Macromolecules **1995**, *28*, 160−164

Analytic Structure of the Solutionlike−Meltlike Transition in Polymer Dynamics

George D. J. Phillies* and Carol Ann Quinlan

Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Received March 16, 1994; Revised Manuscript Received October 7, 1994[⊗]

ABSTRACT: Solutions of some very-high-molecular-weight polymers exhibit a solutionlike−meltlike rheological transition—a crossover from a lower-concentration stretched-exponential regime ($\eta \sim \exp(\alpha c^{\nu})$) to a high-concentration power-law ($\eta \sim c^{x}$) regime at large concentration c. We report a detailed study of this transition for (hydroxypropyl)cellulose:water, with extensive sets of measurements in both concentration regimes and in the transition region. The transition between regimes is extremely sharp. Our experimental data are sufficiently fine-grained as to allow us to confirm the hitherto-untested result that η is analytic (i.e., the logarithmic derivative $\partial \log(\eta)/\partial \log(c)$ is continuous) through the transition.

Introduction

A current theme in polymer physical chemistry is the search for an adequate model of polymer dynamics in solution. A correct, complete model would yield transport coefficients as functions of polymer concentration c, polymer molecular weight M, and detailed chain properties, without requiring empirical prefactors, adjustable parameters, or restrictions to asymptotic validity. A wide variety of treatments of polymer dynamics, most incomplete or approximate, are found in the literature; Skolnick and Kolinski[1] provide an extensive review.

Models of polymer solution dynamics have been extensively tested by examining how transport coefficients are affected by c, M, chain architecture, and solvent quality. A model-free reanalysis of the published literature[2,3] shows that the polymer self-diffusion coefficient D and the shear viscosity η usually follow stretched-exponential forms

$$D = D_0 \exp(-\alpha c^{\nu}) \qquad (1)$$

and

$$\eta = \eta_0 \exp(\alpha c^{\nu} M^{\gamma}) \qquad (2)$$

for polymer concentrations ranging from the highly dilute to concentrations far above the nominal[4] chain overlap concentration c^*. Here α is a scaling prefactor, ν and γ are scaling exponents, η_0 is the solvent viscosity, and D_0 is approximately the diffusion coefficient of an isolated chain.

A derivation of eq 1 from a semimicroscopic (Kirkwood−Riseman[5] level) model of polymer solutions, including quantitative estimates of the scaling exponents ν and γ and scaling prefactor α, has been given previously.[6] The calculated dependences of α and ν on M are in good agreement with experiment. The derivation makes clear that the stretched-exponential concentration dependence of D should not persist to arbitrarily low polymer concentrations; some experimental data[7] exhibit low-c behavior consistent with this theoretical prediction.

On the other hand, in polymer melts η scales with polymer molecular weight as[4]

$$\eta = \bar{\eta}_M M^{\gamma} \qquad (3)$$

for $\gamma \in (3.2, 3.6)$. An apparent paradox lurks between eqs 2 and 3. As $M \rightarrow \infty$, a stretched exponential in M always grows more rapidly than a power law in M. Therefore, if eqs 2 and 3 remained valid out to sufficiently large M, one would find that the melt viscosity of a polymer was less than the viscosity of some of its solutions, contrary to reasonable expectations.

Furthermore, the semimicroscopic derivation of eq 1 involves polymer chains floating in a simple Newtonian fluid responsible for momentum transport. As the melt is approached, momentum transport is performed by the viscoelastic medium of the other polymer chains. With increasing chain concentration, the physical image underlying the derivation of eq 1 ceases to resemble reality. Consequently, it is reasonable to expect that with increasing chain concentration eqs 1 and 2 will be replaced with another behavior.

One of us[8] previously found that in some published data[9] the apparent paradox is potentially averted by a transition from low-concentration stretched-exponential behavior to high-concentration power-law

$$\eta = \bar{\eta} c^{x} \qquad (4)$$

behavior at some transition concentration c^{+}. The transition usually occurs at very large η (typically $\eta/\eta_0 > 10^3$) and M (typically $M > 1$ MDa). In some systems the transition is not seen.

We[8,10] have previously described these small- and large-concentration behaviors as "solutionlike" and "meltlike", respectively. We emphasize that these descriptors are *names* for regimes that are defined by eqs 2 and 4. Both regimes refer to polymers in solution; we do not claim that the meltlike regime is actually like a melt in any other sense. The solutionlike/meltlike descriptors were employed here (as opposed, e.g., to "semidilute" and "concentrated") in order that a reader can tag our phenomenological results without using terms already entangled in references to previously-proposed models.

As defined here, a system is phenomenologically in a solutionlike or meltlike regime if η follows eq 2 or 4, respectively, over an extended range of concentrations. It is important to distinguish data that actually follow eq 4 over an extended range of c from data having power-law curves as tangents. One can draw power-

---

* To whom correspondence should be addressed. E-mail: phillies@wpi.wpi.edu (Internet).

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

0024-9297/95/2228-0160$09.00/0

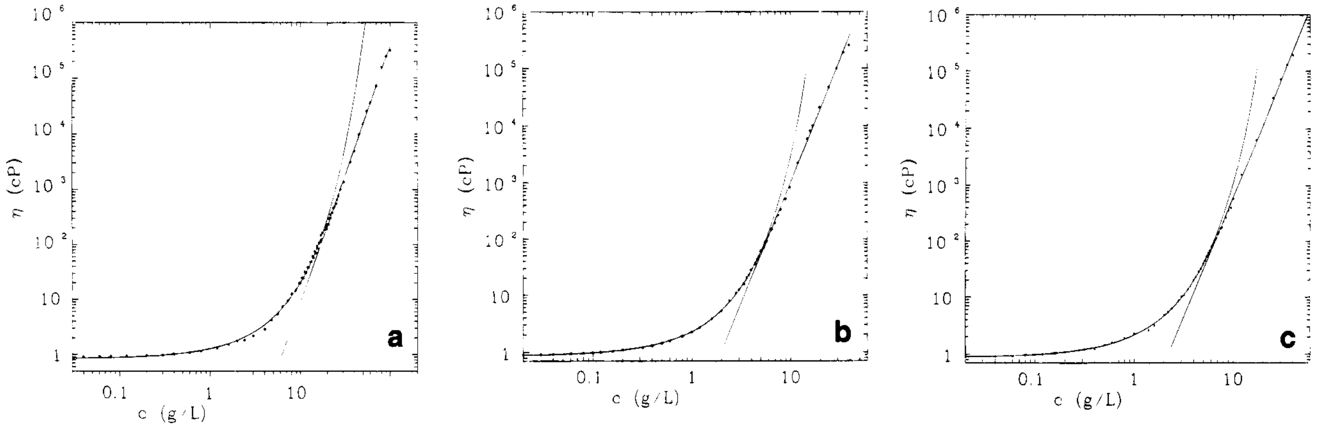

Figure 1. Shear viscosity η of (hydroxypropyl)cellulose:water against polymer concentration c at nominal polymer molecular weights of (a) 300 kDa, (b) 1 MDa, and (c) 1.15 MDa.

law tangents to solutionlike data, but these data are not in the meltlike regime. Most literature data on η refer to $c < c^+$; some exceptions are discussed below.

From previous work, the details of this transition remain unclear. Is the transition broad or narrow? Is the transition universal; for example, does it occur at a fixed $c[\eta]$, $[\eta]$ being the intrinsic viscosity? While one expects η to be continuous near c^+, it is theoretically interesting to ask if η is analytic through the transition. For example, one could inquire if $\partial\log(\eta)/\partial\log(c)$ or higher derivatives are continuous near c^+.

Here we report a study of the shear viscosity of (hydroxypropyl)cellulose (HPC):water. η of HPC solutions shows the transition at relatively small η, simplifying the task of covering wide ranges of c in both regimes. Unlike many previous studies, near c^+ our measurements are sufficiently densely spaced that we are able to examine the analytic structure—the continuity of $\partial\log(\eta)/\partial\log(c)$—near the transition. The following sections describe our experimental methods, the data and its analysis, a comparison with the literature, and our conclusions.

Experimental Section

We studied solutions of (hydroxypropyl)cellulose, a chemically-modified semirigid nonionic polymer remarkable for the unusually low viscosity ($\eta/\eta_0 \approx 10^2$) at which the solutionlike–meltlike transition occurs. Polymer samples had nominal M of 3×10^5, 1×10^6, and 1.15×10^6 Da. We have previously reported[10] probe diffusion, spectral lineshape studies, and preliminary measurements of η against c and M for the 3×10^5 and 1×10^6 Da polymers. Interpolating our previous data to 25 °C, we find $c^* \equiv 1/[\eta] \approx 2.4$ and 1.4 g/L, respectively, for the 3×10^5 and 1×10^6 Da polymers. Measurements of η reported here are much more closely spaced in c than were the previous measurements. In the previous paper, we were able to estimate c^+ but not to discuss the behavior of η near the transition.

Viscosities were obtained using Cannon-Fenske and Ostwald capillary viscometers mounted in a stirred temperature bath ($T = 25 \pm 0.1$ °C). Flow times were sufficiently long to avoid kinetic energy corrections. We checked for shear rate effects by studying the same sample with several different sizes of viscometer. When flow times were varied by a factor of 5, η changed only slightly; shear-thinning effects were not important in the c–M–flow rate conditions that we studied.

Viscosity Measurements

This section presents our experimental data. Figures 1a–c show η as a function of c for each polymer that we studied. Concentrations ranged from extreme dilution to c/c^* of 70 and 30, respectively, for the 3×10^5 and 1×10^6 Da polymers. η/η_0 ranged from 1.0 up to $\geq 1 \times 10^5$. Qualitatively, our measurements cover a regime where η is little different from the solvent viscosity, a regime where $\partial\log(\eta)/\partial\log(c)$ increases smoothly with increasing c, and a broad regime where (on a $\log(\eta)$–$\log(c)$ plot) the data are close to a straight line. It might have been possible, at least approximately, to superpose the three curves by choosing appropriate units for η and c. We elected not to do so because the number of data points for each polymer sample is already quite large (50–70 points).

Table 1. Fitting Parameters for the Viscosity of (Hydroxypropyl)cellulose:Water at 25 °C Using $\eta = \eta_0 \exp(\alpha c^\nu)$ for $c < c^+$ and $\eta = \bar{\eta} c^x$ for $c > c^+$[a]

			$c < c^+$				$c > c^+$	
M_w (MDa)	c^+ (g/L)	c_m (g/L)	η_0	α	ν	% RMSE	x	% RMSE
0.3	18	0.04	0.84	0.42	0.88	7.3	4.64	7.7
1.0	6	0.02	0.85	0.97	0.93	2.4	4.33	10.3
1.15	6	0.02	0.87	0.90	0.90	3.2	4.27	10.1

[a] % RMSE = root-mean-square fractional error in the fit, expressed as a percent. c_m is the lowest concentration at which η was measured.

Solid lines in Figures 1a–c represent stretched-exponential and power-law functions. The parameters that yield these lines were obtained from nonlinear least-squares fits. Data with $c < c^+$ were fit to eq 2, while data having $c > c^+$ were fit to eq 4. Low-concentration measurements are fit well by stretched exponentials (smooth curves); high-concentration data follow power laws (straight lines) accurately. On the scale of the figure, the lines very nearly pass through the points to which they were fit.

Table 1 reports optimal fitting parameters and other data for each polymer. The transition concentrations are substantially larger than the nominal overlap concentration $1/[\eta]$, so that $c^+[\eta] \approx 7$ or 4, respectively, for the two lower-molecular-weight chains. The stretched-exponential parameter α increases markedly with increasing M, but ν is independent of M. The power-law exponent x is in the range 4.3–4.6. RMS fractional errors are in the range 2–10%.

The validity of our fitting procedure may be judged from Figure 1. At small c, the stretched exponential fits the data well. Above c^+, the smooth curve representing eq 2 soon deviates substantially from the measurements. Similarly, at large c $\log(\eta)$ is linear in $\log(c)$. The data deviate substantially from this linear

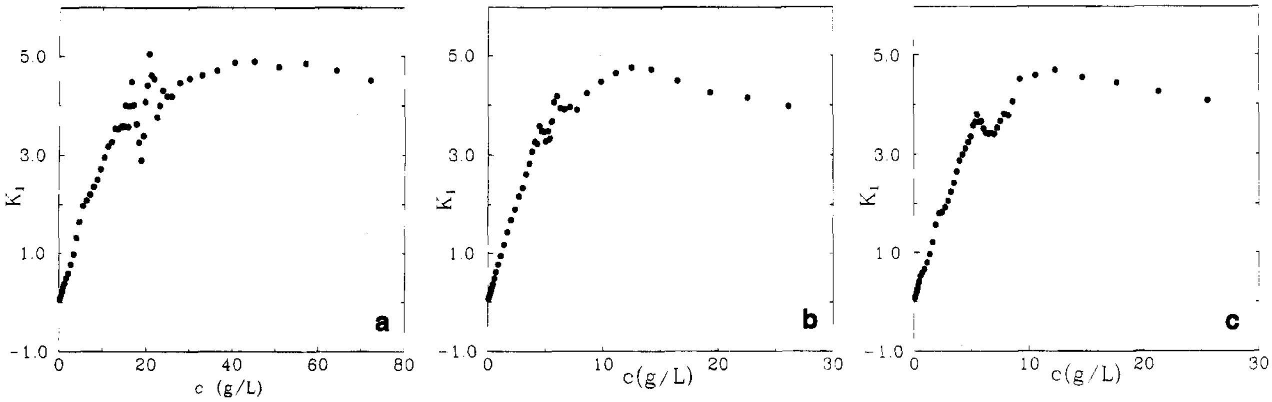

Figure 2. Local numerical derivatives $K_1 = \partial\log(\eta)/\partial\log(c)$ based on Figure 1. Nominal polymer molecular weights are (a) 300 kDa, (b) 1 MDa, and (c) 1.15 MDa.

(i.e., power-law) behavior at concentrations even moderately below c^+.

The quality of the fits and the exact value obtained for each fitting parameter depend on the choice of the transition concentration c^+. A good approximate choice can be obtained by inspection. To identify the optimal c^+, we systematically varied c^+ and computed the total RMS fractional error while fitting points with $c < c^+$ to eq 2 and points with $c > c^+$ to eq 4. The optimum c^+ was chosen to minimize the error. A fit of either function to a range of c significantly wider than the range used here drastically increases the total RMS fractional error.

At the transition concentration c^+ the stretched-exponential and power-law curves are very nearly tangent, a small gap or bridge marginally being visible between the curves. The transition regime between solutionlike and meltlike behaviors is extremely narrow. If one identifies the transition regime with the visible gap between the two curves, the width δc of the transition satisfies $\delta c/c \leq 0.05$.

Analytic Structure of η

This section considers the analytic structure, i.e., the derivatives, of $\eta(c)$. Our procedure is to obtain the derivative with respect to c numerically and examine its behavior. The behavior of the derivative argues for the reality of the apparent transition at c^+; it also constrains the mathematical form of any theory that purports to explain meltlike and solutionlike behavior simultaneously.

Simple numerical derivatives of real data tend to be somewhat noisy. To reduce the noise, we took every set of seven adjoining data points (for N data points, there are $N - 6$ such sets), computed the average concentration $\bar{c}$ of the points, and fit each set of data points via linear least squares to

$$\log(\eta) = K_0 + K_1[\log(c) - \log(\bar{c})] + K_2[\log(c) - \log(\bar{c})]^2 \quad (5)$$

the K_i being the fitting parameters. K_1 is the numerical first logarithmic derivative of η at $\bar{c}$.

For the fitting process, pairs of points at virtually the same concentration were smoothed into a single point. Fits were made with the three K_i as free parameters and with $K_2 = 0$ forced, the former being used in the following discussion. Forcing $K_2 = 0$ increased the scatter in the points but had no obvious qualitative effects. We also tried fitting eq 5 to groups of five instead of seven adjoining points; this change simply increased the scatter in the fits.

K_1 from seven-point fits with K_2 a free parameter appears in Figures 2a–c. For $c < c^+$, K_1 increases sharply with c, rising linearly (in log(c)) from $K_1 \approx 0$ at $c \approx 0$ to $K_1 \approx 4$ near $c = c^+$. Above c^+, K_1 is approximately constant, as expected for data that follow eq 4.

It is reasonable to ask if Figures 1a–c actually show evidence for a transition at c^+ or if one could readily imagine a single function that would fit the entirety of the data. This question is implicitly answered by Figures 2a–c. From these figures, $\partial^2\log(\eta)/\partial\log(c)^2$ is a positive constant for $c < c^+$, is nearly zero for $c > c^+$, and near c^+ changes nearly impulsively from one value to the other. This sudden and dramatic change of slope is precisely the behavior seen in more familiar phase transitions (say, in c_p at a second-order transition), where at the boundary there is a sudden change from one value of c_p to another.

From Figures 2a–c, $\lim_{c\to c^+} K_1$ has the same value for $c < c^+$ and for $c > c^+$. The slope $\partial\eta/\partial c$ is therefore continuous across the solutionlike–meltlike transition.

In each system, there is some structure in $K_1(c)$ near c^+, corresponding to a narrow transition between solutionlike and meltlike behavior. The transition region is about twice as wide as the resolution (in c) of the numerical derivative procedure. Above c^+, K_1 is not quite constant. Above c^+, in all three systems K_1 first slightly overshoots the best-fit power-law slope x of Table 1 and then decreases slightly with increasing c. At the largest concentrations studied, K_1 is falling slowly with increasing c.

Discussion

Some previous studies of zero-shear viscosity observed phenomena similar to those that we have studied. In chronological order, Utracki and Simha[11] studied poly(dimethylsiloxane):penta(dimethylsiloxane) and polyisobutene:2,2,4-trimethylpentane, Lin and Phillies[12] studied non-neutralized poly(acrylic acid):water, Takahashi et al. studied poly(α-methylstyrenes)[13] and linear polystyrenes[14] in good, Θ, and poor solvents, Nemoto et al.[15,16] studied polystyrenes in dibutyl phthalate, and we[10] reported low-resolution (in c) measurements on HPC:water.

Utracki and Simha[11] observed two polymer:solvent systems over a wide range of molecular weights (up to 2.5×10^6 for the polyisobutenes) for volume fractions $\phi \in 0-1.00$. In the siloxane system, plots of $\log(\tilde{\eta}) = $ log-

($\eta_{sp}/c[\eta]$) against a reduced concentration $\log(\tilde{c})$ compress data over a range of M and c to nearly a single line. Utracki and Simha do not present a mathematical form for their data, but by inspection they obtain a smooth curve for $\tilde{c} < 60$ and a straight line (power-law behavior) for $\tilde{c} > 60$. In contrast, in polyisobutene solutions Utracki and Simha[11] found that their $\tilde{\eta}$ and $\tilde{c}$ variables do not reduce η to a single master curve. Furthermore, η for each polyisobutene lies on a smooth curve. Utracki and Simha present a straight line (on a log–log plot) that is tangent to parts of the $\log(\tilde{\eta})-\log(\tilde{c})$ curves of the polyisobutenes that they examined.

Lin and Phillies' work on poly(acrylic acid):water[12] anticipated results here and in Phillies et al.[10] in identifying a stretched exponential–power law transition between lower and higher concentrations. Their data are consistent with findings here in that (to within the resolution of their data) both η and $\partial\eta/\partial c$ are continuous through their transition concentration. However, non-neutralized, salt-free poly(weak acids) are reasonably expected to show odd behavior, so the significance of their observation was not recognized at the time of publication.

Takahashi et al.[13,14] report very extensive results on η of polystyrene and derivatives under a variety of solvent conditions. Peczak and Phillies[3] show that almost all of the findings of ref 13 on poly(α-methylstyrene) are in the solutionlike regime, with a few data points having $\eta \geq 10^5$ cP showing meltlike behavior. Reference 13 did test their data against power-law forms. Their $\log(\eta_R)-\log(c/c^*)$ plots for good, Θ, and poor conditions show that their data have local tangents of slopes matching particular models. However, from Takahashi et al.'s[13] Figures 1–3, a plot of $\log(\eta)$ against $\log(c)$ for poly(α-methylstyrenes) yields smooth curves, not (except for a few points at very large η) the straight lines seen in the true meltlike regime. Takahashi et al.'s data[13] are therefore almost entirely in the solutionlike regime. In contrast, Takahashi, Noda, and Nagasawa's[14] data on linear polystyrenes do show a clear transition to a meltlike regime at large c and M, with $\eta \sim c^x$ over a 10-fold range in concentration and 3000-fold range of η.

Nemoto et al.[15,16] report η as a function of M at two polymer concentrations. Upon reanalysis, their data are found to follow[8] a stretched exponential in M at low M and a power law in M at larger M. Nemoto et al.'s measurements do not test the concentration dependence of η, but their results are important for unifying different parts of the literature. Namely, it is often though not always found that $\tilde{\eta}$ is a universal function of $c[\eta]$; plotting η (in appropriate units) against $c[\eta]$ reduces data on multiple molecular weights of the same polymer to a single curve. As is well known $[\eta] \sim M^{\gamma}$. If η is a universal function of $c[\eta] \sim cM^{\gamma}$ and if η follows eq 2 below c^+ and eq 4 above c^+, then below c^+ η must follow a stretched exponential in M, while above c^+ η must follow a power law in M. These required dependences on M are previously the results found experimentally by Nemoto et al.[8,15,16] Nemoto et al.'s results on the M-dependence of η show how one can simultaneously have $c[\eta]$ as a frequent universal variable and also have a solutionlike–meltlike transition in the functional dependence of η on c.

There exists an extremely wide variety of theoretical models for treating η in polymer solutions. Some treatments[4] interpret polymer dynamics in terms of a low-concentration dilute regime and an intermediate-concentration semidilute regime, with fundamentally different physics dominating chain motion in the two regimes. The transition described here does show different physical behavior in the solutionlike and meltlike regimes, so c^+ in our data could reflect the onset of some type of overlapping chain behavior, either reptative (as in de Gennes's[4] treatment) or nonreptative (as in Skolnick et al.[17]).

The formation of a transient gel lattice, as hypothesized by some models, is a percolation transition. Percolation transitions are intrinsically sharp, so the sharp transition we find experimentally is consistent with the onset of transient lattice formation. The oft-heard assertion that rheological transitions must be extremely broad does not appear to be accompanied by rigorous supporting theoretical arguments.

It is noteworthy that we observe c^+ at a concentration $c^+[\eta]$ of 4–7. Takahashi et al.'s[14] data imply $c^+[\eta] \approx 10$. From Utracki and Simha's[11] data one infers a transition for polysiloxanes at $\tilde{c} \approx 60$. In terms of $c[\eta]$, the solutionlike–meltlike transition does not occur at a universal concentration in all solutions.

Several authors have proposed to interpret η of polymer solutions by means of renormalization group and related techniques.[18–21] These calculations all yield η in terms of a novel concentration variable related to c by an unknown constant. While details differ from calculation to calculation, in each case a plot of $\log(\eta_R)$ against $\log(c)$ reveals a smooth curve at all c. Power-law behavior is not obtained, except as an asymptote. It is possible that renormalization group calculations are limited to $c < c^+$, in which case numerical adjustment might bring renormalization results into phenomenological agreement with our data.

Shiwa et al.[18] explain very clearly why the renormalization approach cannot remain valid as the melt is approached, so the differences between our large-c data and renormalization group results are not necessarily a refutation of that approach to calculating η. However, even if one obtained fair *quantitative* agreement between renormalization calculations and our data above c^+, at the qualitative level of observing transitions in the functional dependence of η upon c the solutionlike–meltlike transition is apparently not being captured by calculations of this style. These calculations involve a variety of approximations; we do not claim that calculations using this approach are intrinsically incapable of yielding the experimental power-law concentration dependence. Shiwa et al.[18] did obtain the power-law asymptotes to their expression for η, but it is apparent from their calculation that these are true asymptotes, not a functional form to be found for c above some bounding value.

In the meltlike regime, we obtain slightly different values for x for the 300 kDa HPC than for the 1(+) MDa HPCs. It might appear that this difference could plausibly be explained by the wider concentration range studied with the 300 kDa polymer, at least if one expected the local value of x to increase with increasing c in the meltlike regime. However, K_1 of Figure 2 is the same variable as x. From Figures 2a–c, at large c the best-fit local K_1 declines with increasing c, so increasing the uppermost concentration at which x is determined will have the general effect of forcing down, not up, the x determined by fitting to the entire meltlike regime.

Conclusions

In conclusion, we made a high-resolution (in c) study of the rheological properties of HPC:water. Our measurements span 3 orders of magnitude in c and more than 5 orders of magnitude in η. The data show a region in which η unambiguously has stretched-exponential (solutionlike) behavior and a separate region in which η has power-law (meltlike) behavior.

At the transition concentration, both η and its first derivative $\partial \log(\eta)/\partial \log(c)$ are continuous. The mechanism responsible for the solutionlike–meltlike rheological transition preserves the analytic structure of $\eta(c)$. Any model that seeks to explain the observed transition must therefore predict, at least to first approximation, not only that η is a continuous function of c but also that $\partial\eta/\partial c$ is continuous. This requirement that η shows analytic behavior at the transition is a substantial constraint on allowable models.

The transition between concentration regimes is extremely narrow. The sharpness of the transition seen in Figure 1 contrasts with any assumption that rheological transitions between different concentration regimes should be broad.

Acknowledgment. The partial support of this work by the National Science Foundation under Grant DMR91-15639 is gratefully acknowledged. We are grateful to Aqualon Co., Wilmington, DE, for its generous gift of Klucel HF (hydroxypropyl)cellulose. We thank anonymous referees for interesting discussion.

References and Notes

(1) Skolnick, J.; Kolinksi, A. *Adv. Chem. Phys.* **1989**, *78*, 223.

(2) Phillies, G. D. J. *J. Phys. Chem.* **1989**, *93*, 5029.

(3) Phillies, G. D. J.; Peczak, P. *Macromolecules* **1988**, *21*, 214.

(4) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(5) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.

(6) Phillies, G. D. J. *Macromolecules* **1987**, *20*, 558; **1988**, *21*, 3101.

(7) Wheeler, L. M.; Lodge, T. P. *Macromolecules* **1989**, *22*, 3399.

(8) Phillies, G. D. J. *J. Phys. Chem.* **1992**, *96*, 10061.

(9) For full references to an extensive list, see ref 8.

(10) Phillies, G. D. J.; Richardson, C.; Quinlan, C. A.; Ren, S. Z. *Macromolecules* **1993**, *26*, 6849.

(11) Utracki, L. A.; Simha, R. *J. Rheol.* **1981**, *25*, 329.

(12) Lin, T.-H.; Phillies, G. D. J. *J. Colloid Interface Sci.* **1984**, *100*, 82.

(13) Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1002.

(14) Takahashi, Y.; Nodo, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 2220.

(15) Nemoto, N.; Kojima, T.; Inoue, T.; Kishine, M.; Hirayama, T.; Kurata, M. *Macromolecules* **1989**, *22*, 3793.

(16) Nemoto, N.; Kishine, M.; Inoue, T. *Macromolecules* **1991**, *24*, 1648.

(17) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1986**, *84*, 1922; **1987**, *86*, 7164, 7174.

(18) Shiwa, Y.; Oono, Y.; Baldwin, P. R. *Macromolecules* **1988**, *21*, 208.

(19) Stepanow, S.; Helmis, G. *Macromolecules* **1991**, *24*, 1408.

(20) Shiwa, Y. *J. Phys. II Fr.* **1991**, *1*, 1331.

(21) Nystrom, B. *Macromolecules* **1993**, *26*, 3784.

MA9410274