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Shear History Effects in Associative Thickener Solutions

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ABSTRACT: Rheological investigations have revealed the strong dependency of the solution properties of associative thickener solutions on their shear history. Studies involved the measurement of the apparent solution viscosity both as a function of the shear time at constant shear rates and as a function of shear rate. Thixotropic behavior was observed at all copolymer concentrations studied. Furthermore, the effect of shear history on the viscoelasticity of the solutions was studied with stress relaxation and dynamic measurements. Results are explained in terms of the balance between *inter*chain and *intra*chain associations of the copolymer molecules in solution, and the kinetics of the molecular reorganization and dissociation−reassociation processes.

Introduction

Associative thickeners constitute a class of hydrophobically modified water-soluble polymers that in aqueous solution can give rise to enhanced viscosities. These copolymers typically consist of a hydrophilic backbone with a small number of hydrophobic monomer groups either dispersed along the polymer chain,[1−26] or present as terminal groups.[2,27,28] Their thickening ability in aqueous solution arises through reversible *inter*molecular associations caused by the unfavorable solvent conditions for the hydrophobic groups. These *inter*molecular associations form physical linkages between the chains, producing polymolecular structures with a high hydrodynamic volume and, consequently, enhanced viscosification properties.

Many of the studies available in the literature involve the use of copolymers based upon polyacrylamide.[3−18,24,25] Typically, these copolymers are synthesized via an aqueous micellar copolymerization route pioneered by Evani[24] and Valint et al.[25] This copolymerization process overcomes the obvious problem of the inherent water-insolubility of the hydrophobic comonomer. The microheterogeneous nature of the polymerization medium produces a copolymer with a blocklike structure, the hydrophobe being dispersed along the hydrophilic polymer backbone in what can be considered as hydrophobe rich regions. It has been argued previously that these small blocks of hydrophobic monomer will have a much greater hydrophobicity than an equivalent amount of monomer dispersed as discrete units along the polymer chain.[9] These blocky hydrophobic regions along the polymer chain are favorable to the formation of either *inter*chain associations, involving interactions between the hydrophobic regions on different chains, or *intra*chain associations, where the hydrophobic regions on a single chain interact between themselves. *Inter*chain associations produce polymolecular structures that enhance viscosity, whereas *intra*chain associations result in contraction of the copolymer coil, thereby reducing the viscosity. The thickening ability of the associative copolymer therefore depends on the balance between each mode of association.

Previous investigations have demonstrated the complex nature of the solution rheology. All types of non-Newtonian rheological behavior may be observed, namely, shear thinning, shear thickening, thixotropy, and rheopexy, depending on the particular sample utilized and the experimental conditions under which the observations are made. Moreover, substantial viscoelastic behavior is often observed.

A number of studies for the effect of shear rate on the apparent viscosity of aqueous nonionic hydrophobically modified polyacrylamide solutions have been reported.[4,6,9,10,14] These investigations have revealed the general shear thinning behavior of these associative thickeners, in the absence of any additives such as surfactants, resulting from the disruption of *inter*chain associations. At a sufficient rate of shear all of the associations are broken, the apparent viscosity of the solution then becomes identical to that of a similar molecular weight homopolyacrylamide solution at the same concentration and the same shear rate.[9] When the shear rate is sequentially decreased, the associations re-form, with a progressive increase in the apparent solution viscosity. Hysteresis phenomena are typically observed whereby the curves obtained under the increasing and decreasing rates of shear are not superimposed. Frequently, the apparent solution viscosities at each shear rate along the decreasing shear curve are lower than those along the increasing shear curve,[6,9] a thixotropic shear time-dependent phenomenon. It has also been observed that any thixotropic character markedly increases with increased *inter*chain associations.[9] Rheopexy, another time-dependent behavior, has been observed by McCormick et al.,[14] evidenced by the decreasing shear rate curve being above the increasing shear rate curve. These time-dependent behaviors indicate that kinetic effects on the destructuration−restructuration of the system are involved. Shear thickening has also been reported, its behavior arising through a change in the balance between *intra*chain and *inter*chain interactions.[10]

Based on the observed shear time dependency of the apparent viscosity of aqueous associative thickener solutions, the shear history of a particular sample must be taken into consideration when investigating its

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rheology. Other researchers have duly noted the importance of shear history.[4,6,7,9,14,15,26]

In this paper we present the results of a detailed study into the effects of shear history on the rheology of aqueous acrylamide/*N*-(4-butylphenyl)acrylamide copolymer solutions. Rheological behavior as a function of the shear time at constant shear rates has been investigated. Moreover, the effects of time-dependent phenomena on shear rate sweep measurements have been studied in a novel manner by varying the shearing time at each shear rate in the sweep. Effects of shear history on the viscoelasticity of the copolymer solutions are also investigated through stress relaxation and dynamic measurements. The observed rheological phenomena are discussed in terms of the balance between *inter*chain and *intra*chain associations of the copolymer molecules in solution, and the kinetics of the molecular reorganization and dissociation−reassociation processes.

Experimental Section

A. Materials. Acrylamide (Aldrich, 97% purity), sodium dodecyl sulfate (SDS) (Ajax, Technical grade), and ammonium persulfate (Aldrich, 98+% purity) were used as received without any further purification.

N-(4-butylphenyl)acrylamide was synthesized from the reaction of 4-butylaniline (Aldrich, 97% purity) and acryloyl chloride (Aldrich, 96% purity) according to the technique of McCormick et al.,[14] with both reagents used as supplied.

All water used here was of Millipore Milli-Q grade.

B. Copolymer Synthesis and Characterization. The acrylamide/*N*-(4-butylphenyl)acrylamide copolymer was synthesized via a free-radical copolymerization in an aqueous micellar medium. The technique has been described at length elsewhere.[3,9] Experimental conditions were as follows: the total monomer (acrylamide and hydrophobe) concentration in water was 3% w/w, with the hydrophobe (*N*-(4-butylphenyl)-acrylamide) at 1% w/w (or 0.35 mol %) based on the total monomer feed. The surfactant (SDS) concentration in water was 1% w/w, and the initiator (ammonium persulfate) concentration was 0.3% w/w relative to the total monomer feed. The reaction was allowed to proceed for 21 h at 60 °C.

The hydrophobe content of the copolymer sample was determined by UV spectrophotometry using the previously described calibration technique of Candau and co-workers.[3,9] Molecular weight information was obtained using static light scattering. The copolymer used here was found to have a hydrophobe content of 0.35 mol %, which is equivalent to 100% incorporation. Its molecular weight, M_w, was determined to be 2.1×10^6. For comparative purposes, a homopolyacrylamide, synthesized using the same procedure described above was also prepared, it had a molecular weight of 2.5×10^6.

From previous studies in the literature[3,9] on similar copolymers it has been shown that micellar copolymerization yields copolymers that are polydisperse in both molecular weight and hydrophobe incorporation. This is due to a higher hydrophobe incorporation in the early stages of the polymerization. As the polymerization proceeds, the amount of hydrophobe incorporated into each copolymer chain lessens, with both the size of the blocks and their number decreasing. At high levels of monomer conversion (as was the situation in this particular study) a copolymer sample must therefore contain a proportion of homopolyacrylamide, due to the exhaustion of the hydrophobe before the total monomer feed is completely consumed. The copolymer sample prepared in this study is therefore expected to be polydisperse in nature, with polymer chain compositions ranging from hydrophobe rich to pure polyacrylamide. Assuming an aggregation number of 60 for SDS,[3,9] we calculate approximately less than or equal to one hydrophobe per micelle in the polymerization medium. Previous investigations indicate that this will result in relatively small blocks of hydrophobe dispersed along the copolymer chains.

C. Copolymer Solution Preparation. Copolymer solutions were prepared by dissolution of the copolymer, at concentrations of 0.50, 1.00, 1.50, and 2.00% w/w, in pure water at ambient temperature. Agitation by gentle magnetic stirring was applied during dissolution of the copolymer. One to three days was generally required for complete dissolution and elimination of entrained air bubbles, depending on the copolymer concentration.

D. Rheological Measurements. All rheological measurements were performed with a Bohlin VOR controlled-shear rate rheometer. The instrument was interfaced to a personal computer and driven by a software package supplied by the manufacturer.

Different measuring systems were employed depending on the concentration of copolymer so as to ensure adequate sensitivity. The double gap DG 24/27 geometry was used for the 0.50% w/w copolymer solution. The concentric cylinder C25 geometry was used for the 1.00% w/w copolymer solution. For the 1.50% and 2.00% w/w copolymer solutions the concentric cylinder C14 geometry was employed.

The instrument affords control of two measuring parameters termed the delay time and the integration time. Together these parameters constitute the total measuring time for each measurement point. The delay time determines how long shear is applied, at each shear rate, before a measurement at that shear rate is taken. Following this time interval, instantaneous torque readings are taken over a period of time, called the integration time, the average of which yields the measurement point.

Viscosity−time at constant shear rate measurements were performed at shear rates of 0.116, 0.583, 1.16, and 11.6 s^{-1} by repeatedly measuring at a particular shear rate. A delay time of 0 s and an integration time of 4 s were employed for all measurements.

Viscosity−shear rate measurements were performed by sweeping over a particular number of shear rates, the minimum and maximum of which being 0.0146 and 1460 s^{-1}, respectively. For each measurement the shear rate was first increased and then sequentially decreased. An integration time of 5 s was used for all measurements, with a delay time of either 5, 30, 60, 180, or 600 s.

Stress relaxation following cessation of steady shear flow measurements were performed in two modes. The first involved subjecting the copolymer solution to a constant shear rate for 600 s and then measuring the stress relaxation for a period of 2000 s. Shear rates ranged from 0.0116 to 1460 s^{-1}. In the second experiment the solution was subjected to a constant shear rate of 11.6 s^{-1} for different periods of time, after which the stress relaxation was followed for 2000 s. Shear times ranged from 1 to 600 s.

Oscillatory measurements were performed by measuring the absolute value of the complex modulus $|G^*|$, the storage modulus G', the loss modulus G'', and the phase angle δ as a function of time at a constant frequency of 10.0 Hz and a constant strain of 0.14. These magnitudes of frequency and strain were chosen so as to provide a stress of reasonable magnitude for purposes of sensitivity. After taking an initial measurement on an unsheared copolymer solution for 19 min, shear was applied at a shear rate of 1460 s^{-1} for 300 s followed immediately by another measurement for 3 h. Between the measurement of each data point the oscillation was discontinued such that the solution was sheared only during the time interval (2 s) of the reading. For the initial measurement a reading was taken every 60 s, while a reading was taken every 300 s for the measurement following the imposition of shear.

All measurements were performed at 25 °C.

Results and Discussion

Before considering any results it should be recalled that the copolymer solutions had to be magnetically stirred in order to eliminate any entrained air bubbles, as explained in the Experimental Section. The higher the copolymer concentration, the longer the stirring time

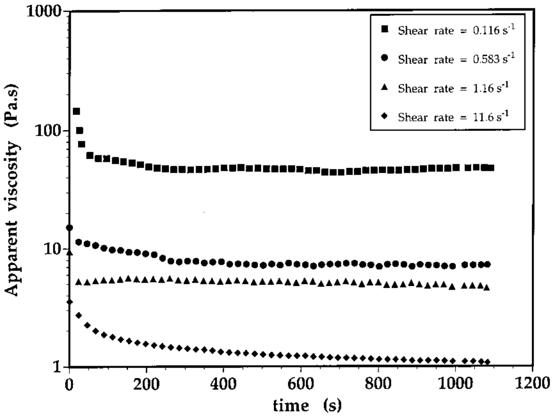

Figure 1. Apparent viscosity as a function of shear time for a 1.50% w/w aqueous copolymer solution at four shear rates. Only one data point out of four is displayed for clarity. (Temperature = 25 °C.)

required. Consequently, each solution had a different shear history before being used in the experiments. As a result of this, direct comparison between the apparent viscosities of different solutions is not easily performed without first considering the effects of this sample history.

A. Viscosity as a Function of Shear Time. Figure 1 shows the apparent viscosity as a function of shear time at four constant shear rates for a 1.50% w/w copolymer solution. The curves displayed in Figure 1 are representative for the concentration range 0.50–2.00% w/w copolymer. Thixotropic behavior is exhibited by the solutions. For comparison, it should be noted that the viscosity of the homopolyacrylamide sample at 1.5% (w/w) is of the order of 0.01 Pa•s at an equivalent shear rate and it does not exhibit a large thixotropic response. For clarity, these data are not shown in Figure 1.

This behavior of the copolymer solutions may be explained by considering the effect of applied shear on the hydrophobic associations. Upon application of a constant shear flow, the copolymer chains will extend under the applied stress. This results in the disruption of *intra*chain and *inter*chain associations, liberating hydrophobic regions. The disruption of *inter*molecular entanglements occurs as well, though are thought not to be as significant as the hydrophobic associations in determining the apparent solution viscosity at these levels of copolymer; hence they are not discussed in any detail. *Inter*chain associations are disrupted predominantly, as the majority of the associations are of this nature. This provides the copolymer chains with increased freedom of movement due to the loss of the conformationally restricting associations. Consequently, the copolymer chains possess an augmented ability to align with the shear flow, effecting a decrease in the apparent solution viscosity. Disruption of *intra*chain associations increases the number of hydrophobic regions available for participation in *inter*chain interactions. However, since such a large number of *inter*chain associations are disrupted, any new such associations formed from hydrophobic regions liberated through *intra*chain disruption would be masked by the large decrease in apparent viscosity. From observation of the curves in Figure 1 it is seen that the decrease in the apparent solution viscosity with shear time is not instantaneous, occurring over a finite time period before reaching a plateau value. This is probably the consequence of time-dependent processes such as the alignment of the copolymer chains with the shear flow and the disruption of associations. The latter would not necessarily occur immediately nor all at the same instant since the energy required to break the associations may vary from association to association. This would be highly probable for polydisperse copolymer samples. Such a copolymer sample is expected in this case since the hydrophobic regions differ in the number of hydrophobic monomer units and hence hydrophobicity, as discussed in the Experimental Section. An increase in shear rate is also seen to result in a lower magnitude of the plateau apparent solution viscosity, a result of the higher shear disrupting more associations than at lower shear. It is also observed that the thixotropic behavior does not change in magnitude substantially with an increasing constant shear rate. However, as the constant shear rate is increased, the thixotropic character should concomitantly increase since a greater number of *inter*chain associations would be disrupted. This apparent invariance in the thixotropic character is most probably caused by the faster alignment of the copolymer chains and the higher rate of disruption of the associations with increasing shear rate.

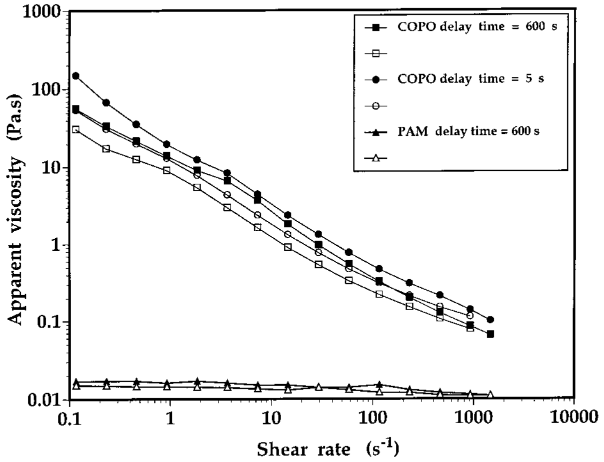

Figure 2. Apparent viscosity as a function of shear rate (sweep up and down) for 2.00% w/w aqueous copolymer solutions with two different delay times during measurement. Filled symbols represent the sweep up data; open symbols, the sweep down data. Data for a homopolyacrylamide sample of equivalent molecular weight are also given for comparison. (Temperature = 25 °C.)

B. Viscosity as a Function of Shear Rate. Based on the observed thixotropy in Figure 1, such time-dependent behavior should also affect the apparent viscosity measured during shear rate sweeps. Presented in Figure 2 is the apparent viscosity as a function of shear rate for a 2.00% w/w copolymer solution. Data collected using two different constant delay times of 5 and 600 s are shown. These curves are representative for the concentration range 0.50–2.00% w/w copolymer. Also shown here are data for the homopolyacrylamide sample at a concentration of 2% w/w. Clearly, the polyacrylamide solution is of a substantially lower viscosity and does not exhibit the large shear thinning response seen for the copolymer samples. In addition, there is only a very small hysteresis between the ascending and descending data sets.

For the copolymer sample, both measurements display the presence of substantial shear thinning, characteristic of associative thickener solutions.[4,6,9,10,14] As

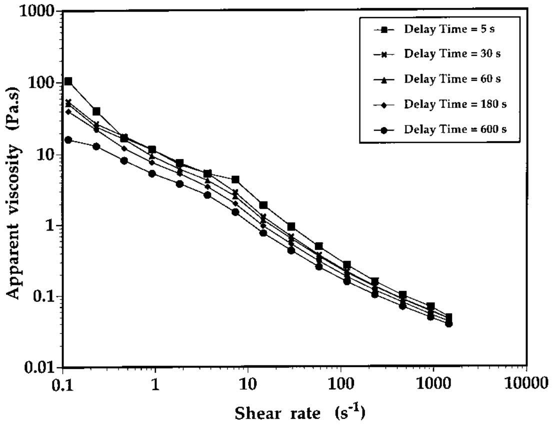

Figure 3. Apparent viscosity as a function of shear rate (sweep up) for 1.50% w/w aqueous copolymer solutions with five different delay times during measurement. (Temperature = 25 °C.)

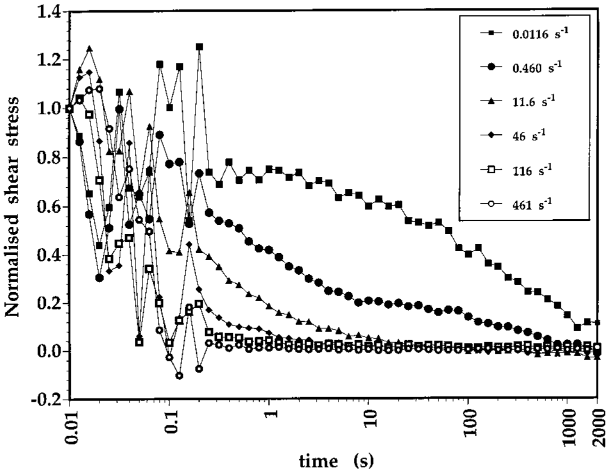

Figure 4. Relaxation of shear stress (normalized) following cessation of 600 s of shear flow at six different shear rates for 2.00% w/w aqueous copolymer solutions. Only one data point out of two is displayed for clarity. (Temperature = 25 °C.)

the shear rate is progressively increased, the shear field disrupts any *inter*chain associations between copolymer chains, which results in a breakdown of the polymolecular structures, effecting a decrease in the apparent solution viscosity. A higher shear rate results in the disruption of an increasing proportion of the associations decreasing the apparent viscosity further. These data support the behavior in Figure 1 where an increase in shear rate resulted in a lower apparent viscosity. Moreover, the sweep up and corresponding sweep down curves for each measurement do not superimpose, reflecting significant hysteresis effects. This hysteresis is due to time-dependent effects that can be explained by considering the kinetics of the dissociation−reassociation process (vide infra). For both the 5 and 600 s delay time measurements the presence of thixotropic behavior is observed, evidenced by the sweep down curve being below the sweep up curve. Furthermore, the curves for the 600 s delay time measurement are below the corresponding curves for the 5 s delay time measurement, again a thixotropic phenomenon, concurring with the corresponding constant shear rate measurements in Figure 1 where thixotropy was seen to occur over a substantial time period. This behavior may be explained, at least in part, in terms of the time dependency of the dissociation−reasssociation process. At the highest shear rate, where most associations are lost, the copolymer chains possess a highly extended conformation. As the shear rate is decreased, the chains can begin to re-coil and the hydrophobic interactions will begin to increase in number. These associations are almost exclusively of an *inter*chain nature. As the shear rate progressively decreases the chains will continue to associate, though the extent of *inter*chain association obtained during the sweep down does not reach that which was present during the sweep up at any particular shear rate. Thus it may be necessary to allow much longer times for the *inter*chain linkages to reach an equilibrium level since the hydrophobic regions have to locate each other in solution against the imposed shear. This results in a lesser degree of polymolecular structure and hence a lower apparent solution viscosity. The observation that the degree of hysteresis has not decreased with an increase in the delay time from 5 to 600 s further illustrates the magnitude of this effect.

The apparent viscosity as a function of shear rate for a 1.50% w/w copolymer solution employing five different constant delay times is displayed in Figure 3. Only the sweep up curves are shown. Generally, as the delay time increases, the apparent viscosity decreases, again a thixotropic effect analogous to the behavior seen in Figure 2. An inflection point is observed at approximately 10 s^{-1}, notably for the 5 s delay time curve. We believe this is an experimental artifact and not a real phenomenon. These curves serve to further illustrate that time-dependent effects occur gradually over long time periods.

C. Stress Relaxation. The presence of physical associations between the copolymer chains strongly influences the viscoelastic character of the copolymer solutions.[10,15,26] Since the degree of association is a function of both shear rate and shear time, these parameters must influence the viscoelastic behavior. Figure 4 shows the stress relaxation following cessation of 600 s of shear flow for 2.00% w/w aqueous copolymer solutions at various shear rates. The ordinate extends to negative values of shear stress due to initial oscillations resulting from resonance oscillation of the detector system following the abrupt cessation of the shear flow. The curves were normalized by dividing each stress value of a particular curve by the initial stress of that curve. It is observed that, in general, as the shear rate increases, the stress relaxes more rapidly, similar to the behavior observed by Klucker et al.[15] At the highest shear rates the stress relaxes completely within approximately 0.2 s, suggesting that the solution is behaving almost as a Newtonian liquid. The highest shear rate shown is 461 s^{-1}, as the same behavior was seen for the higher shear rates studied. At the lowest shear rates, however, the stress has not completely relaxed even after 2000 s, indicative of a viscoelastic liquid. Furthermore, the rate of relaxation decreases with time. An explanation for this behavior is as follows. It was previously shown (Figures 2 and 3) that the aqueous solutions of associative thickeners studied here are shear thinning. Therefore, as the shear rate is increased, the solutions become less viscous and less elastic due to the disruption of hydrophobic associations, the disruption of entanglements, and the alignment of the copolymer chains with the shear flow. The degree of polymolecular structure thus decreases with increasing shear rate, producing a greater proportion of free (unassociated and unentangled) copolymer molecules. Upon cessation of flow at high shear rates, the stress is

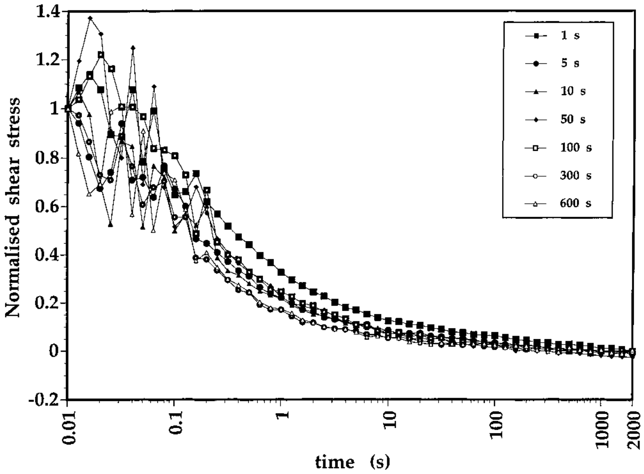

Figure 5. Relaxation of shear stress (normalized) following cessation of seven different periods of shear flow at a shear rate of 11.6 s^{-1} for 2.00% w/w aqueous copolymer solutions. Only one data point out of two is displayed for clarity. (Temperature = 25 °C.)

then able to relax rapidly through relatively unhindered movement of the free copolymer chains and polymolecular structures into positions that free the chains from the constraints originally imposed on them. As the shear rate before relaxation decreases, however, the degree of disruption of the polymolecular structures is reduced, with a concomitant decrease in the proportion of free copolymer chains. These polymolecular structures have a high hydrodynamic volume such that the solution is relatively viscous. Further, the presence of a high degree of association results in substantial elasticity of the solution. Relaxation of the stress is then due to the hindered movement of polymolecular structures and free copolymer chains, and the partial dissociation and reassociation of the chains. Consequently, upon cessation of flow the stress relaxation is relatively slow since these processes do not allow rapid relaxation. The decrease in the rate of decay of the stress is a consequence of two factors. The first is due to the decrease in stress with time, which results in a decrease in the flow rate of the liquid. This effect thus causes a decrease in the rate of movement of the molecules. The second factor is the increase in the apparent viscosity of the copolymer solution with time following the cessation of the shear flow, essentially exacerbating the first effect.

The effect of shear time at a constant shear rate of 11.6 s^{-1} on the stress relaxation behavior of 2.00% w/w aqueous copolymer solutions is shown in Figure 5. The curves were normalized as previously described. It is readily seen from Figure 5 that as the shear time increases the relaxation of the stress generally occurs more rapidly. This behavior may be expected on the basis of the knowledge that these solutions have previously been shown to exhibit thixotropy (see Figures 1−3). Thus, as the shear time increases, the degree of polymolecular structure decreases, resulting in a system that can more rapidly relieve the imposed stress.

D. Viscoelastic Recovery. In Figure 2 it was seen that if the *inter*chain associations are disrupted, they may not necessarily re-form to the extent they were originally. Since the viscoelasticity of the solutions is a function of the degree of this association, the reassociation process may be followed with dynamic measurements. In Figure 6, data for the storage and loss moduli of the copolymer and homopolymer as a function of frequency are presented. The concentration of both polymers is 2% w/w. There are substantial differences between the two data sets. In the case of the copolymer, there is a large increase in both G' and G'' as a function of the frequency due to the hydrophobic interactions in the solution. At frequencies >1 Hz, the storage modulus, G', becomes larger that the loss modulus, G'', indicating the highly elastic nature of these solutions. In contrast, for the homopolymer solution the loss modulus is higher than the strage modulus across the entire frequency spectrum tested. Volpert et al.[10] have also measured the viscoelastic response of a similar copolymer and a homopolymer. Their results are directly analagous to those given here. In this previous investigation, they indicated that the homopolymer solution could be modeled using a bead−spring model, although as is the case here, a larger frequency spectrum is needed to test this model.

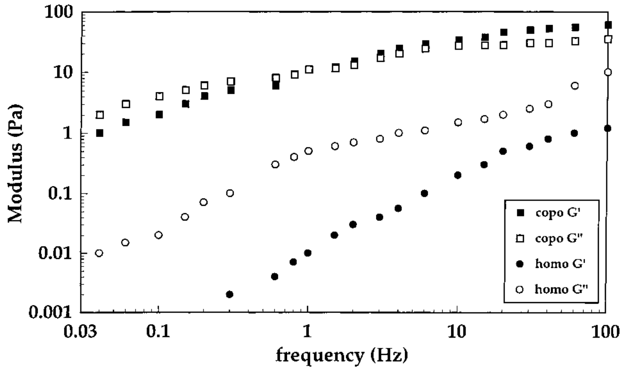

Figure 6. Storage and loss moduli (G' and G'') as a function of frequency for the copolymer sample and the homopolymer sample, respectively.

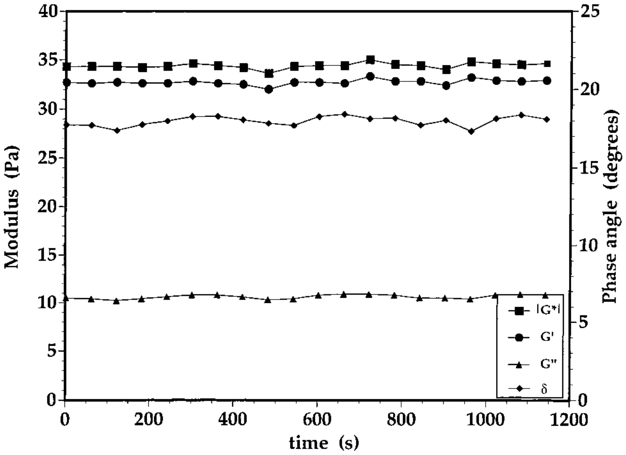

Figure 7. $|G^*|$, G', G'', and δ as a function of time for a 2.00% w/w aqueous copolymer solution under discontinuous oscillation. Strain = 0.14, frequency = 10 Hz. (Temperature = 25 °C.)

Figure 7 shows the absolute value of the complex modulus $|G^*|$, the storage modulus G', the loss modulus G'', and the phase angle δ as a function of time for a 2.00% w/w aqueous copolymer solution under discontinuous oscillation at constant strain and frequency. In this case a reading was taken every 60 s. Observation of these data reveals that all the parameters are essentially constant with time within this time scale of measurement. This infers that under this particular oscillatory shear there are no substantial structural changes of the system within this time scale. The

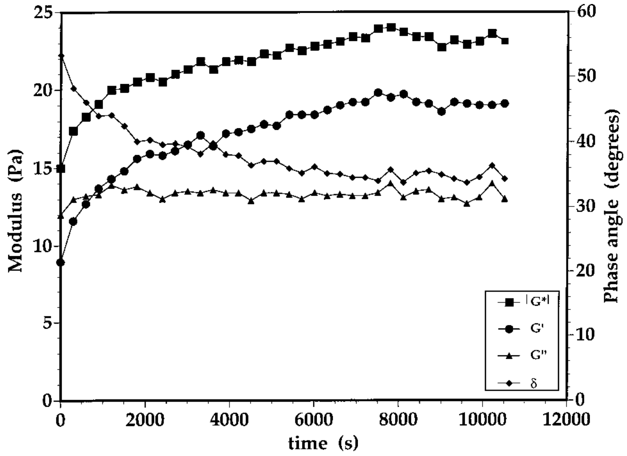

Figure 8. $|G^*|$, G', G'', and δ as a function of time for a 2.00% w/w aqueous copolymer solution under discontinuous oscillation, following 300 s of shear at 1460 s^{-1}. Strain = 0.14, frequency = 10 Hz. (Temperature = 25 °C.)

energy input to the system is thus constant, as reflected in $|G^*|$. Further, the proportions of this energy stored and recovered elastically and dissipated as heat through viscous drag per cycle per unit volume remain constant, as reflected in G' and G'', respectively. G' is greater than G'', indicating that a greater proportion of the input energy is stored elastically, and a lesser fraction is dissipated as heat, which is to be expected due to the high frequency (10 Hz) employed in these measurements and the high elasticity of the solution. The highly elastic nature of the solution at this frequency is also represented by δ, which is closer to 0° than 90°.

In Figure 8 are shown similar measurements, though taken after the solution was sheared at a shear rate of 1460 s^{-1} for 300 s. This shearing resulted in thixotropic behavior, and a plateau apparent viscosity of approximately 64 mPa·s was attained. A reading in this case, however, was taken every 300 s for a total period of 3 h. $|G^*|$ is seen to essentially increase with time to an apparent plateau that is well below the value observed originally before shearing in Figure 6. This indicates that the energy input is increasing with time to an apparent plateau, as a result of an increase in viscosity and elasticity of the solution due to structural recovery. The smaller magnitude of $|G^*|$ as compared to the original value suggests that the sample is now much easier to deform, a consequence of the disruption of the *inter*molecular structure due to shear. G'' has expectedly increased relative to the original value, due to the lower viscosity, and remains constant with time. G', now of similar magnitude to G'', increases concomitantly with $|G^*|$ and is less than its original value, a consequence of the loss of elasticity due to the breakdown in *inter*molecular structure. It thus appears that the amount of energy dissipated, reflected in G'', is not changing. This is contrary to what would be expected, since, as the hydrophobic associations and entanglements between the copolymer chains re-form and the chains resume their random, unconstrained conformations, the degree of flow would decrease, producing a reduction in the magnitude of G'' with time. A greater proportion of the energy would then be stored elastically, effecting an increase in G'. Observation of the corresponding phase angle δ in Figure 8 reveals that it decreases with time. Now, since $G'' = (\sigma_0/\gamma_0) \sin \delta$, where σ_0 is the shear stress amplitude and γ_0 is the strain amplitude, an increase in σ_0 (which is proportional to $|G^*|$) and a decrease in δ would have opposing effects on G''; increasing σ_0 increases G'' and decreasing δ decreases G''. Consequently, G'' appears constant in Figure 8 due to the superposition of these two opposing effects masking one another. These types of effects do not change the qualitative behavior of G' in this case, however, since $G' = (\sigma_0/\gamma_0) \cos \delta$ and an increase in σ_0 increases G' while a decrease in δ also increases G', so that the effects are not masked. The primary consequence of these considerations is that whether G' and G'' appear to increase, decrease, or remain constant with time is most often meaningless in this form of experiment. Only by comparing the relative magnitudes of G' and G'' (as with δ, where $\tan \delta = G''/G'$) can genuine information be acquired. The decrease in δ with time is expected since, as the system recovers from the shear, less flow and greater elastic energy storage should occur. The phase angle is, nevertheless, substantially larger than it was originally, indicating that a greater proportion of the energy is dissipated and a lesser proportion is stored and recovered compared to the unsheared solution. These results indicate that the preshearing caused a substantial breakdown in the structure of the system which, once the shear was ceased, began to re-form rapidly at first and more slowly with time until an apparent plateau was reached. It thus appears that, even after 3 h of what is essentially rest, the degree of *inter*molecular structure in the system is substantially less than that present originally. The decrease in the rate of recovery is probably due to the loss of freedom of movement of the chains as they begin to reassociate such that at longer times the hydrophobic regions are hindered from locating each other.

Conclusions

Detailed studies on the influence of shear history on the observed rheological properties of associating copolymer solutions have been performed. The associative thickener solutions employed here have been shown to exhibit significant thixotropic behavior, such that the observed apparent solution viscosity is very dependent on the shearing time. As a result, we have explicitly shown that the apparent viscosities measured during shear rate sweep measurements are a function of the time each shear rate of the sweep is applied. The viscoelastic character of the copolymer solutions was also found to depend strongly on shear history, as revealed through stress relaxation and dynamic measurements. Further, the dynamic studies illustrated that long times are required for the associations to re-form following their disruption. Thus, due to the reversible nature of the association process the solution properties depend strongly on what, in terms of shear, the solution has been subjected to previously. Consequently, the shear history of associative thickener solutions must be rigorously controlled if reproducible rheological measurements are to be obtained.

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