

# Synthesis and Characterization of Model Associative Polymers

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## SYNOPSIS

Model linear associative polymers with number average molecular weights in the range of 16,600 to 100,400 were prepared by connecting blocks of commercially available poly(oxyethylene) with isophorone diisocyanate, followed by capping with either hydroxyl, dodecyl, or hexadecyl linear alkyl end groups. The molecular weight distributions measured by gel permeation chromatography are somewhat broad, as expected from the synthetic method. In a 40/60 by weight solvent mixture of diethylene glycol monobutyl ether (Butyl Carbitol) and water, the relative viscosities of model associative polymers and poly(oxyethylene) standards collapsed to a single master curve; viscosity average molecular weights obtained from the intrinsic viscosities measured in this solvent mixture compare favorably to those obtained by size exclusion chromatography. In water, the model polymers with alkyl end groups interact at extremely dilute concentrations to produce a pronounced increase in reduced viscosity that increases as concentration and alkyl end group length increase. The Huggins parameters for solutions of model associative polymers with the hexadecyl and dodecyl end groups vary between 1 and 16, and decrease as molecular weight increases, as hydrophobe length decreases, and as temperature increases. The concentration at which the viscosity data deviate from the Huggins equation is less than the polymer coil overlap concentration, which is on the order of 1–3 g/dL, as estimated from the reciprocal of the intrinsic viscosity data. This suggests that we can define a critical network concentration  $c_n^*$  as the concentration at which the associative polymers hydrophobic end groups first interact to form a rheologically significant network. However, the transition occurs over a concentration range, rather than at a particular critical micellar concentration, as is the case of ordinary surfactants or hydrophobically modified hydroxyethylcellulose. The dimensions of the associative polymer coils in solution, and the signs and relative magnitudes of heat and entropy of dilution as estimated from classical molecular theories, are similar to those obtained by other authors for poly(oxyethylene) homopolymers. A physical model based on equilibrium kinetics for the association process correctly mimics the dependence of viscosity on molecular weight and concentration, and indicates that the free energy of association must become larger as the length of the alkyl end groups becomes larger relative to the hydrophilic backbone. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Associative polymers are hydrophobically modified water-soluble block copolymers composed of both water-soluble and water-insoluble components; the water-insoluble components interact in solution, and

can also adsorb onto latex particles, to form a microstructure that improves the rheological properties of a latex paint. In principle, any water-soluble polymer can be modified to produce an associative polymer; associative polymers have been based on hydroxyethyl cellulose,<sup>1</sup> poly(oxyethylene),<sup>2,3</sup> poly(acrylamide),<sup>4</sup> or polymers that contain acid functionality, such as copolymers of methacrylic acid and ethyl acrylate,<sup>5</sup> and copolymers of styrene and maleic acid.<sup>6</sup> The hydrophobic blocks can terminate

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the polymer backbone, or can reside in, or extend from, the backbone to form a comb-like molecular architecture. The more Newtonian rheology imparted to the latex paint by interactions among the associative polymers, as compared to the rheology imparted by unmodified cellulosic thickeners, improves the application characteristics of the paint. The literature compares the performance of associative polymers and conventional thickeners in common latex paint formulations<sup>7</sup> and provides practical latex paint formulation strategies.<sup>8</sup>

Due to the complex nature of the interactions among associative polymers and standard latex paint ingredients, a growing body of literature has developed around model associative polymers to understand, from fundamental first principles, the relationships among associative polymer structure, dispersion rheology and stability, and formulation. (for example, see ref. 9). Our previous work investigated the relationships between polymer structure and the rheology of aqueous solutions and dispersions, the influence of added surfactant and solvents on rheology, and adsorption of the polymers to latex particles.<sup>10-12</sup> This article describes the synthesis and molecular weight characterization of the model associative polymers used in the previous investigations and presents results from intrinsic viscosity experiments: scaling correlations between viscosity and concentration, estimates of the dimensions of the polymer chains in solution, and semiquantitative information on the dilute solution thermodynamics of associative polymers.

### Corresponding States: Scaling Behavior of Polymer Solutions

The definition of intrinsic viscosity has its roots in the Einstein equation for the relative viscosity of a dilute suspension of unsolvated spherical particles:

$$\frac{\eta}{\mu} = 1 + \frac{5}{2} \Phi_2 \quad (1)$$

where  $\eta$  is the viscosity of the suspension,  $\mu$  is the viscosity of the solvent,  $\Phi_2$  is the particle volume fraction given by  $N_2 V_h / V$ , and  $N_2$  is the number of particles, each of which has hydrodynamic volume of  $V_h$ , in the total suspension volume  $V$ . Polymers in solution likewise enhance the viscosity of the solvent due to their hydrodynamic size. If a polymer in solution is analogous to a particle suspension, then  $N_2$  equals  $V c_2 N_A / M_2$ , and the relative viscosity is then:

$$\frac{\eta}{\mu} = 1 + \frac{5}{2} \frac{4\pi}{3} \frac{N_A c_2 R_h^3}{M_2} \quad (2)$$

where  $V_h$  equals  $(4\pi/3)R_h^3$ ,  $c_2$  is the polymer concentration in grams/cm<sup>3</sup>,  $N_A$  is Avogadro's number, and  $M_2$  is the molecular weight of the polymer. Extrapolation of the specific viscosity  $[\eta/\mu - 1]$  defines the intrinsic viscosity, or limiting viscosity number  $[\eta]$ , as a measure of the hydrodynamic volume of the polymer coil in solution:

$$\lim_{c_2 \rightarrow 0} \frac{\left[ \frac{\eta}{\mu} - 1 \right]}{c_2} = \frac{5}{2} \frac{4\pi}{3} \frac{N_A}{M_2} R_h^3 \equiv [\eta] \quad (3)$$

In general, the viscosity theories for polymers in solution are less well developed than those for colloidal particles in suspension, mainly due to the compressibility of the polymer coils at moderate concentrations, entanglement effects, and the formation of polymer aggregates. The dependence of solution viscosity on polymer coil size and concentration is often expressed in terms of empirical master correlations of the form  $\eta/\mu = f(c[\eta])$ .<sup>13-15</sup> One such equation is the Huggins equation:

$$\frac{\eta}{\mu} = 1 + c[\eta] + K' c^2 [\eta]^2 + \dots \quad (4)$$

where  $\eta/\mu$  is the relative viscosity,  $c[\eta]$  is the overlap parameter (i.e., a dimensionless coil volume), and the constant  $K'$  characterizes the first effects of polymer interaction on the viscosity. The Huggins' parameter  $K'$  is usually independent of polymer molecular weight for long polymer chains, and has a value of about 0.4 for polymers in good solvents without interaction effects, and a value of about 0.8 for polymers in theta solvents.<sup>16,17</sup> Equations like eq. (4) often unify viscosity data over a broad range of molecular weights for a given dilute polymer-solvent system where polymer-polymer interactions do not dominate.

The overlap concentration  $c^*$  denotes the concentration where polymer coils begin to interpenetrate in solution, and distinguishes between the different solution states: dilute ( $c < c^*$ ), semidilute ( $c \approx c^*$ ), and concentrated ( $c > c^*$ ). It is commonly assumed that  $c^*$  occurs when the overlap parameter  $c[\eta]$  approximately equals 1. However, this neglects changes in coil dimensions with concentration: for polymers that contract to theta dimensions before they interpenetrate,  $c^* = 0.74/[\eta]$ .<sup>18,19</sup> In the semidilute concentration regime, interaction occurs among many polymer chains so that solution vis-

cosity no longer follows scaling laws that were derived for isolated polymer chains. de Gennes showed that rheological data of semidilute polymer solutions scale as a power of the reduced variable  $\bar{c}/c^*$ , where the overbar denotes molar concentration, and that  $c^*$  scales with molecular weight to the  $-4/5$  power for a real chain following a self-avoiding random walk.<sup>20</sup> Thus, we can use these scaling laws to determine the boundaries of the various solution states, and to identify the concentrations at which networking begins.

### Polymer Chain Dimensions from Intrinsic Viscosity

Even though the concentration dependence of the relative viscosity of polymer solutions is determined empirically, the dimensions of flexible linear macromolecules in solution can still be extracted from the relationship between intrinsic viscosity and molecular weight. The dimensions of polymer coils in solution are determined by short-range and long-range interactions: short-range interactions that occur between atoms that are separated by only a few bond lengths produce torques that inhibit internal rotation about bonds, and, hence, govern the flexibility of the polymer coil; long-range interactions that occur between segments of the polymer chain that are separated by many valence bonds result from van der Waals interactions. Long-range interactions produce an osmotic swelling of the polymer coil through polymer-solvent interactions, so that the volume of the solvent swollen polymer increases over that for a polymer that is unperturbed by the solvent. An expansion coefficient  $\alpha$ , which is the ratio of the root mean square end-to-end distance of the polymer coil in the solvent  $\langle r^2 \rangle^{1/2}$  relative to the root mean square end-to-end distance in the unperturbed state  $\langle r^2 \rangle_o^{1/2}$ , describes this effect:

$$\alpha = \frac{\langle r^2 \rangle^{1/2}}{\langle r^2 \rangle_o^{1/2}} \quad (5)$$

In a Flory "theta" solvent, long-range interactions are absent, and the polymer chain assumes its unperturbed dimensions. Thus,  $\alpha$  characterizes the "goodness" of solvent for the polymer:  $\alpha < 1$  for a poor solvent,  $\alpha = 1$  in a theta solvent, and  $\alpha > 1$  in a good solvent.

With these considerations, the hydrodynamic volume of the polymer coil can be written as  $V_h = (V_h)_\theta \alpha^q$ , where  $(V_h)_\theta$  is the volume assumed by the unperturbed coil, and  $q$  depends on the chain's conformation: 2.43 for a spherical coil and 2.18 for an

elliptical coil. The intrinsic viscosity in eq. (3) then becomes:

$$\begin{aligned} [\eta] &= \frac{5}{2} N_A (V_h)_\theta \frac{\alpha^q}{M_2} \\ &= \frac{5}{2} N_A \Phi \left( \frac{\langle r^2 \rangle_o}{M_2} \right)^{3/2} M^{1/2} \alpha^q = KM^{1/2} \alpha^q \quad (6) \end{aligned}$$

where  $\Phi$  is a proportionality factor between the radius of gyration and the hydrodynamic volume, and  $K$  is

$$K = \frac{5}{2} N_A \Phi \left( \frac{\langle r^2 \rangle_o}{M_2} \right)^{3/2} = \Phi \left( \frac{\langle r^2 \rangle_o}{M_2} \right)^{3/2} \quad (7)$$

Experiments have shown that  $\Phi$  does not depend on the constitution or configuration of the polymer or solvent, but only on the relative expansion of the coil in solution, and that  $\Phi$  equals  $2 - 2.5 \times 10^{21}$  when traditional units of (dL/g) are used for the intrinsic viscosity. Chain statistics that consider the finite thickness of the polymer chain and interaction between segments of the polymer show that  $\langle r^2 \rangle \sim M^{1+\epsilon}$  when in nontheta solvents. When this is substituted into the previous expression, there results the Kuhn-Mark-Houwink-Sakurada equation:

$$[\eta] = K_{MH} M^a \quad (8)$$

where  $K_{MH}$  and the exponent  $a$  are constants obtained by calibration with standards of known molecular weight. The exponent  $a$  is related both to the solvent quality and to the conformation of the polymer chain:  $a = 0$  for unsolvated spheres,  $a = 2$  for rigid rods, and  $a = \frac{1}{2}$  for polymer coils in a theta solvent.

To determine unperturbed chain dimensions from intrinsic viscosity data, we must uncouple the relative contributions of long-range interactions, which determine  $\alpha$ , and short-range interactions, which determine  $\langle r^2 \rangle_o$ , to total volume of the polymer coil. One obvious way to do this is to measure the intrinsic viscosity in a theta solvent. Then the right-hand side of eq. (7) calculates the unperturbed dimensions:  $K_\theta = \Phi[\langle r^2 \rangle_o/M]^{3/2}$ . Even if a theta solvent for the polymer in question is not known, the unperturbed dimensions from intrinsic viscosity measurements in a nontheta solvent can still be estimated, provided that the correct allowance for the excluded volume of the polymer chain due to long-range interactions is made in the expansion coefficient  $\alpha$ .

Most theories to calculate the perturbation in chain dimensions that results from the excluded

volume effect represent the interactions among nonbonded segments of the polymer chain with the binary cluster integral assuming pair-wise interactions. As a result, the expansion coefficient depends only on the excluded volume parameter  $z$ :

$$z = \frac{\beta m_s^2}{(4\pi)^{3/2}} \left( \frac{\langle r^2 \rangle_o}{M} \right)^{3/2} \sqrt{M} \quad (9)$$

where  $\beta$  is the excluded volume of a pair of chain segments that have a molecular weight  $m_s$ . The excluded volume parameter is related to the second virial coefficient  $B(T)$  via  $B = \beta m_s^2 / (6\pi)^{3/2} = \bar{v}^2 (1 - 2\chi_1) / V_1 N_A$ , where  $\chi_1$  is the familiar Flory interaction parameter. Hence, at the Flory theta temperature, where no long-range interactions exist, the excluded volume parameter is zero.

A number of expressions relate the excluded volume parameter to chain dimensions to determine the unperturbed dimensions from intrinsic viscosity measurements made in good solvents.<sup>21-25</sup> We use the Kurata-Stockmayer and Stockmayer-Fixman equations.<sup>25,26</sup> Kurata and Stockmayer suggested the approximate equation  $\alpha^3 - \alpha = Cg(\alpha)z$ , where  $g(\alpha) = 8\alpha^3 / (3\alpha^2 + 1)^{3/2}$  and  $C$  is a constant, for the relationship between excluded volume and the expansion coefficient of the polymer coil. In terms of intrinsic viscosities  $\alpha^3$  is:

$$\alpha^3 = \frac{\langle r^2 \rangle^{3/2}}{\langle r^2 \rangle_o^{3/2}} = \frac{[\eta]}{[\eta]_\theta} = \frac{[\eta]}{K_\theta \sqrt{M}} \quad (10)$$

which is the ratio of the intrinsic viscosity of the polymer in the solvent of interest to the intrinsic viscosity of the polymer in a theta solvent. When these two equations are combined, the results are:

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_\theta^{2/3} + 0.363\Phi B \left[ g(\alpha) \frac{M^{2/3}}{[\eta]^{1/3}} \right] \quad (11)$$

Equation (11) is applied by first plotting  $[\eta]^{2/3}/M^{1/3}$  against  $M^{2/3}/[\eta]^{1/3}$ , while ignoring  $g(\alpha)$  to determine an approximate value of  $K_\theta$ . This value of  $K_\theta$  is used to calculate  $g(\alpha)$ , and  $[\eta]^{2/3}/M^{1/3}$  is now plotted against  $g(\alpha)M^{2/3}/[\eta]^{1/3}$  to find an improved estimate of  $K_\theta$ . The method is applied iteratively until convergence, and the final value of  $K_\theta$  determines the unperturbed dimensions of the polymer coil from  $K_\theta = \Phi[\langle r^2 \rangle_o/M]^{3/2}$ . Stockmayer and Fixman used  $\alpha^3 = 1 + 2z$  to derive an algebraically explicit equation that applies to flexible chains that immobilize solvent:

$$\frac{[\eta]}{\sqrt{M}} = K_\theta + 0.51\Phi B \sqrt{M} \quad (12)$$

According to eq. (12), plotting the intrinsic viscosity divided by the square root of the number average molecular weight against the square root of number average molecular weight yields a line where the intercept is  $K_\theta$ . The temperature at which the slope of the line in a plot of either the Kurata-Stockmayer equation or the Stockmayer-Fixman is zero is the ideal Flory theta temperature  $\Theta$ . Despite their entirely different origins, eqs. (11) and (12) usually yield similar results.

### Thermodynamic Parameters

Intrinsic viscosity measurements can estimate the thermodynamic properties (i.e., equilibrium properties) of a polymer solution through the Flory swelling equation, even though the intrinsic viscosity is measured from a nonequilibrium experiment.<sup>27</sup>

$$\alpha^5 - \alpha^3 = 2C_m \psi_1 [1 - \Theta/T] \sqrt{M} \quad (13)$$

where

$$C_m = \left( \frac{27}{2^{5/2} \pi^{3/2}} \right) \left( \frac{\bar{v}_2^2}{N_A V_1} \right) \left( \frac{\langle r^2 \rangle_o}{M} \right)^{-3/2} \quad (14)$$

$V_1$  is the molar volume of the solvent,  $\bar{v}_2$  is the partial specific volume of the polymer, and  $\psi_1$  is the entropy of dilution parameter. The enthalpy of dilution is  $\Delta H_1 = RT\kappa_1 \bar{v}_2^2$ , where the enthalpy of dilution parameter  $\kappa_1$  equals  $\psi_1 \Theta/T$ , and the entropy of dilution is  $\Delta S_1 = R\psi_1 \bar{v}_2^2$ . These parameters characterize the thermodynamic interactions between polymer and solvent. According to eq. (13), plotting  $\alpha^5 - \alpha^3/\sqrt{M}$  against  $1/T$  yields a line with an intercept equal to  $2C_m \psi_1$  and a slope equal to  $-2C_m \psi_1 \Theta$ . Thus, measurement of  $\alpha$  via intrinsic viscosity eq. (10) permits calculation of the ideal theta temperature  $\Theta$ , and the enthalpy  $\Delta H_1$  and entropy  $\Delta S_{A1}$  of dilution.

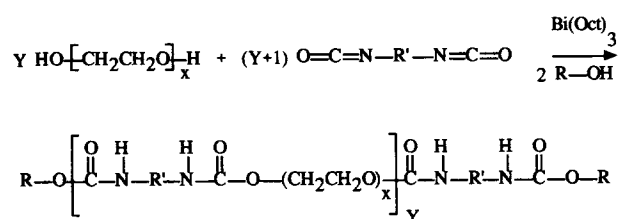
## EXPERIMENTAL DETAIL

### Model Associative Polymer Synthesis

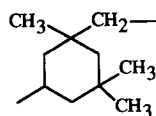
As presented in Table I, the model-associative polymers are linear water-soluble poly(oxyethylene) backbones of a number average molecular weight between 16,600 to 100,400 that have been capped with either hydroxyl, dodecyl, or hexadecyl linear alkyl end groups. The notation  $C_{n-m}$ , where  $n$  rep-

represents the number of carbon atoms in the alkyl end group, and  $m$  represents the polymer number average molecular weight in thousand Daltons, describes the structure of the polymer molecule. The hydroxyl-terminated polymers serve as a control group by which we can measure the influence of the presence of linear alkyl hydrophobic end groups on solution and latex rheology.

Because poly(oxyethylene) of the desired molecular weights are not commercially available, the model associative polymers were prepared by chain extending, and subsequently capping, blocks of commercially available poly(oxyethylene) with diisocyanates,<sup>2,3</sup> as shown by the following reaction schematic:



where  $x$  is approximately 190,  $\text{Bi}(\text{Oct})_3$  is bismuth octoate catalyst, and  $\text{R}'$  is isophorone:



We used isophorone diisocyanate due to the hydrolytic stability of the resulting urethane linkage in the polymer backbone, and due to its relatively lower volatility and toxicity as compared to other aliphatic diisocyanates. As an unavoidable consequence of this synthetic route, the polymers have molecular weight distributions that are not monodisperse. Nonetheless, because we examine a series of polymers that vary systematically in molecular weight, the breadth in the molecular weight distribution does not invalidate our qualitative conclusions.

Because water reacts with diisocyanates to terminate the chain extension reaction, even trace water must be removed from the reaction vessel prior to polymerization. This is accomplished through azeotropic distillation of a toluene solution of Carbowax® 8000 (Union Carbide Corporation) brand of poly(oxyethylene) in a four-neck, 1 liter, round-bottom reaction flask equipped with a heating mantle, Dean-Stark trap, condenser, thermometer, nitrogen bubbler, nitrogen purge line, addition funnel, and stirrer. After refluxing to dryness at approximately 113°C under nitrogen purge, the reaction solution

is subsequently cooled to 90°C, and a stoichiometric amount of isophorone diisocyanate and a urethane catalyst (bismuth octoate) are charged and allowed to mix well in the toluene solution. Prior to the reaction, the molecular weight of the poly(oxyethylene) is determined by hydroxyl number, and the equivalent molecular weight of the isophorone diisocyanate is determined by free isocyanate analysis. The reaction mixture becomes viscous after an exotherm, and the reaction proceeds an additional hour at 90°C to ensure that an isocyanate terminated prepolymer forms before adding a toluene solution of the capping alcohol to the reaction mixture by way of the addition funnel. After the capping reaction proceeds at 90°C for an hour, the product is cooled to 70°C, 0.12 grams of 2,6-Di-*tert*-4-methyl phenol (BHT) preservative are added, and the toluene solution is poured into a stainless steel pan with large surface area to facilitate drying.

Performing the chain extension and capping reactions at 100% poly(oxyethylene) solids in the melt avoids the use of solvent, but this process requires a high-speed air mixer capable of delivering enough torque to ensure good mixing during the polymerization. The poly(oxyethylene) must be melted and sparged with nitrogen before charging the reactants to drive off as much water as possible, and the catalyst and capping material are added to the molten poly(oxyethylene) simultaneously. The mixture is stirred until the melt becomes too viscous to allow further stirring, after which the sample is cured in an oven for several hours. After curing, the beaker is broken away to reveal the solid model polymer.

### Size Exclusion Chromatography

The model-associative polymers were dissolved as 0.5 wt % solutions in tetrahydrofuran, and were filtered with a large pore-sized membrane to remove residual catalyst. The size exclusion column was calibrated with monodisperse poly(oxyethylene) standards at ambient temperature, and had a resolution of 14,000 plates.

All of the chromatograms (which are presented elsewhere)<sup>12</sup> have two features in common. First, the molecular weight distributions are large with a long low molecular weight tail, as expected from the synthetic method. The molecular weight distributions of commercial associative polymers are likewise broad, and we suspect that the model polymers synthesized through urethane chemistry by other researchers also had broad molecular weight distributions. Poly(oxyethylene) can degrade mechanically in tetrahydrofuran while in a size exclusion column.<sup>28</sup> According to Beech and Booth,<sup>23</sup> such

**Table I Structure and Molecular Weight Summary of Model Associative Polymers as Obtained from Various Methods**

Reference	Structure		Calculated $M_n^c$	Gel Permeation Chromatography					Intrinsic Viscosity <sup>e</sup>	
	R	Y		$M_n$	$M_w$	$M_v^d$	$M_z$	PDI	$M_n$	$M_w$
C <sub>0-16</sub>	H	2	16,600	15,600	38,600	34,400	72,700	2.5	10,200	23,100
C <sub>0-33</sub>	H	4	33,400	29,300	77,800	69,400	146,000	2.6	18,400	44,000
C <sub>0-50</sub>	H	6	50,200	29,400	105,000	93,000	208,000	3.6	20,500	67,000
C <sub>0-67</sub>	H	8	67,000	31,300	128,000	112,000	263,000	4.1	22,700	82,200
C <sub>0-84</sub>	H	10	84,000	36,000	140,000	123,000	285,000	3.9	26,400	95,400
C <sub>0-100</sub>	H	12	100,400	40,200	168,000	146,000	348,000	4.2	30,800	117,000
C <sub>12-17</sub>	C <sub>12</sub> H <sub>25</sub>	2	17,400	22,000	51,700	47,200	82,100	2.4	20,600	45,600
C <sub>12-34</sub>	C <sub>12</sub> H <sub>25</sub>	4	34,200	27,700	77,800	70,900	122,000	2.8	25,900	66,700
C <sub>12-51</sub>	C <sub>12</sub> H <sub>25</sub>	6	50,400	23,700	87,400	78,400	148,000	3.7	25,400	85,300
C <sub>12-68</sub>	C <sub>12</sub> H <sub>25</sub>	8	67,700	29,100	101,000	91,800	158,000	3.5	30,200	96,000
C <sub>12-85</sub>	C <sub>12</sub> H <sub>25</sub>	10	84,500	30,000	107,000	96,800	169,000	3.6	32,000	102,000
C <sub>12-100</sub>	C <sub>12</sub> H <sub>25</sub>	12	99,900	28,800	109,100	98,900	173,000	3.8	36,000	124,000
C <sub>16-18</sub>	C <sub>16</sub> H <sub>33</sub>	2	17,500	20,100	54,500	49,400	89,900	2.7	22,800	56,500
C <sub>16-34</sub>	C <sub>16</sub> H <sub>33</sub>	4	34,200	13,500	65,300	58,500	108,000	4.9	15,300	68,100
C <sub>16-51</sub>	C <sub>16</sub> H <sub>33</sub>	6	51,000	35,100	97,000	88,200	155,000	2.8	31,000	79,700
C <sub>16-68</sub>	C <sub>16</sub> H <sub>33</sub>	8	67,600	13,100	93,000	81,600	167,000	7.1	15,800	99,600
C <sub>16-84</sub>	C <sub>16</sub> H <sub>33</sub>	10	84,300	31,000	113,000	103,000	177,000	3.7	32,600	118,000
C <sub>16-100</sub>	C <sub>16</sub> H <sub>33</sub>	12	100,400	29,300	105,000	695,800	164,000	3.6	35,800	117,000

<sup>a</sup> DI is isophorone diisocyanate, and PEG is Carbowax 8000 with a nominal molecular weight of 8200.

<sup>b</sup> The first subscript indicates the length of the alkyl end group, denoted R, and the second subscript indicates the molecular weight of the model associative polymer in thousands.

<sup>c</sup> Number average molecular weight calculated from reaction stoichiometry. R = Type of end group on polymer backbone. Y = Number of Carbowax blocks in thickener backbone.

<sup>d</sup> The Mark-Houwink exponent for poly(oxyethylene) is used to calculate the viscosity average molecular weight.

<sup>e</sup> Molecular weights determined from  $[\eta] = 2.84 \times 10^{-4} M_v$  for monodisperse poly(oxyethylene) standards in a 40/60 diethylene glycol monobutyl ether/water solvent mixture.

degradation does not occur if a 50/50 mixture of ethanol and water is used to elute the poly(oxyethylene). This makes us wonder if the model polymers are, indeed, as polydisperse as the chromatograms indicate. Even though the molecular weight distribution of the polymers are broad, one can easily discern a trend with respect to the peak molecular weight of the chromatogram, which corresponds closely to the viscosity average molecular weight. Second, the chromatograms have a shoulder, or a second peak for some of the lower molecular weight model polymers, that corresponds to a molecular weight of about 10,000. The shoulder grows smaller as the target molecular weight of the polymer increases. This suggests that the shoulder possibly results from some unreacted poly(oxyethylene) starting material. A small amount of unreacted starting material will, of course, influence intrinsic viscosity measurements, but should not significantly affect rheological measurements in larger concentrations where an association network exists.

Table I compiles the molecular weight averages that are calculated from the chromatograms. Although the breadth of the molecular weight distributions makes the selection of a characteristic molecular weight somewhat difficult, we use the number average molecular weight calculated from reaction stoichiometry for several reasons. First, it lies close to the peak molecular weight in the chromatograms, and seems to best represent the trends in the molecular weight progression in the model polymer series. Second, no other molecular weight average appears to serve any better. Third, we wish to retain uniformity of nomenclature with our previous publications that used the number average molecular weight calculated from reaction stoichiometry. In any event, none of the general conclusions presented in this dissertation are affected by an error in the absolute magnitude of the benchmark molecular weight that we choose. It is enough for most purposes that the molecular weights within a given polymer series increase systematically.

### Intrinsic Viscosity Technique

Stock solutions of 5% by weight-associative polymers were prepared by adding a weighed amount of solid polymer to distilled deionized (DDI) water. Because poly(oxyethylene) degrades by a free radical mechanism,<sup>29</sup> we added 5–20 ppm of hydroquinone inhibitor to these solutions, and stored the solutions in the dark to stabilize them against degradation; the solid polymers were stored in a refrigerator at 4°C to promote their long-term stability. The intrinsic viscosities that followed were determined by diluting these stock solutions.

The intrinsic viscosities of the associative polymers were measured with Ubbelohde dilution viscometers situated in a thermostated bath. The efflux time for the solvents were large enough to ignore the Hagenbach–Couette kinetic energy correction, and the densities of the solutions were nearly those of the solvents. Thus, the efflux times of the solutions were converted to reduced viscosity and inherent viscosities from the following definitions:

$$\eta_{\text{reduced}} = \frac{\eta_{\text{specific}}}{C} = \frac{t - t_o}{Ct_o};$$

$$\eta_{\text{inherent}} = \frac{\ln(\eta_{\text{relative}})}{C} = \frac{\ln(t/t_o)}{C} \quad (15)$$

where  $t_o$  is the solvent efflux time, and the resulting reduced and inherent viscosities were plotted against concentration in the traditional units of g/dL. Extrapolation of the linear regions of the reduced and inherent viscosity curves for  $1.2 \leq \eta_{\text{relative}} \leq 1.6$  to zero concentration with the familiar Huggins and Kraemer equations, respectively:

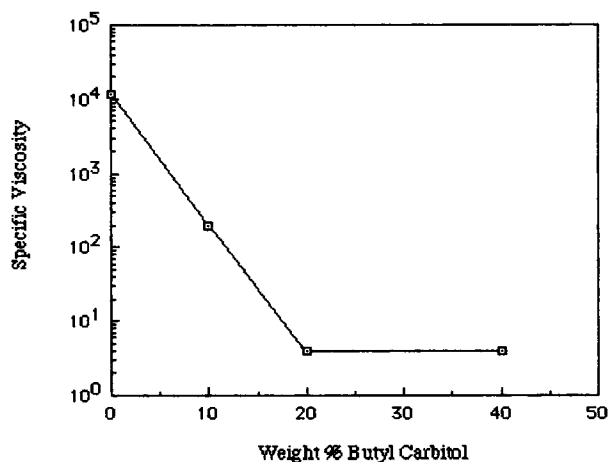
$$\eta_{\text{reduced}} = [\eta] + K'[\eta]^2C;$$

$$\eta_{\text{inherent}} = [\eta] + K''[\eta]^2C \quad (16)$$

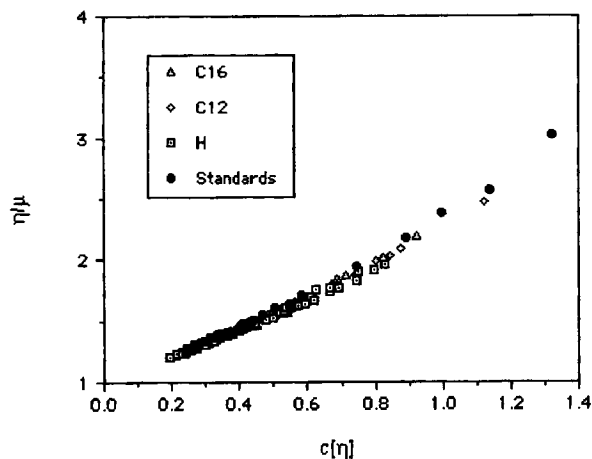
produced intrinsic viscosities in units of dL/g that were equivalent within the precision of the experiment. Rheological measurements on concentrated solutions performed with a Bohlin Rheometer indicated that solutions containing less than 0.5% associative polymer by weight were Newtonian at shear rates from  $40 \text{ s}^{-1}$  to  $8000 \text{ s}^{-1}$ .<sup>10</sup> Because the shear rates at which the dilute solutions reach Newtonian behavior are similar in magnitude to the shear rate at the wall in our Ubbelohde viscometer, no shear rate correction was applied to the measured intrinsic viscosities.

To independently verify the molecular weights of the model-associative polymers, we measured their

viscosity average molecular weights in a 40/60 mixture of Butyl Carbitol and water. Water miscible cosolvents, such as Butyl Carbitol (diethylene glycol monobutyl ether), disrupt the hydrogen bonding among water molecules to suppress the interactions among associative polymer hydrophobic groups in solution, and, hence, reduce the viscosity and viscoelasticity of associative polymer solutions. Because the driving force for the association process is hydrogen bonding among water molecules to expel the hydrophobes of an associative polymer from an aqueous medium, the term “hydrophobic” bonding is a misnomer that reverses cause and effect; the hydrophobes do not attract and seek each other out in solution but are, instead, forced out of solution by the water molecules. In this respect, the association phenomenon and surfactancy are strongly related because entropy contributes largely to the free energy of both processes (i.e., “entropic” bonding).<sup>30</sup> Figure 1 shows the effect of adding Butyl Carbitol on the specific viscosity of a 2.5 wt % aqueous solution of a hexadecyl-terminated associative polymer with a number average molecular weight of 51,000. Because Butyl Carbitol has a relatively large viscosity on its own, the specific viscosity of the polymer in solution is used to eliminate the variation in the viscosity of the solvent mixture from the comparison. The specific viscosity decreases sharply as the concentration of Butyl Carbitol increases up to 20% by weight in the solvent mixture, whereupon it reaches a plateau where additional Butyl Carbitol has no effect on the specific viscosity. As shown in Figure 2, the relative viscosities of model-associative polymers, both hydroxyl and hydrophobe termi-



**Figure 1** The influence of diethylene glycol monobutyl ether (Butyl Carbitol) on the specific viscosity of 2.5% by weight hexadecyl-terminated associative polymer with a number average molecular weight of 51,000 at 24.5°C.



**Figure 2** The dilute scaling behavior of all 18 model associative polymers and monodisperse poly(oxyethylene) standards of molecular weights from 20,400 to 400,00 in a mixed solvent system composed of 40% diethylene glycol monobutyl ether (Butyl Carbitol) and 60% water at 30°C.

nated, and poly(oxyethylene) standards in a 40/60 Butyl Carbitol and water solvent mixture collapse to a single master curve, and are indistinguishable from those of the poly(oxyethylene) standards. The Huggins parameter of all of the model polymers have a "normal" value of 0.4 in the cosolvent mixture, and a plot of the reduced viscosity against concentration is linear for all of the model polymers. These results suggest that the cosolvent mixture has suppressed the formation of an association network. Table I shows that the viscosity average molecular weights obtained by intrinsic viscosity compare quite favorably to those obtained by size exclusion chromatography.

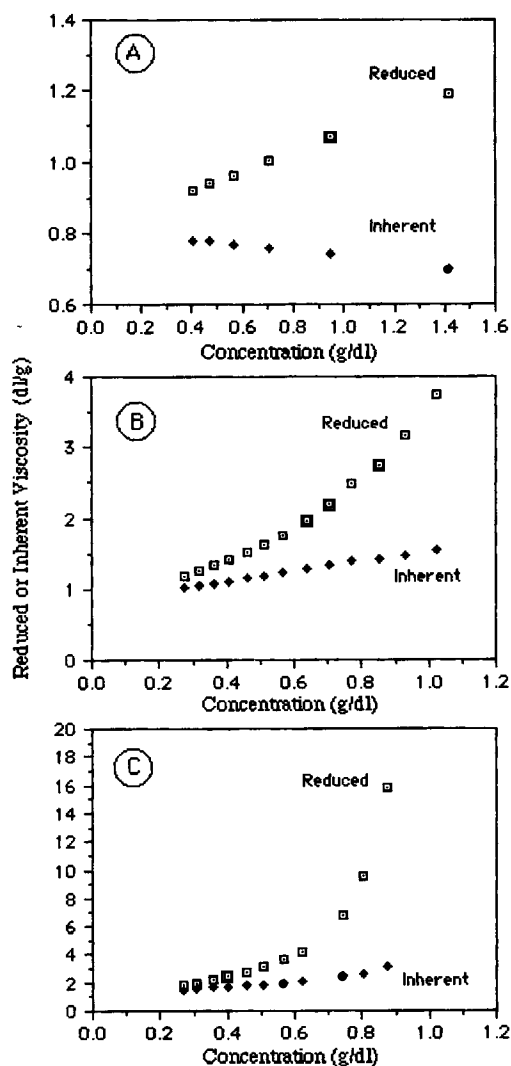
The average molecular weight calculated from intrinsic viscosity is sensitive to the molecular weight distribution of the sample. Hence, we must correct the Mark-Houwink parameter  $K$  for the molecular weight distribution if we wish to calculate the number average molecular weight of the polymer from intrinsic viscosity data. Newman et al.<sup>31</sup> and Kurata et al.<sup>32</sup> give methods to calculate this correction. The magnitude of the correction depends both on the magnitude of Mark-Houwink exponent and on the polydispersity index. We know both of these from the intrinsic viscosity data for poly(oxyethylene), and from the size exclusion chromatography. As an example of a typical value of the correction for the model polymers, when the Mark-Houwink exponent equal to 0.7, and when the polydispersity index equals 3, the correction  $K_n/K_{exp}$  equals 2.0, where  $K_n$  is used to calculate the number average molecular weight of the polymer, and  $K_{exp}$

is the experimentally measured value of the Mark-Houwink parameter. Table I shows that the number average molecular weights calculated from this method agree fairly well from the number average calculated from size exclusion chromatography.

## RESULTS AND DISCUSSION

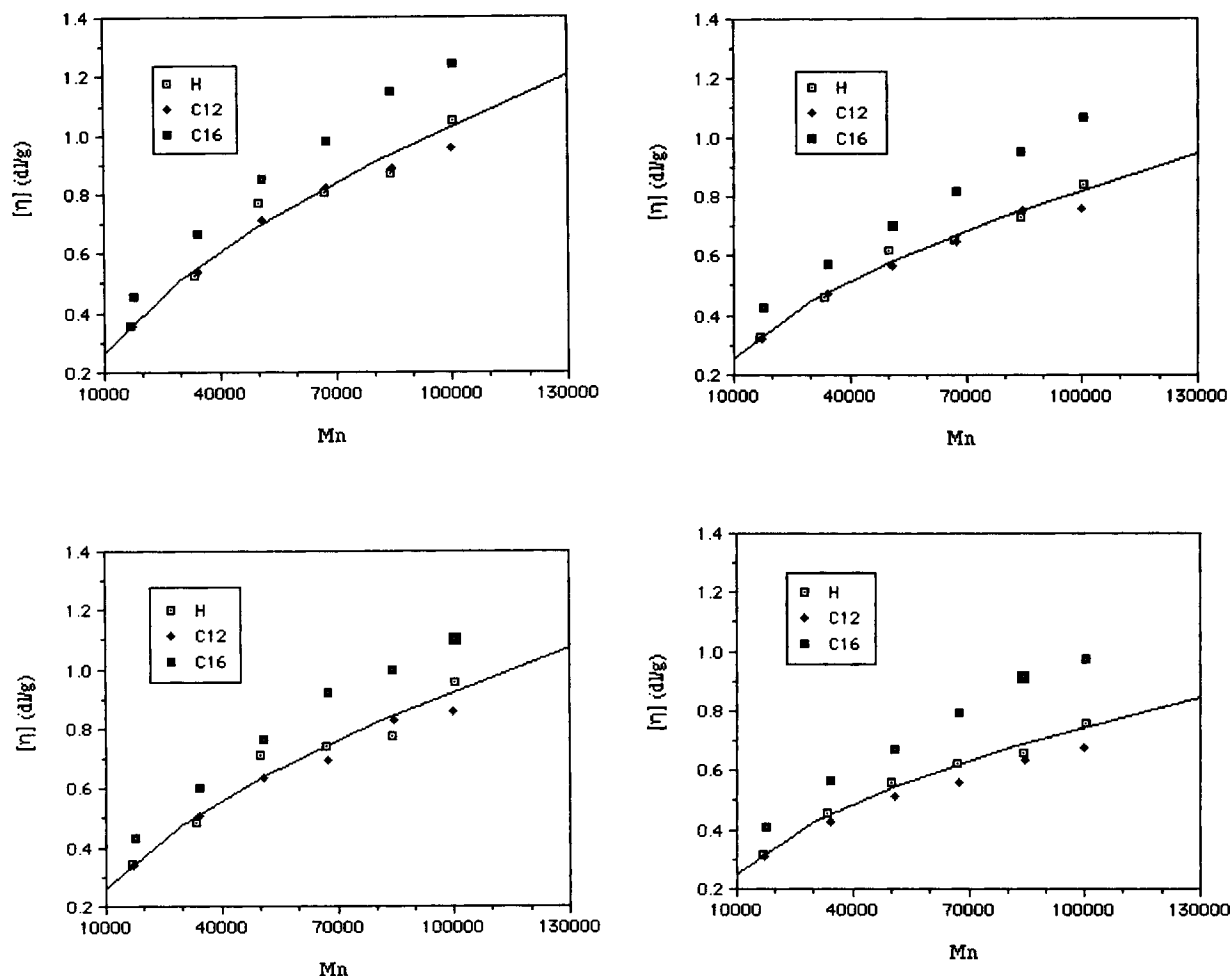
### Intrinsic Viscosities of Aqueous Solutions

Figure 3 compares how the reduced and inherent viscosity functions depend on concentration for hydroxyl, dodecyl, and hexadecyl terminated polymers, respectively. As seen in Figure 3(a), the reduced vis-



**Figure 3** Concentration dependence of the reduced and inherent viscosities at 30°C of model-associative polymers of 67,000 number average molecular weight terminated with either (a) hydroxyl, (b) dodecyl, or (c) hexadecyl end groups.





**Figure 4** (a) Intrinsic viscosities of model-associative polymers in water at 30°C. The line represents the Mark-Houwink equation as applied to the hydroxyl-terminated polymers. (b) Intrinsic viscosities of model-associative polymers in water at 40°C. The line represents the Mark-Houwink equation as applied to the hydroxyl-terminated polymers. (c) Intrinsic viscosities of model-associative polymers in water at 50°C. The line represents the Mark-Houwink equation as applied to the hydroxyl-terminated polymers. (d) Intrinsic viscosities of model-associative polymers in water at 60°C. The line represents the Mark-Houwink equation as applied to the hydroxyl-terminated polymers.

cosity of a hydroxyl terminated model-associative polymer remains linear over the measured concentration range, and has a value of  $K'$  near 0.35. In contrast, model polymers with alkyl end groups interact at extremely small concentrations to produce a rapid increase in reduced viscosity, which deviates from the linear behavior predicted by the Huggins equation. Figures 3(b) and (c) show how the reduced viscosity, which measures the specific capacity of the polymer to enhance viscosity, increases as both concentration and alkyl end group length increase. The viscosity enhancement becomes quite dramatic at concentrations that exceed 0.5 g/dL, which heralds the formation of an extensive association network in solution, and shows that the rate of addition

of associative polymer to the network with respect to polymer concentration increases as the length of the hydrophobic end group relative to the polymer backbone increases. This concentration is less than the polymer coil overlap concentration, which is on the order of 1–3 g/dL, as estimated from the reciprocal of the intrinsic viscosity data shown in Figure 4. Thus, an interaction occurs between hydrophobes at a concentration that is less than that required to make the polymer coils physically touch. This suggests that we should define a new critical network concentration  $c_h^*$  as the concentration at which the associative polymers hydrophobic end groups first interact to form a rheologically significant network.<sup>33</sup> For hydrophobically modified hydroxyethylcellulose,

this concentration is distinct, and distinguishes between the limited aggregation that occurs in the dilute regime from the more extensive aggregation at larger concentrations that lead to an association network. In contrast, the shape of the curves in Figure 3 suggests that the network builds up over a range in concentration, rather than at a particular critical micellar concentration, as in the case of ordinary surfactants or hydrophobically modified hydroxyethylcellulose.

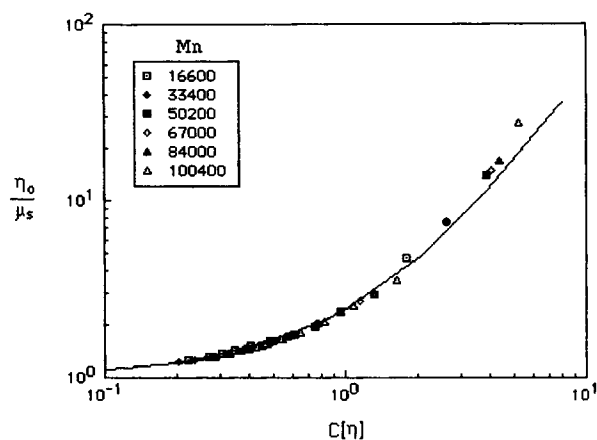
The Huggins parameters  $K'$  for solutions of model-associative polymer with the hexadecyl and dodecyl end groups are abnormally large, and vary between 1 and 16. In general, the Huggins parameter decreases as molecular weight increases, as hydrophobe length decreases, and as temperature increases. This behavior is usually attributed to the association phenomenon.<sup>34</sup> Brown and Glass<sup>35</sup> used absorbance measurements on model star-shaped associative polymers to find that large values of  $K'$  for associative polymer solutions corresponded to the formation of a hydrophobic domain in solution. Hence, the large values of the Huggins parameter, and the rapid increase in specific viscosity with increasing polymer concentration in Figure 3 indicate association of the model polymers with dodecyl and hexadecyl end groups, and suggest that the free energy of association becomes larger in magnitude as the length of the hydrophobic end group increases relative to the hydrophilic polymer backbone. The decrease in the Huggins parameter, and its approach to the value expected for a polymer–theta solvent system as temperature increases, is not surprising. It is well known that poly(oxyethylene) contracts on heating because the hydrogen bonds between the ether oxygens and water molecules are disrupted.<sup>36</sup> This compression of the polymer coil helps to suppress interactions between neighboring coils, and, thus, lower  $K'$ . Hoy et al.,<sup>2</sup> estimate the chemical potential of an associative polymer's hydrophobe  $\Delta\mu$  from Scott–Hildebrand theory:

$$\Delta\mu = 2RT - \frac{V_s + V_p}{2} (\delta_s - \delta_p)^2 x^2 \quad (17)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $V_s$  and  $V_p$  are the molar volumes of the solvent and hydrophobe, respectively,  $\delta_s$  and  $\delta_p$  are the solubility parameters of the solvent and hydrophobe, respectively, and  $x$  is the volume fraction of the hydrophobe in solution. As discussed by Hoy et al., the driving force for forming and sustaining intermolecular associations increases as the chemical potential of the hydrophobic groups becomes more negative. Increasing the temperature of an associa-

tive polymer solution, decreasing the size of the hydrophobe, matching the solubility parameter of the solvent to that of the hydrophobe, or increasing molecular weight (which decreases the volume fraction of hydrophobes for a given mass concentration) should decrease the degree of intermolecular association. Thus, the Huggins parameter is an indicator for the degree of intermolecular association.

Figure 4 shows the dependence of the intrinsic viscosities of the model-associative polymers on molecular weight and temperature. The molecular weight dependence of the intrinsic viscosities of the model polymers is nearly the same, regardless of hydrophobe length, and the intrinsic viscosities of the model polymers are similar in value to those presented by Bailey and Koleske<sup>36</sup> and Amu<sup>21</sup> for poly(oxyethylene) in water. The intrinsic viscosities decrease as temperature increases, irrespective of hydrophobe length, and as was discussed in the previous paragraph, this results from a decrease in coil dimensions as temperature increases. The intrinsic viscosities of the polymers with hexadecyl hydrophobes are slightly larger than those of the other polymers, which is noteworthy because the intrinsic viscosity of a hydrophobically modified polymer is usually lower than that of the corresponding homopolymer due to intramolecular associations that contract the chain dimensions.<sup>17</sup> This suggests that the larger intrinsic viscosities possibly result from measuring the hydrodynamic volume of an aggregate, rather than that of a molecularly dispersed associative polymer. Undoubtedly, the solutions contain a distribution of species: some polymers that are aggregated, and some that are not. This distribution will depend on associative polymer concentration, structure, and solution temperature. However, aggregation cannot be a major contribution to the intrinsic viscosities reported here for two reasons. First, the intrinsic viscosities of the hexadecyl terminated polymers are systematically larger in a solvent composed of 40% Butyl Carbitol and 60% water, where intermolecular association is apparently suppressed. Second, the molecular weight distributions are polydisperse, resulting in some uncertainty in the number average molecular weight. These facts indicate that the discrepancies in the intrinsic viscosities between polymers with different end groups are probably due to differences in model polymers' molecular weight distributions. In any event, the intrinsic viscosity results show that the average molecular weights of the model associative polymer samples increase systematically in the way expected from reaction stoichiometry, and that the molecular weights of the different hydrophobe series are, indeed, close.



**Figure 5** The concentration dependence of the relative viscosities of hydroxyl-terminated model-associative polymers in water at 30°C. The line in the figure is eq. (2.4) with the Huggins parameter  $K'$  equal to 0.4.

### Scaling Behavior

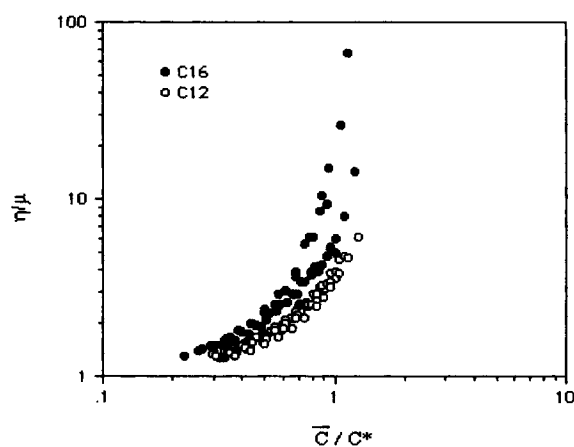
How the rheological properties of associative polymers scale with concentration and molecular weight depends on the solvent medium, and on associative polymer structure and concentration. Dilute solution theories adequately describe the viscosity behavior of aqueous solutions of the hydroxyl-terminated model-associative polymers, even up to concentrations of 5% polymer by weight. In Figure 5, the relative viscosity data for all six molecular weights of the hydroxyl-terminated model-associative polymers in water at 30°C superimpose to form a master curve when plotted against the overlap parameter  $c[\eta]$ . The master curve follows the Huggins equation when a value of 0.4 is used for  $K'$ . In contrast, dilute solution theories cannot adequately represent the viscosity data for aqueous solutions of model-associative polymers with hexadecyl or dodecyl end groups:  $c[\eta]$  fails to standardize data because significant interaction occurs among the hydrophobic alkyl end groups. Instead, the data scale via the de Gennes  $c^*$  theorem for semidilute solutions:  $\eta_0/\mu_s = F[\bar{c}/c^*]$ , where  $\bar{c} = c/M$  molar concentration of associative polymer, and  $c^*$  is proportional to  $M^{-4/5}$  for polymer chains that follow a self-avoiding random walk in a good solvent. Figure 6 shows the resulting standardization, where the relative viscosities of the model polymers with either dodecyl or hexadecyl hydrophobes in concentration between 0.2% and 0.8% by weight superimpose to a set of master viscosity curves, one for the dodecyl terminated polymers (open symbols) and one for the hexadecyl terminated polymers (closed symbols). These curves have more scatter than the curve in Figure 5, which results from the uncertainty in the number average

**Table II** Mark-Houwink Parameters of Model Associative Polymers in Water<sup>a</sup>

End Group	Temp (°C)	$K_{MH} \times 10^3$ (dL/g)	$a$
H	30	1.29	0.581
	40	1.71	0.547
	50	2.38	0.508
	60	3.31	0.471
C12	30	1.32	0.576
	40	1.84	0.539
	50	2.09	0.518
	60	4.07	0.445
C16	30	1.59	0.579
	40	2.18	0.541
	50	2.48	0.524
	60	3.08	0.500

$$^a [\eta] = K_{MH} M^a.$$

molecular weights of the polymers due to their broad molecular weight distributions. Also, solutions of hexadecyl terminated polymers are non-Newtonian when the polymer concentration exceeds 0.5%, and the relative viscosity depends on the shear rate in the capillary. This causes additional scatter in the data in the curve at the larger polymer concentrations. The important conclusion from Figures 5 and 6 is that interactions among associative polymer hydrophobes in water cause significant nonclassical rheological behavior, even when the concentrations are dilute enough that an unmodified homopolymer of identical molecular weight exhibits single chain behavior. Apparently, intermolecular interactions between hydrophobes in water occur at extremely dilute concentrations, definitely at concentrations on the order of a few tenths of a wt %.

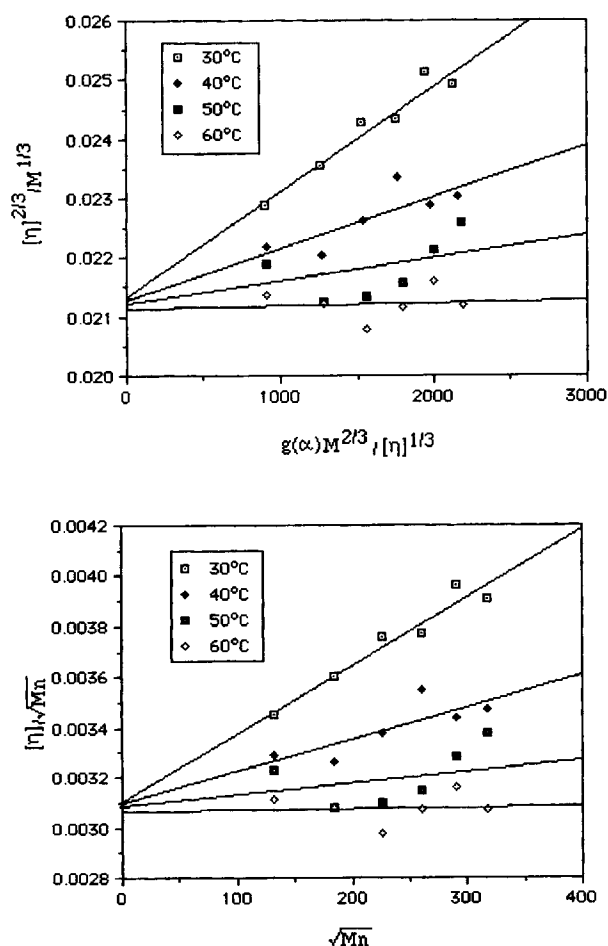


**Figure 6** The semidilute scaling behavior of the relative viscosities of dodecyl (open symbols) and hexadecyl (closed symbols)-terminated model-associative polymers in water at 30°C.

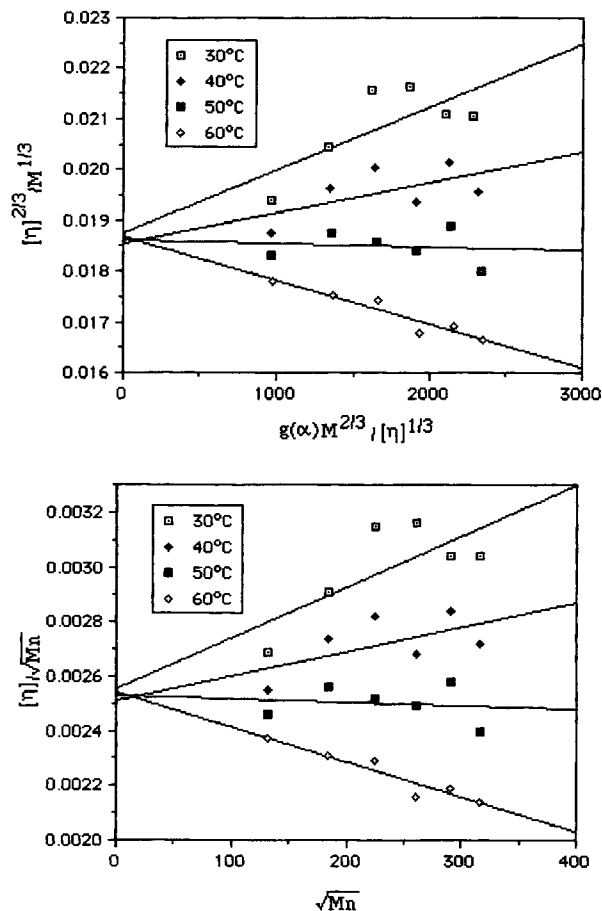
### Molecular Dimensions

As described in the Introduction, we can use the analysis developed by Kurata and Stockmayer [eq. (11)] and by Stockmayer and Fixman [eq. (12)] to estimate the unperturbed dimensions of the associative polymer coil in solution. Figures 7 through 9 show the intrinsic viscosity data plotted by this analysis for the model-associative polymers; all of the plots have two features in common. First, regardless of the temperature of the solution, the lines in each figure extrapolate to the same intercept  $K_\theta$ , which measures the unperturbed dimension of the model polymers in water from  $K_\theta = \Phi[\langle r^2 \rangle_0/M]^{3/2}$ . Second, the lines in the figures have positive slopes, and, thus, positive second virial coefficients at room temperature, and these slopes decrease to zero as the temperature increases.

As shown in Table III, the two different extrapolation equations, as applied to model associative polymers of a given length for the alkyl end group,



**Figure 7** Plot of the Kurata-Stockmayer (a) and Stockmayer-Fixman (b) equations as applied to hexadecyl-terminated model-associative polymers in water.



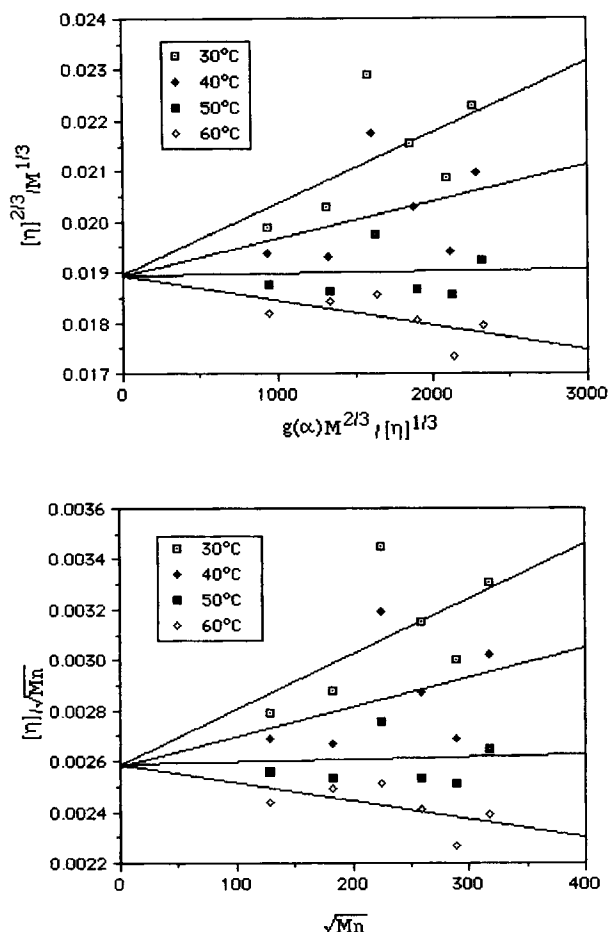
**Figure 8** Plot of the Kurata-Stockmayer (a) and Stockmayer-Fixman (b) equations as applied to dodecyl-terminated model-associative polymers in water.

provide similar estimates of  $K_\theta$ . Because we used number average molecular weights in the extrapolation equations, and because the model associative polymers are not monodisperse, we must correct the intercepts for the polydispersity before we can calculate the unperturbed dimensions of the model polymers from them. This is done by multiplying  $K_\theta$  in eqs. (11) and (12) with  $q_n$ , which is a correction factor that depends on the shape of the molecular weight distribution.<sup>25,32,37</sup> The equation of Newman et al. estimates the correction factor directly from the moments of the molecular weight distribution:

$$q_n \cong \frac{I_1^2 I_3^{3/2}}{I_{3/2} I_2^{5/2}} \quad (18)$$

where

$$I_m = \sum_i M^m N_i \quad (19)$$



**Figure 9** Plot of the Kurata-Stockmayer (a) and Stockmayer-Fixman (b) equations as applied to hydroxyl-terminated model-associative polymers in water.

For a Gaussian distribution,  $q_n$  is approximately equal to the ratio of the weight average molecular weight to the number average molecular weight. Fortunately, the method should provide a fair estimate of the chain dimensions even though the correction factor for the model polymers is rather large (about 2.1), because the linear unperturbed dimensions are only proportional to  $K_\theta^{2/3}$ . The unperturbed root mean square end-to-end distances of the model polymers in water (Table IV) are on the order of 100–300 Å, which are similar to the dimensions of poly(oxyethylene) that were obtained by other workers.<sup>23,28,38,39</sup>

Once the dimensions of the unperturbed coil are known, the effect of short range interactions on the thermodynamic flexibility of the polymer chain can be estimated through the “steric hindrance” parameter  $\sigma$ :  $\sigma^2 = \langle r^2 \rangle_o / \langle r^2 \rangle_{o,free}$ , where

$$\langle r^2 \rangle_{o,free} = Nb_e^2 \left( \frac{1 - \cos \phi}{1 + \cos \phi} \right) \quad (20)$$

is the dimension of a polymer with completely free rotation about its bonds, and  $N$  is the number of bonds of length  $b_e$  and valence angle  $\phi$  in the polymer backbone. Because steric or electrostatic interaction among segments prevent a polymer coil from sampling all of the possible internal bond rotations available to it, the coil expands to dimensions that are larger than those that the coil would assume in the absence of steric hindrance. Thus, the steric hindrance parameter is greater than one, and usually has a value of between 1.5 to 2.5 for most polymers. In poly(oxyethylene), the internal resistances are steric rather than electrostatic, and the chain is relatively flexible about its ether oxygens due to the absence of hydrogen atoms substituents.<sup>25</sup> Neglecting the presence of the isophorone diisocyanates in the associative polymer backbone, and assuming a carbon-carbon bond length of 1.54 Å, a carbon-oxygen bond length of 1.43 Å, and tetrahedral bonds in the polymer backbone, the steric hindrance parameter for the associative polymer is 1.47. This is consistent with values of 1.4 through 1.6 calculated from the data of poly(oxyethylene) from other workers.<sup>23,25,28,38,39</sup> The ratio of the fully extended length of the polymer coil  $L_{max}$  to the calculated end-to-end distance  $\langle r^2 \rangle_o^{1/2}$  provides an estimate for the degree of coiling of the polymer coil in solution. Assuming again that poly(oxyethylene) approximates the associative polymers’ molecular structure, and that the fully extended length of the model associative polymer monomer unit is 3.6 Å, the ratio of the fully extended polymer chain to the end-to-end distance of the polymer coil is over 12 for the lowest molecular polymer, and over 30 for the highest mo-

**Table III** Thermodynamic Parameters of Model Associative Polymers in Water<sup>a</sup>

Item	End Group		
	C16	C12	H
$K_\theta \times 10^3$ (dl/g) (SF)	3.10	2.37	2.54
$K_\theta \times 10^3$ (dl/g) (KS)	3.10	2.57	2.60
$K_\theta \times 10^3$ (dl/g) <sup>b</sup>	1.48	1.12	1.21
$B_o \times 10^{27}$ (cm <sup>3</sup> ) (SF)	-2.67	-3.06	-2.77
$B_o \times 10^{27}$ (cm <sup>3</sup> ) (KS)	-2.66	-2.87	-2.58
$\theta$ (°C) (SF)	58.1	55.4	53.0
$\theta$ (°C) (KS)	60.0	50.9	51.7
$\theta$ (°C) (MH)	60.6	51.9	53.7
$\theta$ (°C) (FF)	52.5	54.5	58.4

<sup>a</sup> Letters in parenthesis indicate method of evaluation: SF = via Stockmayer-Fixman analysis. KS = via Kurata-Stockmayer analysis. MH = via interpolation on the Mark-Houwink exponent. FF = via Flory-Fox analysis.

<sup>b</sup> Average experimental value, corrected for polydispersity.

**Table IV** Theoretical Root Mean Square End-to-End Distances of Model-Associative Polymers in Water at 30°C

End Group	$M_n$	$\langle r^2 \rangle^{1/2}$ (Å)			
		Stockmayer-Fixman	Peterlin	Kirkwood-Riseman	Debye-Bueche
H	16,600	110	136	136	94
	33,400	158	195	194	135
	50,200	207	255	253	176
	67,000	231	285	283	197
	84,000	255	314	312	217
	100,400	288	355	353	246
C12	17,400	112	137	137	95
	34,200	161	197	197	136
	50,700	201	247	247	170
	67,700	232	286	285	197
	84,500	257	316	315	217
	99,900	278	344	342	228
C16	17,500	122	150	149	103
	34,200	172	213	212	147
	51,000	214	264	262	182
	67,600	246	304	302	210
	84,300	279	345	343	238
	100,400	304	375	373	259

lecular weight polymer. These calculations indicate that the model associative polymers are flexible, highly coiled chains in solution, and can be modeled in dilute solution as having a Gaussian segment distribution.

During the last several decades, many models that account for the intensity of interaction between the polymer and solvent have been developed for the conformation of the polymer coil in solution: non-draining coils for polymers that interact strongly with solvent molecules, and free-draining coils for polymers that interact weakly with the solvent. The molecular theories of Debye and Bueche,<sup>40</sup> Kirkwood and Riseman,<sup>41</sup> and Peterlin<sup>42</sup> can infer the dimensions of such a polymer chain in solution. Debye and Bueche modeled the polymer coil as a solvent-permeable sphere that has a constant polymer segment distribution function (i.e., a sieve-like permeable equivalent sphere), and solved the resulting hydrodynamic problem. Their result is:

$$\langle r^2 \rangle^{1/2} (\text{cm}) = \left( \frac{36}{10} \right)^{1/2} \left( \frac{3M[\eta]}{4\pi N_A \phi(\sigma)} \right)^{1/3} \quad (21)$$

where  $[\eta]$  has the units  $\text{cm}^3/\text{g}$ , and the function  $\phi(\sigma)$  accounts for the permeability of the equivalent sphere and depends on the Mark-Houwink exponent. When the solvent and polymer do not interact strongly, the polymer only slightly inhibits the flow of the solvent through the polymer coil, with the

result that the average velocity of the solvent differs from that of the polymer coil. Kirkwood and Riseman model the polymer chain as a "pearl necklace" where the frictional resistance of the polymer was concentrated in beads spaced along a completely flexible polymer backbone, and expressed the hydrodynamic interaction between beads given with the Oseen tensor. Their result is:

$$\langle r^2 \rangle^{1/2} (\text{cm}) = \left[ \frac{36M[\eta]}{N_A \sqrt{6\pi^3} X F(X)} \right]^{1/3} \quad (22)$$

where the intrinsic viscosity has the units  $\text{cm}^3/\text{g}$ ,  $X$  is the "draining parameter" found from the Mark-Houwink exponent, and the function  $F(X)$  is given in the revised tables of Kurata and Yamakawa.<sup>43</sup> Peterlin modeled the polymer as a random coil that had a high segment density at its center that partially immobilized the solvent. His result for the root mean square end-to-end distance is:

$$\langle r^2 \rangle^{1/2} (\text{cm}) = 1.21 \times 10^{-8} \left[ \frac{[\eta]M}{(1-a)} \right]^{1/3} \quad (23)$$

where "a" is the Mark-Houwink exponent, and the intrinsic viscosity has units of  $\text{cm}^3/\text{g}$ . Table IV compares the root mean square end-to-end distances calculated by these theories to those determined by experiment (i.e., the Kurata-Stockmayer and

Stockmayer–Fixman analyses). Although the models have various deficiencies and simulate the polymer coil with varying degrees of realism,<sup>14,25</sup> the dimensions calculated from them agree fairly well with those calculated from the extrapolation equations. The draining characteristics of the polymer coils calculated from these models are small; thus, all of the theories indicate a large degree of solvent inhibition by the polymer backbone in solution.

### Thermodynamic Parameters

The second virial coefficient, Flory theta temperature, and the enthalpy and entropy of dilution parameters quantify the degree of polymer–solvent interaction. For solutions of model associative polymers, Ballard et al.<sup>44</sup> modified Flory–Fox theory<sup>27</sup> to account for the effects of association on these parameters by including a term in the free energy due to association  $\Delta F_{\text{association}}$ :

$$\Delta F = \Delta F_{el} + \sum_{j \text{ segments}} \Delta F_m + \Delta F_{\text{association}} \quad (24)$$

$\Delta F_{el}$  and  $\Delta F_m$  are calculated from the Flory's familiar expressions. To derive an expression for contribution of association to the overall free energy, Ballard et al. assumed that the kinetics of association followed:



where  $m$  and  $d$  represent monomers and dimers, respectively. The equilibrium constant for this physical reaction is given by:

$$K_A = [d]/[m]^2 \quad (26)$$

and is related to the standard molar free energy of association  $\Delta F_a^\circ$  through:

$$\Delta F_a^\circ = -RT \ln K_A \quad (27)$$

By assuming dilute conditions, which are valid for small degrees of association, and by assuming that the polymers coils are Gaussian, they derived the contribution of association to the overall free energy:

$$\Delta F_{\text{association}} = -2kTC_m(d_p^2 V_1 f^2 K_A \ln K_A/m_s^2)M^{1/2}\alpha^{-3} \quad (28)$$

where  $k$  is Boltzmann's constant,  $C_m$  is given by eq. (14),  $d_p$  is the density of the polymer, and  $f$  is the

mol fraction of hydrophobes in the associative polymer. When eq. (28) is substituted into eq. (30) along with Flory's expressions for  $\Delta F_{el}$  and  $\Delta F_m$ , the results are:

$$\begin{aligned} \alpha^5 - \alpha^3/M^{1/2} \\ = 2C_m(\psi_1 - \Theta/T - f^2 d_p^2 V_1 K_A \ln K_A/m_s^2) \end{aligned} \quad (29)$$

which reduces to the Flory swelling equation when no association is present.

Equation (29) states that association, as reflected in positive values of  $K_A$ , actually decreases the dimensions of the polymer coil. As discussed previously, this is ostensibly due to intramolecular association. A plot of  $\alpha^5 - \alpha^3/\sqrt{M}$  against  $1/T$  should then produce a family of parallel lines with equal slopes that are proportional to the Flory theta temperature and with intercepts that decrease as the free energy of association increases. Although the quantity  $\alpha^5 - \alpha^3/\sqrt{M}$  should not depend on molecular weight, it is well known that it does because of the approximate nature of the Flory swelling equation.<sup>25</sup> For the model-associative polymers,  $\alpha^5 - \alpha^3/\sqrt{M}$  passes through a maximum in the middle of the molecular weight series. Hence, when we plot the results for our model polymers according to eq. (31) in Figure 10, we use the average value of  $(\alpha^5 - \alpha^3/\sqrt{M})$  that is obtained from the series of molecular weights for a given alkyl end group. The error bars in Figure 10 mark the extremes of the values used to obtain this average. It is not clear in Figure 10 that the length of the alkyl end group has made any difference at all.

If the data are regressed separately by hydrophobe type, what results are lines that have nearly the same intercepts and slopes that depend on the length of

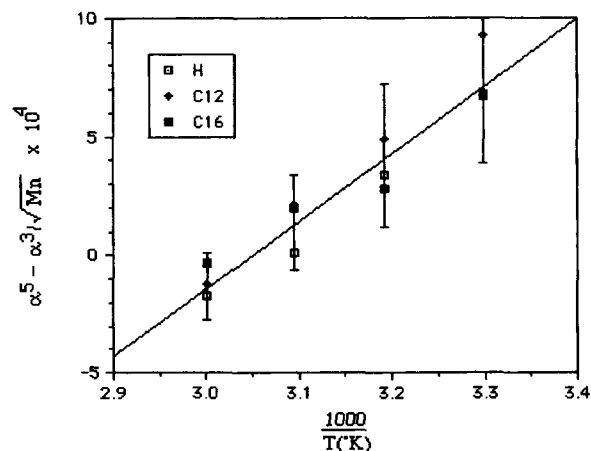


Figure 10 Flory–Fox plot for model-associative polymers in water.

the alkyl end group. This suggests that the equilibrium constant for association depends on temperature,  $K_A = F(T)$ . In classical thermodynamics, the Gibbs–Helmholtz equation expresses the effect of temperature on an equilibrium reaction:

$$\frac{\partial \left[ \frac{\Delta F_a^\circ}{T} \right]}{\partial T} = -R \frac{\partial \ln K_A}{T} = -\frac{\Delta H_A}{T^2} \quad (30)$$

where  $\Delta H_A$  is the standard enthalpy of reaction: it is negative for an exothermic reaction and positive for an endothermic reaction. Substitution of eq. (30) into Ballard's analysis results in:

$$\alpha^5 - \alpha^3/M^{1/2} = 2C_m \left[ \psi_1 - \Theta/T + \frac{f^2 V_1}{v_2^2 m_s^2} \frac{\Delta H_A}{RT} e^{-\Delta H_A/RT} \right] \quad (31)$$

If the standard enthalpy of the association reaction is small, and the exponential can be approximated by its Taylor series, then a plot of eq. (31) should produce a line whose slope depends on the standard enthalpy of association. If the enthalpy of association is larger, then a curve results. Like Ballard's equation, eq. (31) indicates that the standard enthalpy of association is negative, and the association is, therefore, spontaneous, the effect of association is to contract the dimensions of the polymer coil. Equation (31) can be considered the generalization of Ballard's equation to include the effect of temperature on the distribution of aggregates at equilibrium in solution.

Unfortunately, it is difficult to unambiguously distinguish between the various data for polymers with different termini in Figure 10 because the polymers have broad molecular weight distributions. We are, thus, resigned to the fact that the equations described above must be applied to well-fractionated samples before they can produce a precise analysis of effect of hydrophobe on dilute solution thermodynamics. In addition, eq. (19) asserts that the free energy of association and, hence,  $K_A$  depends both on concentration and temperature so that it might be difficult to measure the free energy of association from data obtained from extrapolation to infinite dilution. As elegant as Ballard's analysis is, we must look elsewhere for a means to estimate free energy of association.

In the meantime, we settle for a semiquantitative evaluation of the enthalpy and entropy of dilution parameters from classical Flory–Fox analysis, which means that we set  $\Delta H_A$  in eq. (31) to zero, and draw

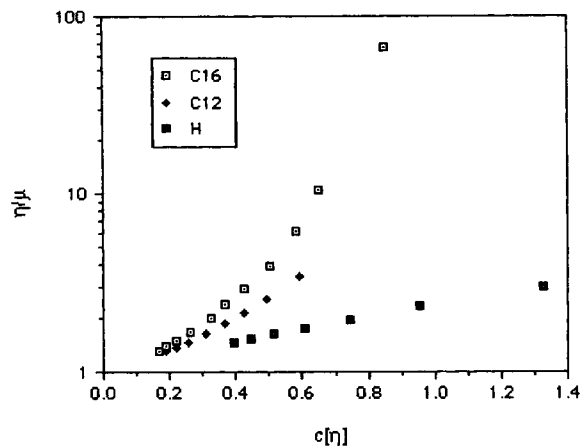
a single line of best fit through all of the data in Figure 10. This assumption does not affect the signs on the enthalpy and entropy of dilution parameters that we calculate. Due to the assumptions made in the Flory–Fox theory, the absolute values of the enthalpy and entropy of dilution parameters may differ in absolute magnitude from those obtained by osmotic pressure or light-scattering measurements. However, as pointed out by Flory and Fox,<sup>27</sup> the relative contributions of  $\psi_1$  and  $\kappa_1$  to the thermodynamic interactions between polymer and solvent are correct. The slope of the line in Figure 10 equals  $-2C_m\psi_1\Theta$ , and its intercept equals  $2C_m\psi_1$ . Because the slope of the line is positive, and because  $\Theta$  is positive, the entropy of dilution parameter  $\psi_1$  is negative. Although a negative entropy of dilution parameter is opposite in sign to those of most polymer–solvent systems, it is typical of water-soluble polymers, and of poly(oxyethylene).<sup>21</sup> The negative entropy of dilution parameter results from orientation effects produced by the hydrogen bonding between water molecules and the ether oxygens in the model polymer backbone,<sup>25</sup> and indicates that the dissolved polymer shrinks on heating. This was observed as a decrease in the intrinsic viscosities of the model-associative polymers on heating, as was presented in Figure 4. Calculation of a numerical value for the entropy of dilution parameter from the line in Figure 10 requires a numerical value for the partial specific volume of the model polymers so that  $C_m$  can be calculated from eq. (14). Although this is unknown at present, it can be estimated because the model polymers have a composition similar to poly(oxyethylene), which has  $\nu_2 = 0.846$ .<sup>32</sup> The partial specific volume should not vary appreciably from this value, and the values of  $\psi_1$  and  $\kappa_1$  relative to each other are not affected by this assumption. The enthalpy and entropy of dilution parameter for the model-associative polymers estimated in this manner are  $164/T(^{\circ}K)$  and  $-0.5$ , respectively.

Because  $K_\theta$  does not depend on temperature, the slopes of the lines in Figures 7 through 9 are proportional to  $(\frac{1}{2}-\chi)$ ,<sup>25</sup> and the Flory equation can be used to determine  $\Theta$ :

$$B(T) = B_o[1 - \Theta/T] \quad (32)$$

where absolute temperature is used. As shown in Table IV, these values of the theta temperature agree well with those obtained from interpolation of the exponent in the Mark–Houwink equation as a function of temperature (Table II), and with that obtained from the slope of the line in Figure 10.  $B_o$  is negative because the model-associative polymers form irregular solutions with water, as demonstrated





**Figure 11** Influence of the length of the alkyl end group on the relative viscosity of model-associative polymers with a number average molecular weight of 51,000 in water at 30°C.

by the negative enthalpy and entropy of dilution parameters. Because  $\psi_1$  is negative, the Flory–Huggins interaction parameter:

$$\chi = \frac{1}{2} + \psi_1[\Theta/T - 1] \quad (33)$$

is less than  $\frac{1}{2}$  for  $T < \Theta$ , which confirms that water at room temperature is a good solvent for the model-associative polymers. This also means that the chemical potential of the solvent in the polymer volume element  $\mu_1$  is less than that of pure liquid water  $\mu_1^0$  for  $T < \Theta$ , as shown by the excess chemical potential of the solvent:

$$(\mu_1 - \mu_1^0)E = -RT\psi_1(1 - \Theta/T) \quad (34)$$

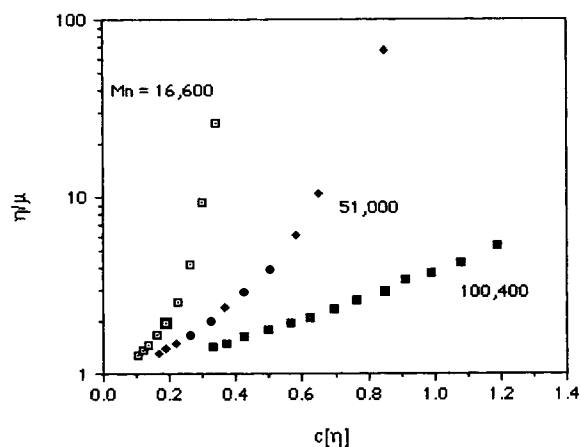
Thus, water swells the model polymer at room temperature in response to a chemical potential gradient. As temperature increases, an increase in the excess entropy of mixing compensates for the favorable enthalpy of mixing, which reduces the chemical potential gradient and dehydrates the polymer backbone. This indicates that the solvent quality decreases as temperature increases.

Our conclusion from this discussion is that either the interactions between the alkyl hydrophobic end groups do not alter the behavior of the associative polymers at infinite dilution enough to invalidate using the classical Flory–Fox analysis, or that the molecular weight distributions of the samples prevent us from seeing such effects. In any event, we must consider a different analysis that accounts for the increase in free energy of association with concentration before we can estimate the free energy of association among the hydrophobic groups in dilute solution.

## Kinetic Model

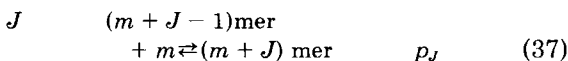
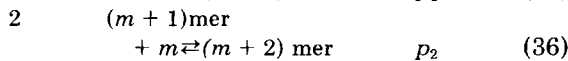
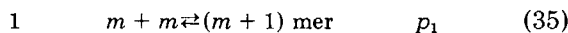
In view of the difficulties in the analysis presented in the previous section on determining the influence of the free energy of association on the viscosity of a dilute solution of associative polymer, eq. (19) and the data in Figures 11 and 12 inspire us to estimate free energy of association by examining the influence of length of the alkyl end group (Fig. 11) and molecular weight of the model polymer (Fig. 12) on the concentration dependence of the relative viscosity. It is self-evident that the differences in the viscosity–concentration curves for the hydroxyl terminated polymers and the hexadecyl and dodecyl terminated polymers must result from an association among the alkyl end groups. This was discussed in a previous section of this chapter in terms of the influence of associative polymer structure on the Huggins parameter  $K'$ . The results of that section indicated that the driving force for association increased as the length of the alkyl end group increased and as the molecular weight of the associative polymer decreased. The association built up a pseudohigh molecular weight in solution, which resulted in a large value for the Huggins parameter and a sharp increase in the relative viscosity with concentration. From these ideas, we build a physical model for the concentration dependence of the relative viscosity.

Like Ballard et al., we model the reaction kinetics of the association process as a reversible equilibrium step polymerization in a closed reaction vessel. Thus, the reaction scheme is:



**Figure 12** Influence of molecular weight on the relative viscosity of hexadecyl-terminated model-associative polymers in water at 30°C.

Reaction Number	Reaction	Extent of Reaction
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which may be written in general form as:

$$n = 1 \cdots J \quad (n-1) \text{ mer} + m \rightleftharpoons (n) \text{ mer} \quad (38)$$

where "m" denotes an unassociated polymer. These equations are general up to any arbitrary number of association reactions  $n = J$ . In this section, the notation "monomer" refers to the unaggregated associative polymer, and "dimer," "trimer," "n-mer," etc., refer to aggregate composed of two, three, and  $n$  associative polymer chains. Weissberg et al.<sup>45</sup> have taken a similar approach in modeling the influence of aggregation of polymers on the concentration dependence of the relative viscosities of dilution solutions, although they restricted their reaction kinetics to dimer and trimers, and the context of our model is different. It is not difficult to show that reactions like dimer + dimer, or dimer + trimer, are simply linear combinations of eqs. (35) to (38), and are, therefore, not needed to completely describe the association process. Our model also differs from the model developed by Bieleman et al. in that we do not assume the existence of a micellar network in solution,<sup>46</sup> an assumption that applies better to more concentrated solutions.

The equilibrium constants for the reactions expressed by eqs. (35) through (38) are given by:

$$K_1^* = \frac{[(m+1) \text{ mer}]}{[m]^2} \quad (39)$$

$$K_n^* = \frac{[(m+n) \text{ mer}]}{[m][(m+n-1) \text{ mer}]}, \quad n = 2 \cdots J \quad (40)$$

The equilibrium constant depends on the standard molar free energy of association, as was given before in eq. (27), and on the molecular weight of the growing aggregate because it is more difficult for the aggregate to diffuse and participate in the reaction. We model the relationship between the size of a polymer in dilute solution and the diffusion coefficient with Hookean dumbbell of polymer kinetic theory:

$$D_{\text{Aggregate}} = \frac{\langle r^2 \rangle_0 N_A k T}{M} \frac{1}{6\mu [\eta]} = \left( \frac{K_\theta}{\Phi} \right)^{2/3} \frac{N_A k T}{6\mu} \frac{1}{K_{\text{MH}} M^a} \quad (41)$$

where the molecular weight used in eq. (2.41) is the molecular weight of the aggregate. Here, we make the physically reasonable and intuitive assumption that the association reaction is diffusion limited so that the equilibrium constants depend on molecular weight in the same way. Thus, Brownian processes build up a dynamic network that can never grow to infinite extent unless the free energy of association is infinite.

A mass balance on the associative polymer in solution yields:

$$[m] = [m]_I - p_1[m]_I - p_2[m]_I - \cdots - p_J[m]_I = [m]_I \left( 1 - \sum_{L=1}^J p_L \right) \quad (42)$$

$$[(m+n) \text{ mer}] = p_n [m]_I \quad (43)$$

$$[(m+n-1) \text{ mer}] = p_{n-1} [m]_I - p_n [m]_I \quad (44)$$

where  $p_i$  is the extent of reaction  $i$ , and  $[m]_I$  is the initial molar concentration of unassociated polymers. Combining these mass balances with the reaction kinetics given in eqs. (39) and (40) yields:

$$K_1^* = \frac{p_1}{m_I \left( 1 - \sum_{L=1}^J p_L \right)^2} \quad (45)$$

$$K_n^* = \frac{p_n}{[m]_I \left( 1 - \sum_{L=1}^J p_L \right) (p_{n-1} - p_n)}, \quad n = 2 \cdots J \quad (46)$$

Thus, if the equilibrium constants are known from the free energy of association, the extent of reaction and the distribution of species in solution can be calculated.

Equations (45) and (46) represent  $J$ -coupled nonlinear algebraic equations:

$$1 - 2 \sum_{L=1}^J p_L + \sum_{L=1}^J p_L \sum_{L=1}^J p_L - \frac{p_1}{K_1^* [m]_I} = 0 \quad n = 1 \quad (47)$$

$$p_n \sum_{L=1}^J p_L - p_n - \frac{p_n}{K_n^* [m]_I} - p_{n-1} \sum_{L=1}^J p_L + p_{n-1} = 0 \quad n = 2 \cdots J \quad (48)$$

which we solved numerically via the Newton–Raphson method elsewhere.<sup>12</sup> Note that increasing the initial concentration of unassociated polymers in solution has the same effect as increasing the free energy of association; increasing either drives the equilibrium reaction toward completion.

Once the extents of reaction have been calculated, the mole fractions  $Y_n$ , where the  $n$  represents the product of the  $n$ th reaction, are calculated from:

$$Y_0 = \frac{1 - \sum_{L=1}^J \frac{P_L}{J}}{1 - \sum_{L=2}^J \frac{P_L}{J}}; \quad Y_1 = \frac{P_1 - P_2}{1 - \sum_{L=2}^J \frac{P_L}{J}};$$

$$Y_{J-1} = \frac{P_{J-1} - P_J}{1 - \sum_{L=2}^J \frac{P_L}{J}}; \quad Y_J = \frac{P_J}{1 - \sum_{L=2}^J \frac{P_L}{J}} \quad (49)$$

where  $Y_0$  is the mole fraction of unassociated polymer. The number average and weight average molecular weights of the distribution are then calculated from:

$$\frac{\langle M \rangle_n}{M_0} = \frac{\sum_{i=0}^J Y_i (i+1)}{\sum_{i=0}^J Y_i};$$

$$\frac{\langle M \rangle_w}{M_0} = \frac{\sum_{i=0}^J Y_i (i+1)^2}{\sum_{i=0}^J Y_i (i+1)} \quad (50)$$

where  $M_0$  is the molecular weight of the unassociated polymer. The ratio of the number average molecular weight to the molecular weight of the unassociated polymer is also the average number of associations in the solution. The total free energy from the association process can simply be calculated from the product of number average of associations and the free energy change for one association given by eq. (27).

The next step is to relate the distribution of aggregate sizes to solution viscosity. Because no analytical theory is available for this, we use the corresponding states principles developed in eq. (4). Here, we assume that the hydrodynamic volume of a dimer composed of two monomers of molecular weight  $M_0$  is the same as a single monomer of molecular weight  $2M_0$ . This neglects branching in the network, and does not account for the functionality of the network junction; however, we can relax this assumption momentarily. This assumption also im-

plies that the enhancement in solution viscosity comes completely from individual clusters that grow as concentration increases, and does not consider the interactions that occur between aggregates. This is a serious flaw, but there is no easy way to mathematically incorporate these interactions into the model. Thus, we can expect no more than qualitative agreement with the data. With this assumption, we can calculate the effective intrinsic viscosity of the aggregate from the Mark–Houwink equation, and then calculate the relative viscosity of the solution from:

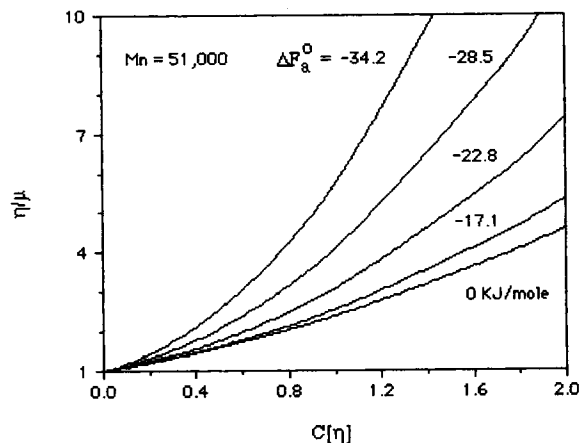
$$\frac{\eta}{\mu} = 1 + c[\eta]_{\text{effective}} + K'c^2[\eta]_{\text{effective}}^2 + \dots \quad (51)$$

where  $[\eta]_{\text{effective}}$  equals:

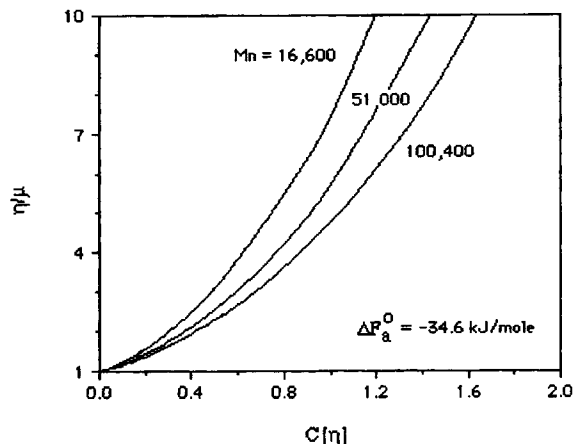
$$[\eta]_{\text{effective}} = K_{\text{MH}} M_0^a \sum_{i=0}^J Y_i I^a \quad (52)$$

Thus, we can calculate how viscosity–concentration relationship for associative polymers in dilute solution varies with the free energy of association.

Figures 13 and 14 show the effect of varying the free energy of association and the molecular weight of the unassociated polymer on the viscosity–concentration relationships calculated by the model. As the free energy of association increases, the number average molecular weight of the aggregated species in solution grows to larger and larger values, which results in a solution viscosity that increases sharply as concentration increases. Here we have used free energies that are comparable to the free energy of micellization of nonionic surfactants. When the free



**Figure 13** Influence of the free energy of association [eq. (2.29)] on the kinetic model's viscosity–concentration relationship of associative polymers with a number average molecular weight of 51,000.



**Figure 14** Influence of molecular weight on the kinetic model's viscosity-concentration relationship of associative polymers with a free energy of association of  $-34.6$  kJ/mol.

energy of association is zero, the model follows the Huggins equation, and when the free energy of association is nonzero, the viscosity-concentration relationship becomes more dramatic. For a fixed free energy of association, the viscosities of solutions that contain small molecular weight associative polymers are more sensitive to changes in concentration than are solutions that contain large molecular weight associative polymers. Both effects mimic experimental data, where the unmodified polymer followed the Huggins equation, and the hydrophobically modified polymers had large values of  $K'$  that depended on lengths of both the associative polymer backbone and the alkyl end groups. Thus, the model indicates that the free energy of association of the model-associative polymers increases as molecular weight decreases, and as the length of the hydrophobic end group increases.

Although the qualitative agreement between the model and the data is pleasing, the model has neglected many things. First, it has neglected the influence branching on the hydrodynamic resistance of the aggregate. As shown by Zimm and Stockmayer,<sup>47</sup> branched macromolecules have a higher average segment density than linear macromolecules of the same molecular weight, and, therefore, have a lower coil volume. The effect of branching on the chain dimensions is expressed by:

$$\frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}} = g^{*3/2} = \frac{\langle r^2 \rangle_{\text{branched}}}{\langle r^2 \rangle_{\text{linear}}} \quad (53)$$

where  $g^*$  depends on the functionality and number of the branching sites. For example, for a polymer with tetrafunctional branches,  $g^*$  is:

$$g_4^* = (1/n_w)\ln(1 + n_w) \quad (54)$$

where  $n_w$  is the number of branch points per molecule by weight. Thus, the resistance of a branched polymer in solution is less than the resistance of an unbranched polymer of similar molecular weight. When eqs. (53) and (54) are used in the model, the growth in the viscosity tapers off at large concentrations. This was observed experimentally, where the rate of increase of the viscosity enhancement by the associative polymer tapers off at large concentrations.<sup>10</sup> Second, the model neglects polydispersity in the unassociated polymers. Third, the model has assumed that the aggregates are like unassociated polymers in that they assume a spherical or Gaussian segment distribution in solution. It does not consider that the aggregates might be nonspherical in shape. Fourth, the current model also neglects the increase of the local viscosity on the diffusion of the growing aggregates. The effect would be to retard the growth of the aggregate, and we can account for this by using the local solution viscosity in eq. (41) rather than the solvent viscosity. This effect will keep the aggregate from growing into an infinite cluster, and causes the viscosity enhancement to taper off at large concentrations. Hence, concentrated solutions of associative polymer are not true gels, although they are gel-like. These effects are better probed through rheology.<sup>10</sup>

We have also neglected interactions between neighboring aggregates, which should build a network that has striking rheological properties. At a certain critical concentration between one-half and 1 wt %, solutions of associative polymers exhibit remarkable and strongly non-Newtonian rheologies; these solution rheologies are best and most naturally interpreted and modeled with network theories.<sup>12</sup> So it is not surprising that although the model predicts a sharper increase in the solution viscosity as concentration, the experimental data exhibit an even larger viscosity enhancement than the model can predict using the values we have used for the free energy of association. Thus, much of the enhancement in viscosity in the data must be due to multibody interactions between aggregates.

In short, we have constructed a physical model for viscosity-concentration relationship of dilute associative polymer solutions that is based on equilibrium kinetics of association. Because we are unaware of any theory that has been derived from fundamental origins on how solution viscosity relates to associative polymer structure, we have used a principle from corresponding states to connect molecular weight to occupied volume to viscosity. The

model incorporates the effects of diffusion and branching of the aggregates through physically reasonable, but somewhat ad hoc, assumptions. The most serious shortcomings in the model as it now stands are its inability to account for multibody interactions among aggregates, and its inability to predict the formation of a coherent network. When these features are introduced into the model, it should represent the data better. Nonetheless, the model does correctly predict the qualitative influence of the structure of the associative polymer on the viscosity-concentration relationship in dilute solution.

## CONCLUSIONS

Analysis of the data presented here has yielded some useful information, even if some of it is semiquantitative because of the polydispersity of the model-associative polymer samples. We have measured the signs and relative magnitudes of heat and entropy of dilution, and have demonstrated that water-miscible cosolvents can disrupt the networking behavior of associative polymers by modifying the solubility characteristics of the solvent. This has allowed us to verify the molecular weights of the model polymers, and to prove that the dramatic enhancement of solution viscosity by associative polymers, and the dependence this enhancement on polymer structure, are due to association behavior. We have constructed a physical model based on equilibrium kinetics for the association process, and have used it to monitor how the free energy of association influences the distribution of aggregates in solution. Although the model neglects some important features, and is, therefore, only qualitative, it does exhibit the correct dependence of viscosity on molecular weight and concentration, and indicates that the free energy of association must become larger as the length of the alkyl end groups becomes larger relative to the hydrophilic backbone. Combination of these results with those obtained from dynamic light-scattering measurements will provide complementary characterizations of the associative polymer in dilute solution.

Because some of the analysis presented in the chapter depends on having samples of monodisperse polymers of known molecular weight, it can be improved by fractionating the model-associative polymer sample. This can be achieved either through dialysis or through precipitation of the associative polymer from benzene with isooctane.<sup>38</sup>

Setting questions on polydispersity aside, the dilute solution viscosity behavior shows that once the

concentration of associative polymer exceeds the overlap concentration, water excludes the hydrophobes from solution to form a hydrophobic domain. This concentration is less than the coil overlap concentration. This congregation of hydrophobes, which we call an association cluster, consists of the approximate aggregation of two or more hydrophobes from different model polymers to form an association network. The three-dimensional shear sensitive association network increases the apparent molecular weight of the associative polymer in solution to enhance rheological properties.

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