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Rheological and Rheooptical Studies of Shear-Thickening Polyacrylamide Solutions

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ABSTRACT: The shear-thickening behavior of partially hydrolyzed polyacrylamide (HPAM) solutions was investigated as a function of polymer concentration, solvent composition (glycerol/water ratio), temperature, and prior shear history. Delayed-step rheological and rheooptical methods were used to generate new insights into kinetic aspects of the shear-thickening process. When a critical shear rate is exceeded after an initial overshoot upon a start-up shear, a second slow growth in stress and flow birefringence is observed, and the solution achieves a higher shear viscosity. Delayed-step flow experiments support the existence of shear-induced interchain structures in the shear-thickening state. By varying the precritical flow history of the solution, we identify two stages of the shear-thickening mechanisms, i.e., chain stretching and disruption of preexisting network association, followed by convective buildup of the shear-thickened state. With increasing glycerol content, the critical shear rate first decreases and then the trend is reversed at a specific solvent composition where the solution shows a discontinuous change in its rheological properties. The relative viscosity at low shear rates and the critical shear rate both increase with temperature. These observations are interpreted to indicate that the solvent quality is poorer at higher glycerol contents and at higher temperatures.

Introduction

Rheopexy (or negative thixotropy) and shear-thickening behavior have been reported in associating polymer solutions since the 1950s.[1] Subsequently, it has emerged that such phenomena are one aspect of a broad range of unusual flow behavior involving flow-induced changes in solution structure, including flow-induced phase separation (i.e., demixing), crystallization, and flow-enhanced mixing.[2–8] Shear-thickening behavior of self-associating polymers in solution has continued to attract considerable attention over the past few years.[9–13] Despite such efforts, the molecular origin of shear thickening remains a subject of controversy. Two types of mechanisms have been proposed to account for the phenomenon. One picture involves shear-induced intermolecular bonding, first suggested by Eliassaf et al.[1] to explain the drastic increase in solution viscosity upon agitating a poly(methacrylic acid) (PMA) solution. It was argued that a shear flow can shift the balance between intra- and intermolecular bonding toward a greater amount of intermolecular cross-linking by hydrogen bonds between carboxyl groups on neighboring PMA chains. This interpretation was often adopted to account for rheopexy or shear-thickening behavior in other polymer solutions.[14–16] Another possible origin of shear thickening arises from the shear deformation of flexible coils to an extent that results in nonlinear retraction forces and in a higher shear stress due to the stiffening of the flow-stretched macromolecules.[17–21] This mechanism of coil stretch in sheared polymer solutions was also implicated in a recent study of a self-associating polyelectrolyte in solution, viz., partially hydrolyzed polyacrylamide (HPAM).[13]

Although the coil-stretch chain transformation has been observed in dilute polymer solutions under elongational flow,[22,23] whether such a transition can be induced by a simple shear flow remains unknown. Due to the rotational component of simple shear, a very large chain deformation is unlikely when the chain rotates with an angular velocity equal to half the shear rate $\dot{\gamma}$. Sophisticated rheooptical studies must be performed to evaluate the chain stretching as the origin of shear thickening in nonassociative polymer solutions. While interchain association seems to be a more common process leading to shear thickening in associating polymer solutions such as poly(methacrylic acid)[1] and sulfonated polystyrene in hydrocarbon solvents,[24] and hydrolyzed polyacrylamide[25] in aqueous media, there remains a need for further experimental study to more fully define the characteristic rheological behavior of these solutions.

In order to visualize the molecular processes leading to shear thickening in self-interacting polymer solutions, it is desirable to be able to vary the strength of segment–segment interactions within and between chains. For partially hydrolyzed polyacrylamide (HPAM), one can adjust the solvent quality and experimental temperature to change the affinity of the HPAM chains to one another and with respect to the solvent. In this paper, we will study the rheological and rheooptical properties of shear-thickening HPAM solutions as a function of the solvent composition (water plus glycerol) and temperature. We will show, based on a variety of experimental data, that chain stretching is important to produce a large amount of intermolecular association but is not directly the origin of shear thickening.

Experimental Section

Partially hydrolyzed polyacrylamide (HPAM) was purchased from Polyscience Inc. This water-soluble polymer is obtained by hydrolysis of polyacrylamide (PAM) with sodium hydroxide. According to the supplier, the molecular weight of the material is above 10 million. The degree of hydrolysis, defined as the number Y of carboxyl residues (COO^-) replacing the amide groups ($CONH_2$) (X) over the total number of the macromolecular residues $Y/(X + Y)$, is 40%. The solvent was a mixture of glycerol (from Fisher Scientific) and distilled water. The polymer powder was always first dissolved in water by gently mixing with a magnetic stirrer. About 10 ppm of sodium azide

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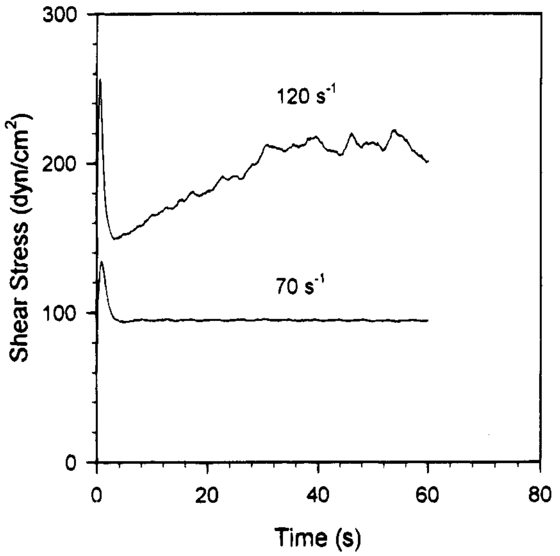

Figure 1. Time evolution of stress in a 0.08% by weight HPAM solution with 3% NaCl at $T = 25$ °C. The solvent is a water/glycerol mixture with 83% glycerol by weight.

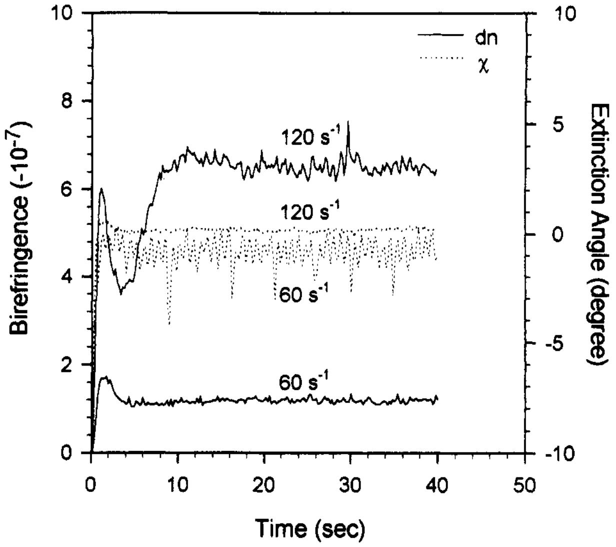

Figure 2. Time evolution of flow birefringence and extinction angle in a 0.08% by weight HPAM solution with 3% NaCl added at $T = 25$ °C. The solvent is a water/glycerol mixture with 81.5% glycerol by weight.

(NaN_3) was added to prevent possible bacterial degradation. Different amounts of sodium chloride were added to control the ionic strength. Weak stirring was maintained during dissolution for at least 1 day to assure the homogeneity of the solutions. Glycerol was added to the solution to control the quality of the solvent after the polymer was completely dissolved.

A Rheometrics fluid spectrometer RFS 8500 was employed to measure stress growth, steady-flow shear stress, and stress relaxation. We used cone and plate geometry with a 50 mm diameter and 0.02 rad cone angle to ensure a uniform shear rate throughout the sample. Rheooptical properties were measured with a Rheometrics optical analyzer (ROA) in a double Couette geometry. The light path length in the sample is 1.16 cm. Growth and relaxation of flow birefringence and extinction angle were measured as a function of time. All the measurements are reproducible from load to load and from batch to batch.

Results and Discussion

Transient Flow Behavior. We begin with a start-up shear experiment to study stress growth. Figure 1 shows the time evolution of shear stress of a 0.08% solution at two different shear rates. At the lower shear rate of $\dot{\gamma} = 70\ s^{-1}$, the stress shows a strong initial overshoot and then levels off to a steady-state value. This stress overshoot would be typical of a semidilute polymer solution. The stress overshoot arises in nonassociative polymer solutions because the polymer chains initially respond affinely to the start-up shear, and the imposed strain on the chains as well as the stress produced by the chain retraction forces grows with time. Beyond the characteristic relaxation time of the solution, the chains contract to a configuration where the retraction force balances the viscous hydrodynamic force, resulting in a decrease in the shear stress. For a semidilute solution of a self-associating polymer such as HPAM, where interchain chain interactions are present in equilibrium, the stress overshoot in Figure 1 may arise from breakup of the interchain associations, while the individual HPAM chains remain essentially undeformed. At a shear rate ($\dot{\gamma} = 120\ s^{-1}$) above the critical shear rate, the stress grows again after the initial overshoot and eventually reaches a fluctuating plateau. In the plateau state, a strong normal force was observed and in the cone/plate flow cell the sample edge tends to become rough. Such a flow instability due to a normal stress buildup in a cone/plate flow cell has been recently discussed in a review paper.[26]

Figure 2 shows the flow birefringence growth and orientation angle of a similar solution having a slightly smaller glycerol content as a function of flow time for two different start-up shear flows. We observed comparable features of the flow birefringence growth in this Couette geometry. At a low shear rate, the birefringence levels off after an initial overshoot. On the other hand, under a higher shear, the initial birefringence overshoot is followed by further growth to a plateau value. Thus our flow birefringence measurements together with the previous rheological measurements[13] indicate that there is a critical shear rate beyond which structural evolution occurs in a simple shear independent of the cell geometry. Note that there is a difference in the growth period between the flow birefringence and stress measurements as can be seen from a comparison between Figures 1 and 2. The origin of this difference might be due to the different flow geometry and can only be resolved by simultaneous measurement of stress and flow birefringence using the same flow fixture.

Since the time scale associated with the second stress or birefringence growth is substantially longer than that characterizing the initial stress or birefringence overshoot, the second growth cannot possibly be due to a subsequent chain stretching. A theoretical account of shear thickening, based on chain stretching beyond the Gaussian chain limit, predicts that the stress growth exhibits only a single overshoot and the stress level remains flat subsequently over time.[27] On the other hand, a recent theoretical calculation[28] based on a shear-induced interchain association model[29] produces a characteristic stress growth curve similar to that shown in Figure 1.

Delayed Transient Flow. To gain some insight into the kinetic process involved in the second stress growth, we perform delayed-step flow experiments. These techniques have been developed previously to study shear thickening in micellar solutions.[30,31] Figure 3a shows a delayed-step flow experiment on the same solution as studied in Figure 1, during which a second flow was turned on 2 s after the cessation of the first steady

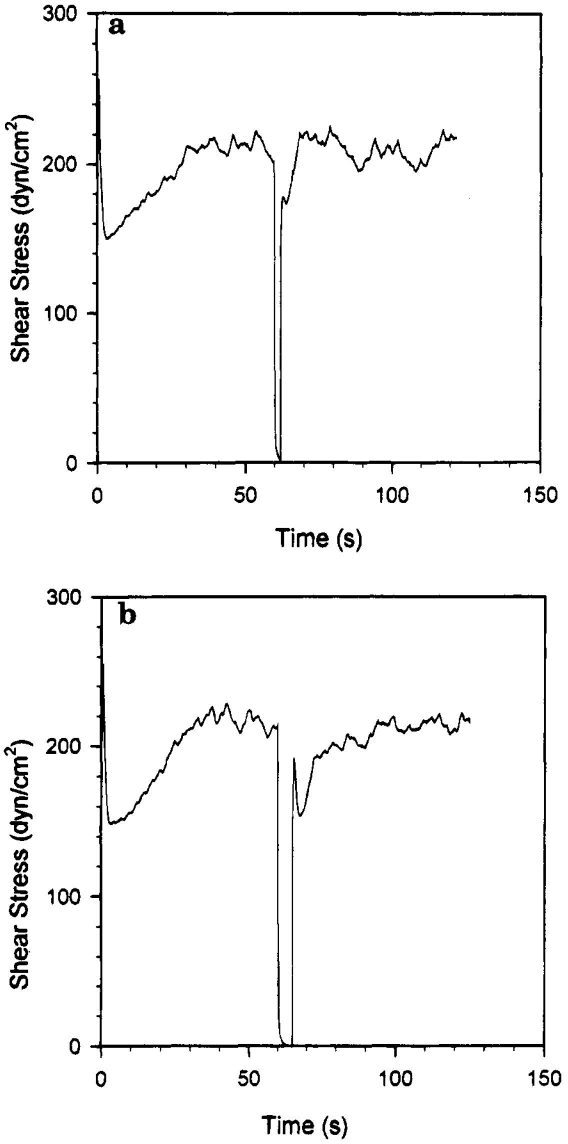

Figure 3. Time evolution of stress in a 0.08% by weight HPAM solution with 3% NaCl at T = 25 °C subjected to two step flows of 120 s^{-1}. The solvent is a water/glycerol mixture with 83% glycerol by weight. The second shear flow is applied (a) 2 s and (b) 5 s after the previous flow had been withdrawn.

shear. Two features should be noted in the stress response to the second flow. First, the overshoot is virtually absent, with the initial stress level notably higher than that of the stress minimum observed in the first start-up shear. This means that a possible structural buildup established in the first start-up shear has not yet broken up and remains strained 2 s after the cessation of the first shear. Second, the stress growth following the second step shear at the same shear rate of $\dot{\gamma}$ = 120 s^{-1} is much faster. In other words, it takes only 8 s to reach the plateau state in comparison to a period of 30 s required in the initial flow. This is not surprising given the first characteristics noted above. Figure 3b demonstrates a similar behavior where the delay time is 5 s. The overshoot upon the second step shear is now quite pronounced, and stress drops almost to the same minimum level as that attained following the initial overshoot. It is remarkable that the stress once again builds up immediately afterward, implying the effect of the first flow is still present. When the solution is allowed to stay quiescent for a sufficiently long period after the first shear, it recovers the equilibrium state. In other words, for a delay time longer than 20 s, the solution responds to a second step shear in quantitatively the same manner as it does to the first shear. Note that, despite the large stress fluctuations and a tendency for flow instability in the shear-thickening state, delayed-step rheological measurements were highly reproducible.

Further insight into the nature of the plateau state can be obtained by performing a different set of delayed-step shear experiments. Here we choose the first start-up shear to have a shear rate below the critical shear rate that is necessary to produce the second stress growth (see Figure 1). At a shear rate of 70 s^{-1}, the solution stress immediately levels off as shown in Figure 1 and Figure 4a after a sharp overshoot. The shear rate is then increased to a level of $\dot{\gamma}$ = 120 s^{-1} 10 s later as shown in Figure 4a. It is very important to notice the absence of any stress overshoot upon increasing the shear rate from 70 to 120 s^{-1}. This seems to rule out the possibility that the overshoot of the solution is chain stretching in origin. Chain deformation would yield a second overshoot following the stepup in shear that is almost 100% stronger than the initial one. Thus Figure 4a supports the conjecture that the effect of shear at low shear rates is to stretch the transient networklike structure formed by intermolecular interactions and break up certain interchain bonding. Since a dominant portion of interchain associations has already been destroyed by the first shear of $\dot{\gamma}$ = 70 s^{-1}, the solution responds to the second shear of 120 s^{-1} without a significant overshoot. Furthermore, any residual temporary network surviving the 70 s^{-1} shear flow should be under considerable strain and may be quickly broken up by the 120 s^{-1} shear,[32] so that the second overshoot may not be resolved on the experimental time scale.

The appearance of an induction period is a new feature in Figure 4a. In contrast to Figure 1 where the network breakup is competing with a shear-induced interchain association process, not much interchain bonding is present in the solution after 10 s of the first shear and interchain association must be rebuilt based on shear flow convection. The initial coagulation is expected to be extremely slow, and an apparent induction phenomenon arises. Figure 4a is reminiscent of the characteristic response of shear-thickening micellar solutions to a start-up shear.[30] The effect of the first shear with $\dot{\gamma}$ = 70 s^{-1} in breaking up the equilibrium solution structures can still be felt 10 s after it is turned off, as shown in Figure 4b, where a second shear of $\dot{\gamma}$ = 120 s^{-1} is applied 10 s after the cessation of the first weaker shear. Unlike Figure 4a, an overshoot appears in Figure 4b. This implies, first, that the residual solution structures surviving the first shear are no longer strained after 10 s of relaxation and, second, some broken intermolecular structures may have reformed. The nearly flat region after the second overshoot in Figure 4b indicates that, after the residual network is stretched and partially broken up, it takes some time for shear-enhanced coagulation to produce sufficient interchain bonding to reestablish the nonequilibrium structures in the solution in the plateau region. A resting period of 20 s is required for the solution (sheared at $\dot{\gamma}$ = 70 s^{-1}) to return completely to its equilibrium state.

It is very interesting to note that an initial shear with $\dot{\gamma}$ = 120 s^{-1} has a similar effect as an initial shear with $\dot{\gamma}$ = 70 s^{-1}, provided it is applied only for a short period (3 s), as shown in Figure 4c, where the characteristic response to the second shear is similar to that in Figure

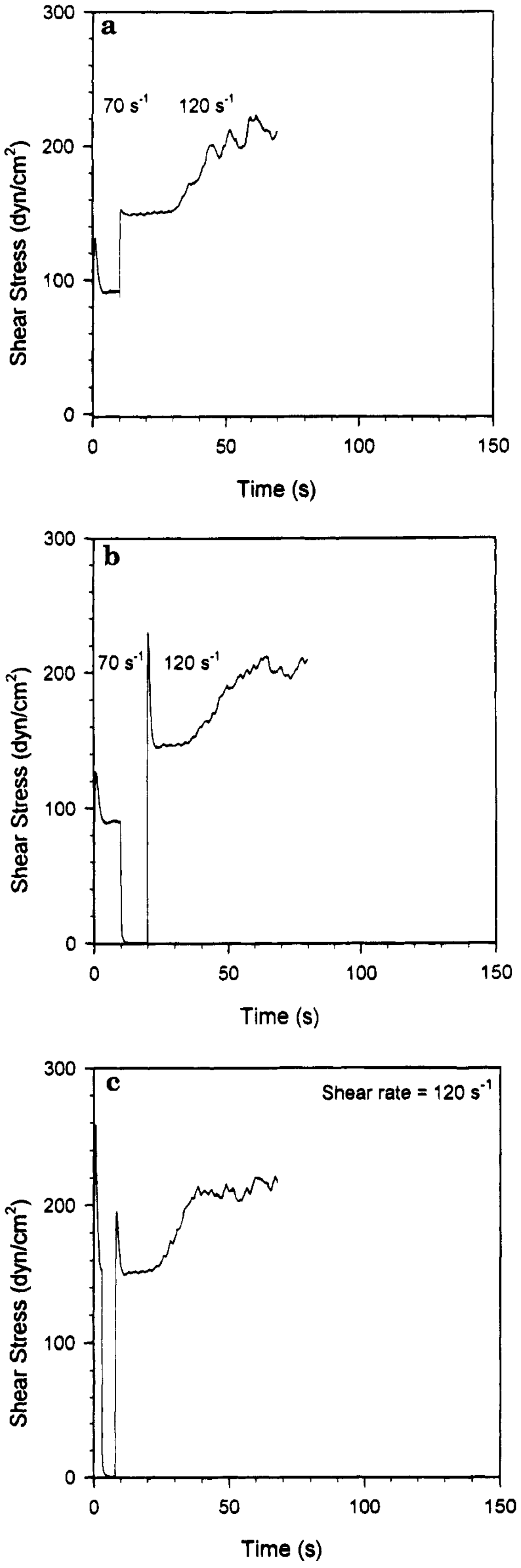

Figure 4. Time evolution of stress in a 0.08% by weight HPAM solution with 3% NaCl at $T = 25$ °C. The solvent is a water/glycerol mixture with 83% glycerol by weight. (a) A second shear flow of 120 s^{-1} is applied immediately following cessation of a first flow of 70 s^{-1}. (b) A second shear flow of 120 s^{-1} is applied 10 s after cessation of a first flow of 70 s^{-1}. (c) A second shear flow of 120 s^{-1} is applied 5 s after cessation of a first flow of 120 s^{-1} which is applied for only 3 s.

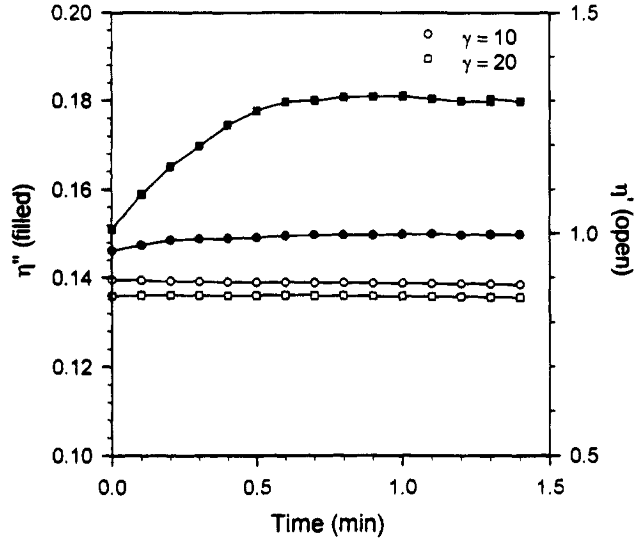

Figure 5. Time evolution of storage and loss viscosities (η' and η'') in a 0.08% by weight HPAM solution with 3% NaCl at $T = 22.6$ °C at $\omega = 50$ rad/s. The solvent is a water/glycerol mixture with 81.5% glycerol by weight.

4b. This behavior can be interpreted in the same way as for Figure 4b. Also, it is striking to compare Figure 4c with Figure 3b. The sharp distinction in the stress response after interruption between Figure 3b and Figure 4c shows that the solution states at the stress minimum and in the plateau region are fundamentally different.

Stress Growth under Oscillatory Shear. The effects of an oscillatory shear flow on the solution structure and viscoelastic properties should be distinctly different depending on whether shear-induced interchain association or chain stretching is the basic process involved. For example, chain extension in oscillatory shear is not expected to change from one oscillation to the next since the sample is returned to its initial position of zero deformation after each cycle. Thus the solution properties should remain constant as a function of time. On the other hand, any coagulation process will continue in an oscillatory shear because the flow-enhanced coalescence is not sensitive to reversal of the shear direction.

We subjected the 0.08% HPAM solution to oscillatory shear and monitored the complex viscosity as a function of time. Figure 5 shows the results of shear at a frequency $\omega = 50$ rad/s and two different strain amplitudes $\gamma = 10$ and 20. Clearly, the increase in the storage modulus $G' = \omega\eta''$ implies some structural change that grows over time. Specifically, interchain association appears to have been induced by the oscillatory shear, resulting in a solution with an increased G'. The comparatively small magnitude of the overall increase in the complex viscosity $|\eta^*|$ reflects the fact that interchain association can occur only to a limited extent in the absence of chain stretching, since the chains are hardly stretched in such a fast oscillating shear.

Influence of Solvent Composition on Shear Thickening. One important way to study the molecular mechanism for shear thickening of the HPAM solutions is to examine the critical conditions under which the shear-thickening behavior occurs. For a given HPAM, the respective amount of equilibrium interchain and intrachain associations is determined by the thermodynamic properties of the solution. Since water is a

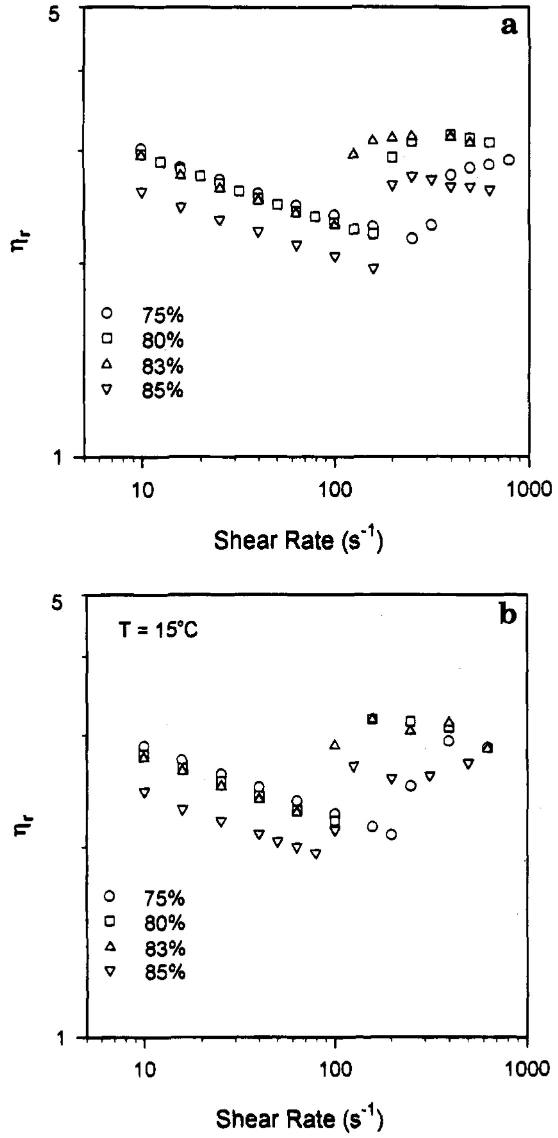

Figure 6. Relative steady-state viscosity of 0.08% by weight HPAM solutions with 3% NaCl and different glycerol concentrations at (a) T = 25 °C and (b) 15 °C.

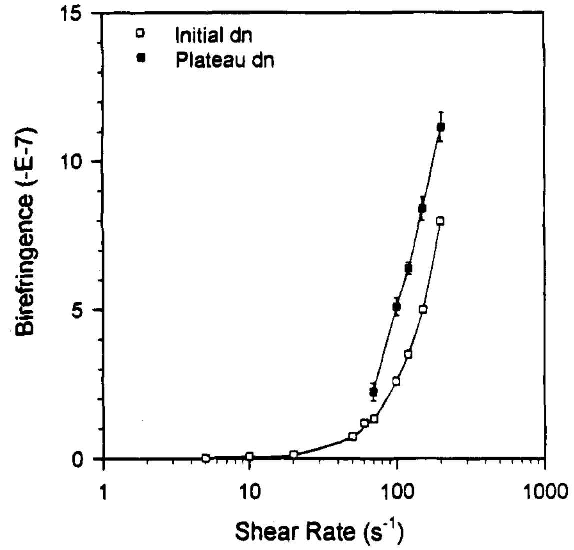

Figure 7. Initial (prior to shear thickening) and plateau flow birefringences as a function of shear rate of a 0.08% by weight HPAM solution with 3% NaCl at T = 25 °C. The solvent is a water/glycerol mixture with 81.5% glycerol by weight.

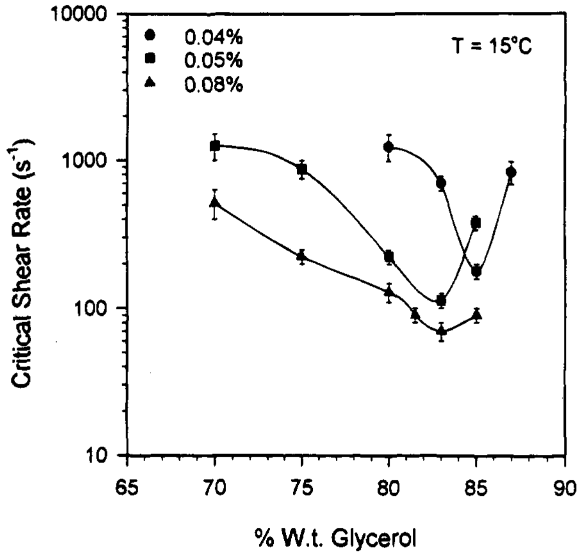

Figure 8. Critical shear rate for three HPAM solutions of different concentrations with 3% NaCl plotted against glycerol concentration at T = 15 °C.

much better solvent for the HPAM than glycerol, we can vary the solvent quality by choosing different glycerol contents in the solvent. Figure 6a shows the steady-state shear viscosity of the 0.08% HPAM solution at T = 25 °C as a function of shear rate for four different solvent compositions. All the solutions display shear thinning in the low shear rate region which is consistent with the observed stress overshoot. The low-shear relative viscosity η_r, defined as the solution viscosity divided by the solvent viscosity η_s, is essentially independent of the glycerol content in the range from 75% to 83%. The nearly identical shear viscosity of the first three solutions suggests that the shear thinning is not dominated by chain stretching as is usually the case for nonassociative polymer solutions. Chain deformation would have produced a lower shear viscosity for the solution with a higher glycerol content because the chain stretching by shear in a more viscous solvent would be larger due to a longer characteristic chain relaxation time. This is further supported by the fact that the magnitude of stress overshoot does not increase with the glycerol content for a fixed shear rate. Thus Figure 6a lends further evidence that the shear thinning in the lower shear rate region arises predominantly from breakup of the interchain associations, rather than from individual chain stretching. Additional information supporting this assertion comes from the flow birefringence data shown in Figure 7. Over the range of shear rate from 5 to 20 s^{-1}, where shear thinning occurs in Figure 6a, there is a negligible amount of flow birefringence.

The remarkable insensitivity of the chain conformation and intra-/inter-chain association to the variation of the solvent composition, as suggested by Figure 6a, is in sharp contrast to the discontinuous change in the low-shear relative viscosity in Figure 6a, from 83% to 85% glycerol content. A drastic change in the equilibrium solution structure has occurred upon increasing the glycerol to 85%. Experiments carried out at 15 °C illustrate similar behavior as shown in Figure 6b. The abrupt thermodynamic change also produces a reverse in the systematic trend that the critical shear rate for shear thickening is lower at a higher glycerol content. Replotting Figure 6b in Figure 8 in terms of the critical shear rate versus the glycerol content, we see that the critical shear rate begins to increase with the glycerol

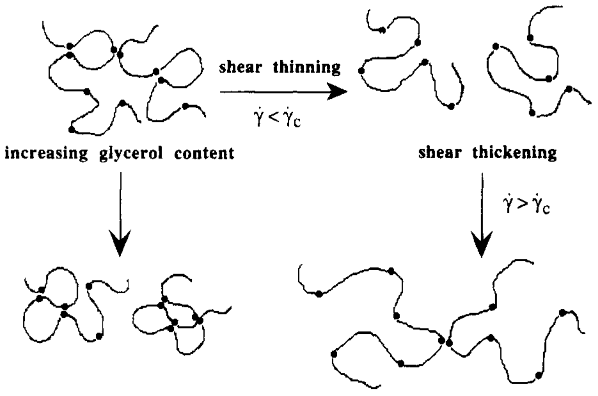

Figure 9. Schematic picture of shear-thinning and shear-thickening processes of HPAM chains under different flow or solvent environments.

content beyond 83%. The results for two other solutions at concentrations 0.04% and 0.05% are also presented in Figure 8. It is important to remark that, when the shear-thickening effect occurs as shown in parts a and b of Figure 6, it is always accompanied by a second stress growth (i.e., a negative thixotropic behavior) after the initial overshoot, i.e., following the characteristic features shown in Figure 1.

With increasing glycerol content, the solvent becomes more viscous and HPAM chain relaxation times increase. The segment–segment interactions may also become stronger since the solvent quality decreases. If shear thickening arises from the shear-induced interchain association and requires a critical amount of chain stretching to allow carboxyl groups on different HPAM chains to associate, then the decrease of the critical shear rate with increasing glycerol content, as shown in Figure 8, is certainly consistent with such a picture. The upturn in Figure 8 and the large separation between the 83% and 85% curves in parts a and b of Figure 6 suggest that the HPAM chains are much more compact at 85% glycerol, presumably due to a sharp increase in the degree of intrachain bonding. The intramolecular interactions are apparently so strong that only a shear flow with a much higher shear rate can stretch open the contracted chains and create interchain associations by enhancing the frequency of collisions between the HPAM chains.

Based on all the rheological data presented and discussed above, we propose the cartoon shown in Figure 9 to depict and summarize the essential behavior of the partially hydrolyzed polyacrylamide solutions under shear. The effect of a simple shear flow is (a) to reduce the number of interchain associations at low shear rates, leading to a stress overshoot and shear thinning, and (b) at sufficiently high shear rates to stretch individual chains and generate interchain bonding by coagulation, leading to shear thickening and a strong flow birefringence. The effect of increasing glycerol content is ultimately to shift the thermodynamic equilibrium among the self-associating chains toward more intrachain bonding so that a much stronger shear flow is required to stretch open the self-interacting chains.

Finally we study the effect of temperature on equilibrium and rheological properties of the HPAM solutions. Figure 10 illustrates the smooth variation of the steady-state shear viscosity over the entire range of shear rate with temperature. A larger low-shear viscosity suggests to us an increase at a higher temperature in the equilibrium intermolecular associations which determine the low-shear rheology. The increase of the critical shear rate with temperature may arise from two possible sources. With increasing temperature, the solvent viscosity and the molecular relaxation times decrease, making the shear flow less effective in stretching the molecular structures and producing convective association. Second, with increasing temperature there is a decrease in solvent quality, so that contraction of isolated chains occurs following the initial stress overshoot, further retarding the shear-thickening process. In contrast to the effect of varying the glycerol content, there is no abrupt change in viscosity and critical shear rate associated with changing temperature from 15 to 35 °C.

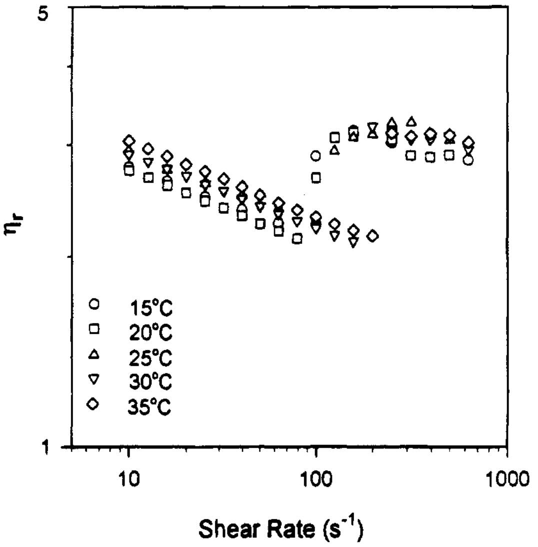

Figure 10. Relative steady-state viscosity of a 0.08% by weight HPAM solution with 3% NaCl at different temperatures as a function of shear rate. The solvent is a water/glycerol mixture with 83% glycerol by weight.

Summary

The rheopexy and shear-thickening behavior of partially hydrolyzed polyacrylamide solutions has been investigated by various rheological and rheooptical measurements. New experimental observations are presented of the stress and birefringence response under start-up shear, delayed-step shear, and oscillatory shear which reveal details of the kinetic processes involved in the formation of the nonequilibrium structures. In particular, we demonstrate for the first time that the shear-thickening kinetics depend strongly on the initial solution structure, which can be manipulated by varying the prior shear history. Thus the kinetics are different upon a start-up shear above the critical shear rate in a solution subjected to an initial flow at a shear rate either above or below the critical level for shear thickening as compared to that under quiescent conditions. In addition, unless the sheared solutions are allowed sufficient time to relax to equilibrium, their flow characteristics are different from those of equilibrium solutions. The equilibrium microscopic structure of HPAM solutions can also be altered by changing solvent composition and temperature. An abrupt change in molecular conformation and intra- vs interchain interactions was inferred at a specific glycerol content from a sudden change in the rheological and shear-thickening properties of the solutions. The relative low-shear solution viscosity is significantly higher at higher temperatures, suggesting a shift toward more intermolecular associations at high temperature.

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(32) It is well-known that a strained temporary network has a shorter lifetime than its equilibrium lifetime. Shear thinning in polymer melts can be accounted for phenomenologically using this concept.

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