an extent neutralization (EN) of 70%. The polymer solutions were then progressively diluted with water and the viscosity measured as a function of shear rate at selected dilutions to yield the reduction curve. Note that although we obtained the reduction curves by the addition of water alone, in practice, some formulations may require additional cosolvent for optimum rheological properties and polymer solubility. In the dilution experiments, double-distilled water was used to minimize the effects of ionic impurities.

Viscometry

The rheological behavior of the polymer solutions during dilution was characterized using a Bohlin VOR rheometer with a concentric cylinder geometry (outer rotating cup of radius 15.4 mm and an inner stationary bob of radius 14 mm). The sample tem-

Table I Properties of Water-reducible Acrylic Copolymers

Resin (Supplier)	Wt % Solids	Solvent ^a	Acid No.	M_n	M_w/M_n
Acryloid WR-97 (Rohm & Haas)	70	83/17 IP/EB	37	8000	2.5
Chempol 10-1706 (Freeman Polymers)	75	EB	49	2800	2.9
WRAC (EMU)	63	EB	37	5800-6600	2.9

^a IP = isopropanol; EB = 2-butoxyethanol.

perature was maintained at $25 \pm 0.2^\circ\text{C}$, and a solvent trap was used to provide a partially vapor-saturated space above the sample that greatly reduced solvent evaporation for several hours. The viscosities of the polymer solutions were measured as a function of shear rate from 0.185 to 185 s^{-1} ,[†] all solutions displayed Newtonian flow behavior in this shear rate range except those with polymer concentrations in the vicinity of the sharp decrease in viscosity (i.e., near 25% polymer in Fig. 1). A capillary viscometer immersed in a constant temperature bath ($25 \pm 0.3^\circ\text{C}$) was used to measure the viscosities of the solvent mixtures (water and EB) in the absence of polymer, which was needed to calculate the relative viscosities of the diluted polymer solutions. Capillary viscometry was also used to obtain the viscosities of the highly diluted polymer solutions (less than 20 wt % polymer).

Light Scattering

Dynamic light scattering (DLS) was used to measure the size of the polymer domains *in situ* at various stages of water dilution. The light-scattering apparatus was equipped with a Brookhaven Instruments digital autocorrelator and an Ar ion laser source (514 nm wavelength). The temperature of the sample chamber was maintained at $25 \pm 0.5^\circ\text{C}$ and the angle of the goniometer was fixed at 90° . The copolymer solutions were extensively diluted (less than 5 g polymer/liter) with solvents of different water/cosolvent ratios to yield solvent environments characteristic of selected points on the reduction curve. The intensity fluctuations of the light scattered by the polymer domains in these solutions were analyzed by the autocorrelator, from which the hydrodynamic radius of the polymer domains (R_h) was calculated using the Stokes–Einstein equation.⁹

RESULTS AND DISCUSSION

Water Dilution of Model and Commercial Acrylic Copolymers

Properties of water-reducible acrylic copolymers such as viscosity and water solubility depend on the relative lengths and concentrations of their hydrophilic and hydrophobic segments. With this in mind, the model water-reducible acrylic copolymers (WRAC) were designed to mimic the molecular

weight and acid number, and, consequently, the reduction (water dilution) curves, of commercial acrylic copolymers. Shown in Figure 2 are the reduction curves for two commercial acrylic copolymers, "Acryloid" WR-97 and "Chempol" 10-1706, and for the model acrylic polymer WRAC-68, where "68" designates the weight percent polymer in the initial polymer solution prior to dilution. Since all polymer solutions exhibit Newtonian flow behavior at low shear rates, we chose to plot the low shear rate (0.185 s^{-1}) viscosity in these reduction curves. In addition, an EN of 70% was chosen as a common neutralization level for comparison since the viscosity depends on the EN.¹⁰

As seen in Figure 2, the reduction curve for the model acrylic copolymer WRAC shows similar viscosity–concentration behavior as that for "Chempol." While the viscosity of the model copolymer does not display a maximum at lower concentrations as seen with "Acryloid," this absence of a viscosity peak is advantageous with respect to processing. A viscosity suitable for application, around 0.1 Pa·s, is attained at a polymer concentration of 20–25 wt % for the model and the commercial copolymers. The similarity in the physicochemical properties (Table I) as well as in the reduction curves of the model and commercial copolymers led us to select WRAC as the model for studying the dilution behavior of water-reducible acrylic copolymers.

The reduction curves shown in Figure 2 can be divided into three regions (reading right to left) of (1) decreasing, (2) constant or increasing, and (3) sharply decreasing viscosity. The viscosity plateau or peak of region 2 is in contrast to the monotonic

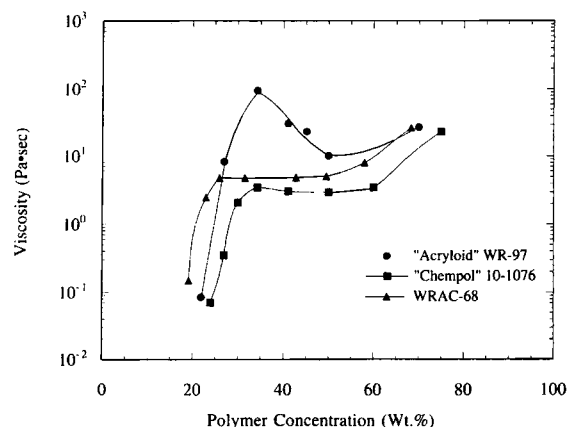


Figure 2 Comparison of the reduction curve of the model acrylic copolymer (WRAC at 68% initial polymer concentration by weight) with those of two commercial water-reducible acrylic copolymers ("Acryloid" and "Chempol").

[†] Whenever not limited by the force measurement element in the rheometer, this range was extended to higher shear rates.

decrease in viscosity expected upon solvent dilution of the polymer solution (see Fig. 1). These plateaus and peaks denote different extents of a positive deviation from a solutionlike viscosity and therefore are phenomenologically the same. To address the problems encountered with reducing VOC below present levels, it is critical to understand these viscosity changes in terms of the microscopic behavior of the polymer molecules. We focused on quantifying the reduction behavior of WRAC, since this copolymer exhibits a reduction curve similar to those of the commercial copolymers, and we can control its physical and chemical properties in a known manner. In the following discussion, we relate the observed reduction behavior of WRAC to the microscopic behavior of the polymer molecules.

Of course, actual coating formulations usually contain a crosslinker and pigment. Such components of the coating will complicate the rheological response. However, these components should not significantly affect the underlying mechanism responsible for the observed rheological behavior upon water dilution, since this mechanism relies on the interactions between the copolymer and the solvent medium.

The Mechanism of Water Dilution of the Model Acrylic Copolymers

Upon the addition of water, a water-reducible copolymer solution is a three-component system consisting of water, cosolvent, and the amine-neutralized polymer. Keeping the EN constant, the properties of such a system can be varied by independently by changing any two composition variables. For example, the viscosity of these diluted systems will have different values at a given polymer concentration if the initial polymer concentrations are different, since the viscosity is a function of the relative water and cosolvent concentrations.

To study the effect of the initial polymer content on the reduction curves, we attained different initial polymer concentrations by removing the cosolvent from a WRAC solution of initial polymer concentration of 50 wt %. Figure 3 shows the reduction curves obtained for these polymer solutions of initial concentrations (by weight) of 50, 62, and 75%. Increasing the initial polymer concentration shifts the viscosity curves to the right toward higher polymer concentrations and up toward higher viscosities. Similar findings have been reported for water-reducible copolymers of acrylic acid and butyl methacrylate with acid numbers that are close to that of WRAC.⁴ As discussed above, the viscosities are not

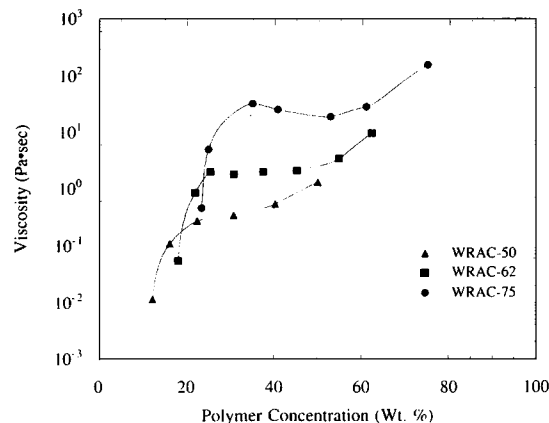


Figure 3 The effect of initial polymer concentration on the reduction curves of the model acrylic copolymer, WRAC. The number after "WRAC" signifies the initial polymer concentration by weight.

equal at a given polymer concentration due to different relative concentrations of water and cosolvent. For example, at a polymer concentration of 50%, the solvent composition of WRAC-50 is 100% EB; of WRAC-62, 61.3% EB; and of WRAC-75, 33.3% EB. In addition, increasing the initial polymer concentration, which reduces the amount of cosolvent and, hence, the VOC, causes large viscosity increases and may even result in a viscosity maximum as noted for WRAC-75. To understand the relationship between the viscosity and the solvent composition, we first need to understand the changes that the polymer molecules undergo during the dilution process that give rise to the viscosity variations.

Adding water to a polymer-cosolvent solution leads to an increase in the water-to-cosolvent ratio. This increase enhances the hydrophilic and dielectric characters of the solution, in contrast to a uniform solvent environment along a (co)solvent dilution curve (Fig. 1). Consequently, not only does the polymer concentration decrease upon dilution, but also the conformation and degree of association of the polymer molecules are altered due to the change in solvent environment. Since the viscosity is a function of the volume fraction of the polymer domains, the viscosity then depends on both the polymer concentration and the solvent environment.² The reduction curves shown in Figure 3 each have different solvent compositions and, hence, different solvent hydrophobicities at equal polymer concentrations. As a result, the polymer chains do not assume the same conformation at equal polymer concentrations. To normalize the data with respect to polymer conformation (size and degree of asso-

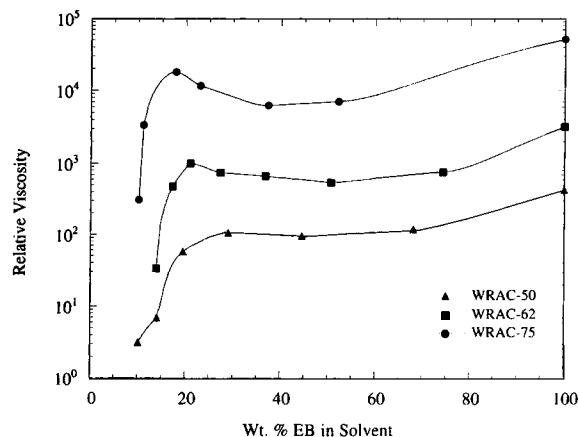


Figure 4 The relative viscosity of the model copolymers as a function of weight percent of the cosolvent, EB, in the solvent medium.

ciation), the viscosity results should instead be compared at similar solvent compositions.

Shown in Figure 4 is the relative viscosity as a function of the solvent composition for the WRAC systems of Figure 3; the use of relative viscosity normalizes the results with respect to the changing solvent viscosity. The three viscosity regions previously observed at different polymer concentrations are now approximately contained within the same windows: (1) a region of slowly decreasing viscosity for EB concentrations greater than 50%; (2) a region of non-decreasing viscosity for EB concentrations between 20 and 50%; and (3) a region of sharply decreasing viscosity for EB concentrations less than 20%. That these three regions can be located within the same solvent composition ranges regardless of initial polymer concentration implies that the mechanism responsible for the features of the reduction curve is largely a result of conformational changes of the copolymer chains upon dilution. Indeed, as discussed below, little aggregation of the polymer chains occurs until Region 3.

To study the effect of solvent composition on the polymer conformation, we diluted the polymer solutions with solvent mixtures of constant water-to-cosolvent ratios. Maintaining a constant solvent composition (and, hence, hydrophobicity) of the dilution medium allows us to assume that the measured viscosity changes can be primarily[‡] associated

[‡] To be rigorous, one should also consider the possibility of preferential partitioning of the cosolvent (or water) between the copolymer domains and the surrounding solvent. Furthermore, the degree of dissociation of the ionic groups in the polymer depends on their concentration in the solution and the pH. While both of these effects can cause small deviations from an ideal dilution process, we are assuming them to be negligible.

with the decrease in polymer concentration during dilution and not with any conformational changes of the polymer molecules. Such dilution curves are given in Figure 5 along with the water-reduction curve for reference. Note that the intersection of the water-reduction curve and the constant solvent-composition dilution curves correspond to media having both the same polymer concentration and the same solvent composition. Since equal viscosities are obtained at identical polymer concentrations and solvent compositions regardless of the preparation history of the diluted polymer system, any aggregation of the polymer molecules that has occurred has attained an equilibrium state at each concentration.¹¹

The constant solvent-composition dilution data enable us to extract quantitative information about the conformation of the polymer chain at any point along the reduction curve. Note that the viscosity data at large polymer concentrations cannot be used, however, since they also contain information about the interactions between the polymer chains. Consequently, the intrinsic viscosity $[\eta]$ is used as a quantitative measure of the conformation of the polymer molecules¹² and can be calculated from measurements of the relative viscosity η_r at low polymer concentrations. Writing the relative viscosity as a Taylor series expansion in polymer concentration c gives

$$\eta_r = 1 + [\eta]c + k'[\eta]c^2 + \dots \quad (1)$$

from which the intrinsic viscosity is defined as follows:

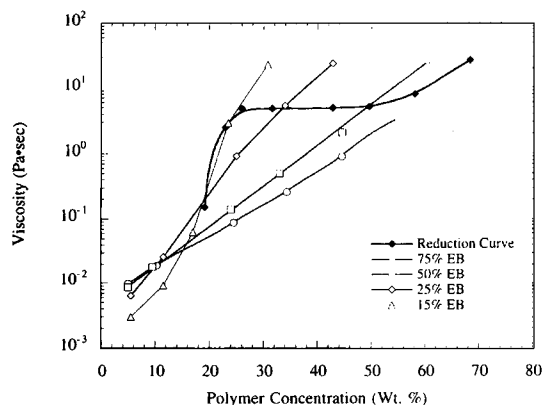


Figure 5 Dilution of WRAC-68 with media of constant solvent composition, showing the viscosity as a function of polymer concentration. Also shown for comparison is the reduction curve for water dilution.

$$[\eta] = \lim_{c \rightarrow 0} \left(\frac{\eta_r - 1}{c} \right) \quad (2)$$

Both $[\eta]$ and the Huggins coefficient k' are independent of polymer concentration.

The viscosity-concentration curve for each constant solvent-composition dilution was extended to low polymer concentrations using capillary viscometry, from which $[\eta]$ (Fig. 6) and k' (Table II) were calculated as a function of cosolvent composition. To analyze the intrinsic viscosity data, we assume that each polymer domain—either a single chain or an aggregate of chains—behaves hydrodynamically like a nondraining sphere. Due to this nondraining assumption, an intrinsic viscosity of 2.5 is assigned to the spheres based on Einstein's equation for hard spheres. Then, defining as d the equivalent diameter of the polymer domain, which contains not only the polymer chain(s) but also entrapped solvent and any charges associated with the chain(s), the intrinsic viscosity $[\eta]$ is expressed as follows:

$$[\eta] = \frac{2.5N_A(\pi d^6/6)}{M} \quad (3)$$

where N_A is Avogadro's number and M is the (viscosity) average molar weight of each spherical domain.⁸ M may be equal to the molar weight of one polymer molecule, in which case the spherical domain is monomolecular, or may be greater than the molar weight of one polymer molecule, in which case the spherical domain is polymolecular. Any change in $[\eta]$ can be due to a change in either the dimension of the polymer domain d or the extent of aggregation of polymer molecules, as reflected by M , caused by changes in the solvent environment. Consequently, it is difficult to determine the extent of aggregation of polymer chains from intrinsic viscosity data alone. This combined effect of the aggregate size and extent of aggregation on the intrinsic viscosity has also presented difficulties in interpreting intrinsic viscosity data in micellizing copolymer solutions.¹³

To study the effect of the solvent medium on the aggregation of polymer chains alone and not on their dimensions, we monitored the latter by dynamic light scattering (DLS). The hydrodynamic diameters obtained by DLS are given in Figure 7 as a function of the weight percent cosolvent in the medium. A relatively constant diameter of 3.5 nm is observed for EB concentrations greater than 50%, followed

⁸ The intrinsic viscosity can simplistically be viewed as an effective volume fraction for a unit weight of polymer in solution.

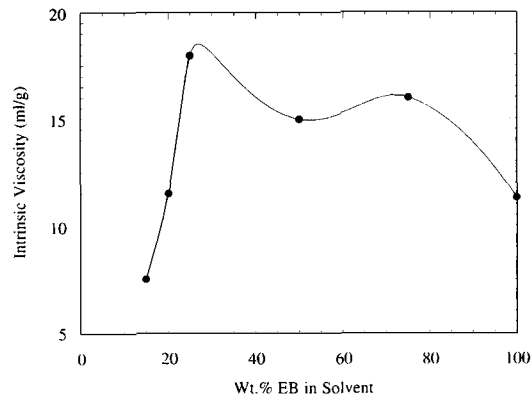


Figure 6 The intrinsic viscosity as a function of solvent composition for WRAC-68.

by an increase to 5 nm for EB concentrations near 25%. As the relative concentration of EB is reduced further, the polymer domain size increases to greater than 150 nm and becomes unstable with time before reaching a relatively constant value of 20 nm at large extents of water dilution (EB concentrations less than 10%).

Note that the shape of the curves in Figures 6 and 7 suggests the same trend as that observed in the reduction curves (Fig. 4), despite the lower polymer concentrations used to obtain the intrinsic viscosities and the hydrodynamic diameters of the polymer domains. Note also that the onset of the increase in domain size and the maximum in the intrinsic viscosity both occur at 25% EB, very close to the solvent composition (approximately 20% EB) at which the onset of the sharp viscosity decrease is observed in the reduction curves. This illustrates that the changes in copolymer conformation along the reduction curve, caused by the changes in water/cosolvent ratio, are responsible for the anomalous shape of these curves. Consequently, we can use the results obtained for the size and association number of polymer domains at low polymer concentration to explain the water-dilution behavior of the copolymers at higher concentrations.

To relate the rheological behavior to the microscopic behavior of the polymer chains, we first calculated the average molar weights for the polymer domains by using the data for $[\eta]$ and d and applying eq. (3). The results of these calculations for different solvent mixtures are given in Table II. Also given in Table II are the average aggregation numbers calculated by dividing M by the molecular weight of an individual copolymer chain. Note that although d should be the viscosity-average diameter of the polymer domains the hydrodynamic diameter obtained from the DLS is very close to the viscosity-

Table II Viscosity and Aggregation Parameters of the Model Acrylic Copolymer WRAC-68

EB %	$[\eta]$ (mL/g)	k'	d (nm)	Molar Weight M ($\times 10^{-3}$)	Average Aggregation No.
2.5	8 ^a	^a	20	1400 ^b	240
11	7.5 ^a	^a	55	24,000 ^b	> 4000
15 ^c	8	6	> 250		
25	18	0.56	5	14	2.3
50	15	0.33	3.5	6	1
75	16	0.41	3.5	6	1
100	11	1.2	3.2	6	1

^a The results at high water concentrations were obtained by fitting the data to a dispersionlike viscosity equation. Accordingly, the Huggins coefficient is not applicable at these concentrations.

^b These very large figures are only approximate values.

^c The system was very unstable with time. The values obtained are for approximately 1 h after sample preparation.

average diameter and can be used as a first approximation.¹² This same method of combining the light-scattering and viscometry data has also been used to calculate the molar weight of block copolymers micelles in selective solvents, and it has been shown that these molar weights are in good agreement with the values obtained from conventional light scattering and electron microscopy (precipitated micelles).¹²

Employing the numerical values in Table II, which correspond to various extents of dilution on the reduction curves, we propose the mechanism described below. Due to the simplifying assumptions of the nondraining sphere model and the inherent errors in the measured values of d , $[\eta]$, and k' , the following can only serve as a semiquantitative model. This model represents an improvement over pre-

vious models^{2,4} in that dynamic light-scattering data is coupled with the rheological data to probe the microscopic behavior of the copolymer chains; in addition, the rheological data are not limited by the available shear rates for a given viscosity.⁴ A more quantitative approach to model the water dilution of water-reducible copolymers, using Monte Carlo simulations, is underway and will be presented in a future publication.

Region 1

Before water dilution, when the solvent medium consists of 100% EB, the copolymer domains are monomolecular. The 3 nm diameter of the spherical copolymer domains is approximately equal to that which would be estimated for a freely rotating polymer chain with an identical degree of polymerization.¹⁴ The Huggins coefficient for the copolymer is approximately 1.6, higher than the 0.3–0.8 range observed for nonionic polymers in good-to-theta solvents. This higher value of the Huggins coefficient can be attributed to the dipole interactions between the salt groups on different chains; these interchain dipolar interactions are also proposed to be responsible for the high viscosities of water-reducible copolymers.⁴ The enhancement of dipole interactions by neutralizing the polymeric acid groups with DMAE is evidenced by the 40–50% increase in viscosity observed upon neutralization. We also observed slight shear thickening for the undiluted WRAC solutions, reflecting the strong intermolecular interactions similar to those reported for ionomers and associative polymers.¹⁵

Upon addition of water to the WRAC solutions, both the viscosity and the relative viscosity initially

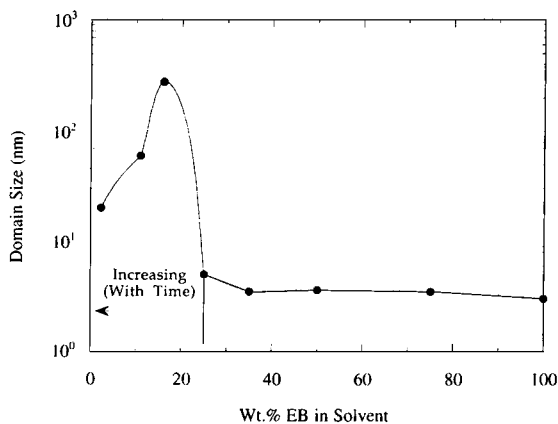


Figure 7 The size of the polymer domains as a function of solvent composition for WRAC-68. The size was measured by dynamic light scattering.

decrease (Figs. 3 and 4). In fact, if the polymer solution is extensively diluted in a solvent of 75% EB/25% water, the domain size d appears to remain essentially unchanged compared to its value in a medium of 100% EB. The absence of any observable significant change in the polymer domain size upon addition of small amounts of water suggests that water acts simply as a diluent during the initial stages of dilution and induces no change in intermolecular interactions. To assess this hypothesis, we compared the cosolvent-only dilution curve with the water-reduction curve for the WRAC, using relative viscosities to account for the different solvent environments (Fig. 8). Initially, the presence of water reduces the relative viscosities below those obtained for the cosolvent-only dilution. Therefore, water is not just a diluent even for the early stages of the dilution. Instead, water is believed to form hydrogen bonds with the cosolvent molecules and, as a result, reduce the dipole interactions between the copolymer molecules, therefore decreasing the relative viscosity in comparison to that for the cosolvent-only dilution. Our observations also show that addition of water eliminates the slight shear-thickening caused by the dipole interactions, producing Newtonian flow behavior in the range of shear rates studied.

In addition, at low polymer concentrations, the addition of water increases the intrinsic viscosity (Fig. 6). This increase in $[\eta]$ is a reflection of the increase in the effective polymer domain size, since the domain molecular weight cannot be less than that for a single copolymer chain [eq. (3)]. Such a change in domain size for EB concentrations from 50 to 100% is not necessarily large, since the intrinsic viscosity varies with the third power of polymer domain diameter and therefore can be difficult to detect by DLS. This can explain why no significant change in domain size was noted in this region using DLS. The expansion of the polymer chains is the result of increasing the dielectric constant of the medium and increasing the extent of dissociation of the neutralized acid groups on the copolymer. Consequently, while the initial addition of water does not significantly alter the domain size, it does alter the intermolecular interactions as reflected by the viscosity.

That the viscosity changes along the reduction curve do not follow the trends in $[\eta]$ in the early stages of dilution is expected since the intrinsic viscosity is only a first-order term in eq. (1) and is a significant contribution to the viscosity only for extremely dilute solutions. As the polymer concentration increases, the second (k') and higher-order terms in eq. (1) become progressively more important in

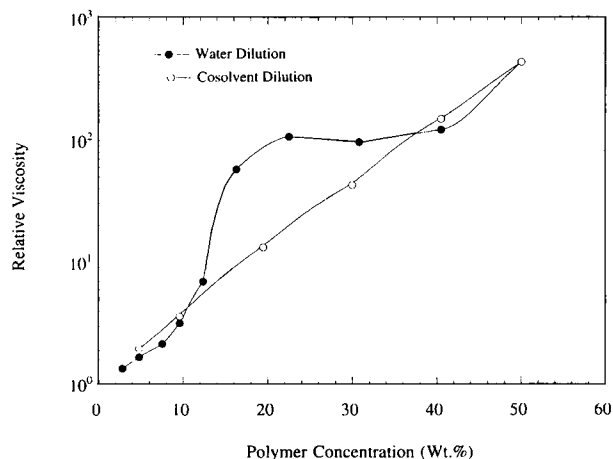


Figure 8 Comparison of the relative viscosity of WRAC-50 as a function of polymer concentration during both water and cosolvent dilutions.

determining the viscosity. It is not surprising, therefore, that in the early stages of water dilution, when the polymer concentration is high, the viscosity follows the decrease in k' rather than the increase in $[\eta]$.

Region 2

Upon the further addition of water, the average aggregation number of each domain increases from 1 to 2.3 (Table II) and the polymer domain size increases from 3.2 to 5 nm (Fig. 7). The incompatibility of the hydrophobic backbone on the polymer chain with the increasingly hydrophilic medium leads to the aggregation of the chains and, hence, more chains per aggregate or domain. The increase in the domain size reflects not only the increase in the number of polymer chains in each domain but also the expansion of the individual chains due to increased electrostatic repulsion between the neutralized acid groups on the chains, which are now ionized in a solvent mixture of higher dielectric constant. Indeed, expansion of the chains is seen by the increase in domain size for relative EB concentrations decreasing from 100 to 35% for which the domains are monomolecular. This expansion is also reflected by the increase in the intrinsic viscosity upon the addition of water (Fig. 6). Our observation that the polymer domains are monomolecular in most of Region 2 as well as in Region 1 is in contrast to the mechanism for dilution previously proposed, which suggests aggregation during most of Region 2.⁴

Similar conformational transitions have been reported for hydrophobic polyelectrolytes upon an in-

crease in chain ionization or a decrease in charge screening (reduction in ionic strength).^{6,7,16} For random copolymers of acrylic acid and ethyl acrylate, Tan and Gasper reported a transition from a compact random coil to a swollen coil upon decreasing the ionic strength.⁷ Helix-coil transitions for ionic polypeptides and globule-coil transitions for poly(methacrylic acid) have also been observed during potentiometric titrations.¹⁶ These transitions are attributed to the competition between the hydrophobic interactions of the apolar segments of the polymer molecules and the electrostatic repulsion between the ionizable acid groups (or their salts when neutralized).^{6,17} In addition, the small values of the Huggins coefficient in this region may result from a polyion expansion effect similar to the that observed for polyelectrolytes.¹⁸

Region 3

At an EB concentration of 25%, the intrinsic viscosity attains a maximum and the hydrodynamic diameter of the polymer domains increases to 5 nm, giving an average aggregation number of 2.3 (2.3 polymer chains per domain). Decreasing the EB concentration below 25% leads to a large increase in the polymer domain size and a decrease in the intrinsic viscosity, indicating incipient aggregation of the copolymer chains. For EB concentrations below 25%, the aggregation of the highly expanded polymer chains is thermodynamically favorable. Presumably, the polymer chain has attained its maximum water solubility and is highly ionized and, hence, highly expanded, exposing a large fraction of its hydrophobic (meth)acrylate backbone segments. Upon further addition of water, hydrophobic effects dominate chain expansion, and the chains associate into polymolecular domains to minimize the contact surface of the (meth)acrylate blocks with the hydrophilic medium.

The increase in domain size and the decrease in intrinsic viscosity for EB concentrations less than 25% indicates the continued formation of large, polymolecular aggregates. For EB concentrations corresponding to the maximum and the sharp decrease in intrinsic viscosity, the polymer solutions were observed to phase separate and to become increasingly cloudy with time. The domain sizes measured by DLS were, consequently, found to increase with time. This indicates kinetically controlled aggregation of the highly ionized and expanded copolymer chains near an EB concentration of 25% for the low polymer concentrations used to measure the intrinsic viscosity and domain size. At the higher

polymer concentrations encountered during typical water reduction, however, this extensive aggregation starts at a lower relative EB concentration. As seen in Figure 4, the sharp decrease in viscosity occurs near a solvent composition of 20% EB. In addition, in contrast to the solutions at lower polymer concentrations, these polymer solutions were found to be stable for weeks with no visual indication of phase separation. Both of these observations suggest the possibility of slow diffusion-limited aggregation due to the higher viscosities in the actual reduced polymer systems; given enough time, phase separation would also be expected in these systems. We have also observed shear thinning for systems in the vicinity of the sharp decrease in viscosity which is probably due to the presence of large aggregates.

Upon aggregation, the continuous phase of expanded, ionic copolymer chains collapses, as evidenced by the sharp decrease in the intrinsic viscosity and the instability in the domain sizes, and a water-rich medium subsequently becomes the continuous phase. This change in the percolative state of the system is analogous to the percolation transition observed for microemulsions. At the percolation transition in a water-in-oil microemulsion, the dispersed aqueous phase (similar to our hydrophilic phase) percolates into a continuous phase, causing abrupt changes in the system properties.¹⁹ For example, the viscosity of microemulsions attains a maximum in the vicinity of this transition due to the existence of a bicontinuous phase structure.²⁰ This analogy to microemulsions suggests the applicability of percolation theories in modeling the viscosity maximum in the reduction curves of water-reducible copolymers.

After the formation of aggregates, the extended copolymer chain acts as an ionic surfactant due to its amphiphilic structure of ionized acid-amine salt groups and long hydrophobic (meth)acrylate segments. From the results presented in Table II, it can be concluded that the large, unstable aggregates formed at the percolation transition break down to more stable aggregates upon further water dilution. The sharp decrease in the viscosity noted on the reduction curves is due not only to the increase in volume of the continuous phase but also to a reduction in the aggregation number. For example, when the solvent composition is 11% EB, the domain diameter is 55 nm and the average aggregation number is 4800; increasing the water content in the medium so as to reduce the EB concentration to 2.5% results in a domain diameter of 20 nm and an average aggregation number of 240. These compact aggregates are more stable than are the larger ones, as evidenced

by smaller changes in aggregate diameter and, hence, solution turbidity over time. This stability may result from the presence of highly ionized groups on the copolymer chains that provide electrostatic stabilization.

In fact, if the effect of dilution (volume increase of continuous phase) is eliminated by maintaining a constant polymer concentration and instead increasing the relative water concentration in the medium, the viscosity of the system may even increase. Shown in Figure 9 are plots of relative viscosity as a function of EB concentration at constant polymer concentrations c . While at lower polymer concentrations the relative viscosity is either approximately constant or follows the general trend of the reduction curves, at higher polymer concentrations the relative viscosity increases as the medium becomes more hydrophilic.

Although the aggregation of the copolymer domains around the percolation transition is likely kinetically controlled, the process is thermodynamically driven at greater extents of water dilution. The breakup of larger micelles to smaller ones can be a result of a high concentration of charged groups in the interior of the micelles which seek contact with the hydrophilic medium. A morphological model recently suggested for a system very similar to ours is the cluster model.^{13,21} In this model as proposed for water-reducible polyesters, the larger micelles are grapelike clusters composed of hundreds of smaller micelles with the same swelling factors and intrinsic viscosities as those of the main cluster.²¹ The cluster model can explain some of the observations made for micellar systems upon changing the temperature¹³ or the ionic strength.²² Further quantitative analysis of postaggregation behavior is required before we can assess the applicability of this model to our systems.

Future Directions

Presented in this article is a descriptive model for the water-reduction behavior of water-reducible amphiphilic copolymers. The effects of the ionic strength and solution pH on the copolymer conformation and the viscosity were not addressed here. We chose to maintain a constant extent of neutralization (amount of amine added to the copolymer solutions) in the dilutions, instead of a constant pH. Furthermore, although double-distilled water was used to dilute the solutions, the ionic strength of the solution will change during the dilution due to the changes in the concentration of the co- and the counterions associated with the ionic carboxylate

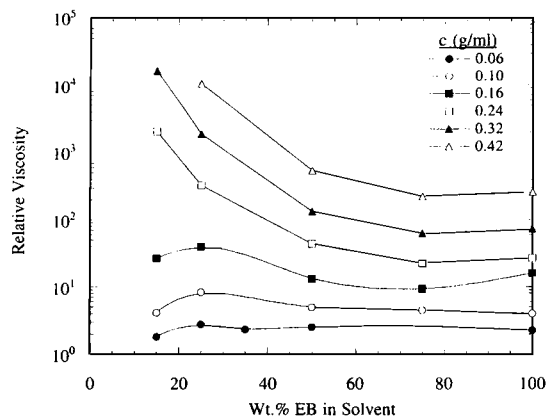


Figure 9 Constant polymer concentration contour plots for WRAC-68 showing the relative viscosity as a function of solvent composition. The polymer concentration is given in g/mL.

groups on the copolymer chains. We are presently studying the effect of both the salt concentration and pH on the reduction behavior of these model resins. In addition, the effect of the copolymer composition (hydrophilic–hydrophobic segment ratio) and its molecular weight on the rheological behavior will be studied. In parallel, Monte Carlo simulations of copolymer chains is underway, the results of which, once coupled with the experimental data, will enable us to predict the rheological behavior of water-reducible coatings. The results of this research can then be used to address the problems encountered in reducing VOC below present levels.

CONCLUSIONS

A descriptive model has been developed, using viscometry and light scattering, that explains the anomalous rheological behavior of water-reducible amphiphilic copolymer solutions upon water dilution. The observed constant or increasing viscosity upon the initial addition of water results primarily from the expansion of the polymer chains due to electrostatic repulsion between the acid groups, not from chain aggregation as previously proposed. Aggregation of the chains occurs when the hydrophobic interactions between the apolar segments of the copolymer dominate the electrostatic repulsions. Maxima in the intrinsic viscosity and the hydrodynamic size of the polymer domains occurs at 20–25 wt % cosolvent in the medium. The locations of these maxima, as well as the viscosity of the solutions, are controlled by the relative strengths of the intramolecular hydrophobic and hydrophilic (elec-

trostatic) interactions. These interactions depend not only on the monomer composition but also on the solvent composition. The composition of the solvent mixture along the reduction curves, therefore, strongly dictates their shape features. Beyond the viscosity maximum, extensive aggregation of the polymer chains into polymolecular domains is observed and is believed to be primarily responsible for the observed sharp viscosity decrease; dilution also contributes to the viscosity decrease. Intermolecular hydrophobic attractions are dominant in this stage of water dilution.

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