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ORIGINAL CONTRIBUTION

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Negative thixotropy of solutions of partially hydrolyzed polyacrylamide

II. The influence of glycerol content and degree of ionization

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Abstract We found that the character of negative thixotropy of partially hydrolyzed polyacrylamide in aqueous glycerol strongly depends on polymer concentration, glycerol content and shear rate applied. At low polymer and glycerol concentrations, shear stress and viscosity slowly increased during shearing to a limiting value. In addition to this behavior, a steep increase in shear stress as well as normal stress followed by their pronounced oscillations occurred at higher concentrations of both components and at higher shear rates. Similarly to the negative thixotropic effect in solutions of other polymers in organic solvents, the hydrodynamic conditions in which the effects set in seem to be controlled by the shear stress acting in the flowing solution; initial kinetics of the effect depends on solvent viscosity and shear stress applied. To explain the influence of the glycerol content and degree of ionization of the polymer on the minimum shear stress at which the effect sets in, a decisive role of intermolecular electrostatic repulsions in association of the polymer molecules in shear field is assumed.

Key words Negative thixotropy–antithixotropy – shear thickening – shear induced structure –polyacrylamide solutions

Introduction

It has been reported [1–3] that dilute solutions of partially hydrolyzed high-molecular-weight polyacrylamide (PHPAA) in water - glycerol mixtures exhibit negative thixotropy on exceeding a certain critical shear rate, i.e., a time-dependent reversible increase of shear stress or viscosity. However, different shapes of the shear stress vs. time of shearing were observed: i) shear stress rose either slowly (time scale of tens of minutes) from the very beginning of shearing [1, 4] or ii) more rapidly after several minutes of shearing [2].

To produce negative thixotropy in aqueous glycerol solutions of PHPAA, the presence of high amounts of glycerol (75–80 wt.%) seems to be necessary. Due to polyelectrolyte character of PHPAA, a strong influence of degree of ionization on its negative thixotropic behavior could be also expected. As the effect of the variables which seem to play an important role in the occurrence of negative thixotropy is not yet clear, we aimed at their systematic investigation.

Experimental part

Polymer and solutions

Partially hydrolyzed polyacrylamide (sodium salt), of molecular weight $\overline{M}_w = 7{\cdot}10^6$ (measured by light scattering in 0.1 M NaCl solution) [5] and of the degree of hydrolysis 0.26 (determined by conductometric titration) was a BASF product. The polymer solutions were prepared by dissolution of PHPAA in twice distilled water followed by glycerol addition to obtain its concentrations 0, 25, 50, 75 and 90 wt.%. The heterogeneous mixtures were gently stirred with steel balls sealed in glass until homogeneous solutions were obtained. Using this procedure the preparation of the polymer solutions took approximately 2 or 3 weeks, but mechanical degradation of the polymer could be excluded. PHPAA concentrations, 300 and 1500 ppm, were higher than the overlap concentration c^* determined by the Simha equation $c^* = 1/[\eta]$ using intrinsic viscosity data from the literature [5].

The degree of ionization of PHPAA, α, adjusted by standard HCl solution was calculated according to $\alpha = (c_{AA} - c_{HCl})/c_{AA}$, where c_{AA} is the molar concentration of acrylic acid monomeric units and c_{HCl} is molar concentration of HCl added. PHPAA concentration in the study was 1440 ppm, glycerol content 85 wt.%. All the solutions were measured after standing for about 24 h.

Shear stress and normal stress measurement

The cone and plate Weissenberg rheogoniometer (model R-18) connected with a recorder which enabled continuous registration of both shear stress, τ, and the first normal stress difference (hereinafter, normal stress), N_1, at constant shear rate was used. The diameter of the cone and plate was 5 cm, the gap angle was ca 2° or 1° to widen the range of shear rates from $1141\ s^{-1}$ to $2314\ s^{-1}$. The instrument was equipped with a special device allowing to keep the temperature of measurement $25 \pm 0.10\ ^\circ C$. All the measurements started 10 min after filling and adjusting the gap width in order to minimize the influence of deformation history on negative thixotropic behavior of the systems. Owing to this "memory" effect and possible polymer degradation during shearing of the negative thixotropic structures, fresh solutions were used at each shear rate.

Results and discussion

The effect of glycerol on shear stress vs. time dependences

Figure 1 illustrates a strong pseudoplastic flow of aqueous glycerol solutions of PHPAA and a weak effect of glycerol content on both viscosity and pseudoplasticity. At certain critical shear rates which decreased with increasing glycerol content and with polymer concentration, negative thixotropy set in. Due to the effect, shear thickening behavior was observed, Fig. 1.

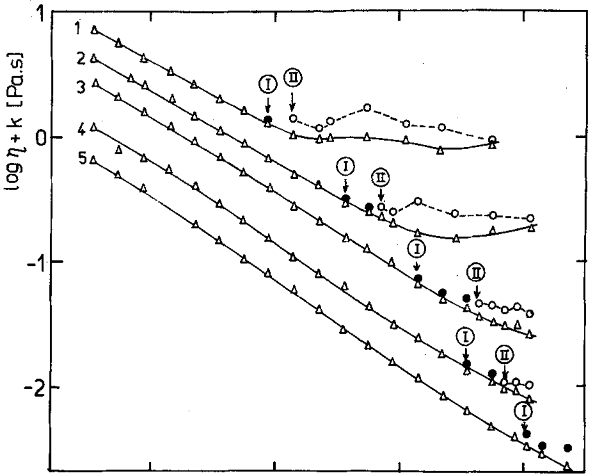
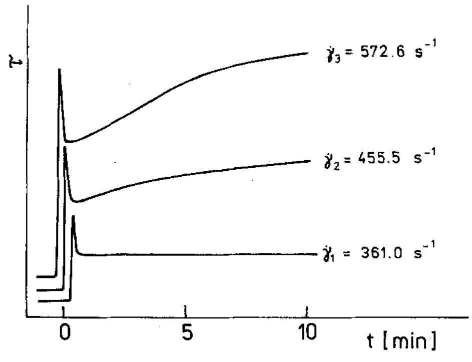


Fig. 1 Dependences of viscosity η on shear rate $\dot{\gamma}$. Viscosity calculated from shear stress τ_0 (△), from the shear stress after 30 min of shearing (●) and from the average shear stress increase $\bar{\tau}$ (○) defined in (Fig. 3b). PHPAA concentration 1500 ppm, aqueous glycerol: 1) 90%, 2) 75%, 3) 50%, 4) 25%, and 5) 0%. The arrows indicate shear rates at which negative thixotropy of the type I or II sets in. The curves were shifted to avoid overlap by: $k = 0$ (90–50% of glycerol), $k = -0.2$ (25% of glycerol) and $k = -0.4$ (0% of glycerol)

The character of negative thixotropy depended on solvent composition, polymer content, and shear rate applied. At 300 ppm of PHPAA in 25–75% glycerol, shear stress increased after overshoot decay with a gradually decreasing slope to a steady-state value or increased continuously, Fig. 2. Such negative thixotropy was denoted type I and the corresponding critical shear rate $\dot{\gamma}^{I}$. In addition to this behavior, a different negative thixotropic effect, Fig. 3a, denoted type II, occurred at 90% glycerol and in 25–90% glycerol with 1500 ppm of PHPAA at critical shear rates $\dot{\gamma}^{II}$, Table 1. In this case a rapid increase in the shear stress followed by pronounced

Fig. 2 Schematic diagram of shear stress τ vs. time dependence for solutions of 300 ppm PHPAA in 25–75% aqueous glycerol



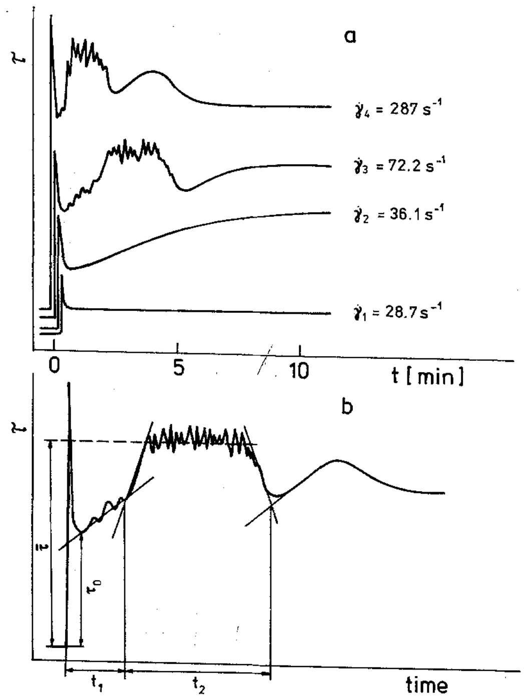


Fig. 3 Schematic diagram of shear stress τ vs. time dependence: a) 300 ppm of PHPAA in 90% aqueous glycerol, b) curve used for definition of the criteria of negative thixotropy of the type II

stress oscillations was observed after some time of shearing. Small vortices or even gel-like particles rotating and partly expelled from the gap appeared during stress oscillations. After several minutes of shearing at higher shear rates, the oscillations of stress diminished, a gel-like structure became liquid and shear stress dropped to a minimum. On further shearing, the shear stress rose again to a steady-state value or, at the highest shear rates, rose to a low secondary maximum, Fig. 3a.

Simultaneous with shear stress, time changes in normal stress were observed, Fig. 4. As can be seen, both stresses changed in the same way at shear rates near to $\dot{\gamma}^{\text{II}}$, Fig. 4a. On the other hand, a considerable difference in their time changes was found at shear rates well beyond $\dot{\gamma}^{\text{II}}$. In this case, the normal stress decayed with time of shearing while the shear stress did not exhibit any decrease, Fig. 4b.

It was found that the time interval from onset of shearing to the steep increase in both shear and normal stress (induction period, t_1) and the time interval from onset of oscillations to the shear stress minimum or to steady-state of normal stress (the period of shear stress oscillations, t_2, defined in Fig. 3b) increased with glycerol content. On the other hand, their values rapidly decreased with shear rate so that at the highest shear velocities the effect changed to several seconds of shear stress oscillations at the beginning of shearing. In comparison to other negative thixotropic systems, an increase in shear stress due to the effect was rather small (up to 70% of τ_0) and did not depend on glycerol content, Fig. 1.

The influence of degree of ionization

Decreasing the degree of ionization led to a lower viscosity and its lower non-Newtonian decrease, Fig. 5. At the same time, negative thixotropic effect of type I diminished and only that of the type II could be found. The critical shear rates $\dot{\gamma}^{\text{II}}$ slowly decreased, Fig. 5, and changes in the shape of shear stress vs. time dependence also occurred: the periods of oscillations at a given flow rate rapidly decreased and secondary maxima gradually diminished. On the other hand, induction periods and the relative increase in viscosity due to the effect did not depend on the degrees of ionization when compared at similar shear rates, Fig. 5.

Hydrodynamic conditions of the occurrence of the effect

Negative thixotropy in polymer solutions is supposed to result from the association of macromolecules activated by their deformation (extension) and orientation in the shear field which leads to formation of a temporary supramolecular structure [2, 4, 6–9]. As the deformation and orientation of macromolecules in the shear field

Table 1 Critical shear rates $\dot{\gamma}^{\text{I}}$, $\dot{\gamma}^{\text{II}}$, critical shear stress τ^{I} and calculated minimum shear stresses τ^{II} at which negative thixotropy I or II sets in. η_s is solvent viscosity

Glycerol		$c_{\text{HPAA}} = 300$ ppm				$c_{\text{HPAA}} = 1500$ ppm			
[wt.%]	η_s [mPa.s]	$\dot{\gamma}^{\text{I}}$ [s^{-1}]	τ^{I} [Pa]	$\dot{\gamma}^{\text{II}}$ [s^{-1}]	$\tau^{\text{II}}_{\text{min}}$ [Pa]	$\dot{\gamma}^{\text{I}}$ [s^{-1}]	τ^{I} [Pa]	$\dot{\gamma}^{\text{II}}$ [s^{-1}]	$\tau^{\text{II}}_{\text{min}}$ [Pa]
0	1.0		no effect up to 2314.0 s^{-1}			1141.1	9.5	–	–
25	1.78	1463.0	6.1	–	–	361.0	7.9	721.9	10.6–13.1*)
50	4.89	455.5	6.4	–	–	143.8	9.6	455.5	15.0
75	26.6	143.8	6.9	–	–	36.1	10.9	72.2	13.8
90	152.7	36.1	10.5	72.2	14.4	9.1	11.4	14.9	13.4

*) Values of critical shear stress due to very small inductions periods

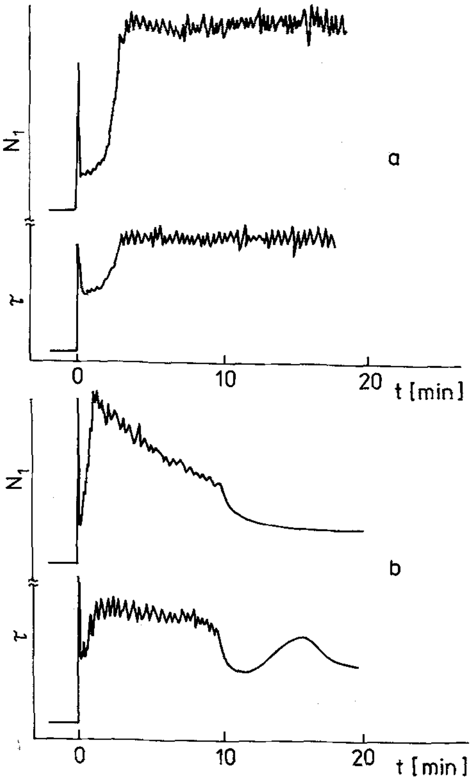
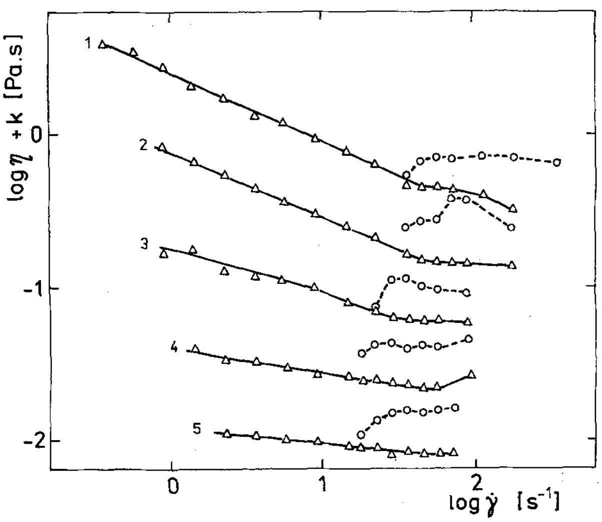


Fig. 4 Schematic diagram of shear stress τ and normal stress N_1 vs. time dependence at: a) 45.5 s^{-1}, b) 72.2 s^{-1}. Polymer concentration 1500 ppm, 75% aqueous glycerol

Fig. 5 Dependences of viscosity η on shear rates $\dot{\gamma}$ at different degrees of ionization α: 1) 1, 2) 0.75, 3) 0.50, 4) 0.25 and 5) 0. PHPAA concentration 1440 ppm, 85% aqueous glycerol. For the meaning of points see Fig. 1. The curves shifted to avoid overlap by: $k = 0$ ($\alpha = 1$), $k = -0.4$ ($\alpha = 0.75$), $k = -0.74$ ($\alpha = 0.50$), $k = -1.0$ ($\alpha = 0.25$) and $k = -1.4$ ($\alpha = 0$)



depend on the shear forces acting on them rather than on shear rate, the hydrodynamic conditions in which the effect sets in are better expressed in terms of critical shear stress than by critical shear rate [7].

It can be seen (Table 1) that while the critical shear rates $\dot{\gamma}^{\mathrm{I}}$ and $\dot{\gamma}^{\mathrm{II}}$ rapidly decreased with glycerol content the differences in the values of both critical shear stresses τ^{I} and minimum shear stresses $\tau^{\mathrm{II}}_{\mathrm{min}}$ were within the experimental accuracy, practically independent of glycerol content and on polymer concentration. Minimum shear stress $\tau^{\mathrm{II}}_{\mathrm{min}}$, at which under given conditions the effect sets in, was used as a more objective criterion of hydrodynamic conditions for the occurrence of the effect instead of critical shear rate which is affected by stepwise increase in the shear rate of the instrument [7]. It was calculated as a product of minimum shear rate $\dot{\gamma}^{\mathrm{II}}_{\mathrm{min}}$, determined from the slope of a linear part of the plot $t_{\mathrm{I}}\dot{\gamma}$ vs. t_{I} [10], and viscosity at $\dot{\gamma}^{\mathrm{II}}_{\mathrm{min}}$. As the solution viscosity increases with solvent viscosity, it is apparent from similar values of both critical and minimum shear stresses that critical shear rates should be inversely proportional to solvent viscosity as was indeed found, Table 1.

One may expect that, due to the deterioration of solvent power with increasing glycerol content [5, 11], the minimum shear stresses should decrease similar to the effect of solvent quality on negative thixotropy in poly(methyl methacrylate) solutions [7]. The results obtained suggest that the solvent quality is not the only quantity which controls the hydrodynamic conditions of the onset of the effect in PHPAA solutions. Association of charged macromolecules requires that, in addition to repulsive interactions arising from polymer excluded volume, electrostatic repulsions between negatively charged carboxylic groups attached to the polymer chains must be overcome by polymer deformation and orientation in shear field. Electrostatic interactions at a given degree of ionization and ionic strength depend on dielectric constant of the solvent. As in water-glycerol mixtures the dielectric constant relatively slowly decreases with glycerol content from 80 (water) to about 50 (90% aqueous glycerol), we assume that the effect of glycerol on electrostatic interactions is rather small. Hence, polymer chain dimension, its flexibility (or rigidity) and electrostatic intermolecular repulsions as well do not change considerably as reflected in small effect of glycerol on flow properties of the solutions, Fig. 1. If the association of the polymer in shear field was suppressed primarily by these electrostatic interactions, minimum shear stress should be little dependent on glycerol content.

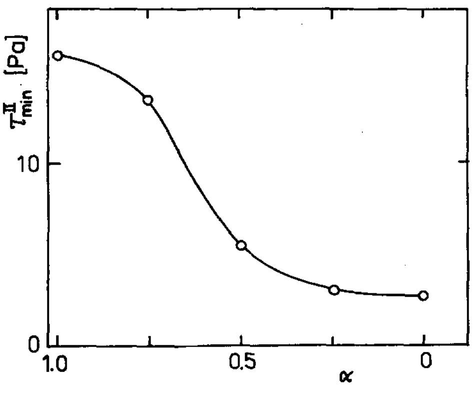
The hypothesis that intermolecular electrostatic repulsions control the hydrodynamic conditions in which negative thixotropy occurs seems to be supported by the strong decrease in $\tau^{\mathrm{II}}_{\mathrm{min}}$ when decreasing degrees of ionization, Fig. 6. Changing this quantity the number of charges on the polymer chain decreases, which brings about a pronounced reduction of the chain expansion as follows from a rapid viscosity decrease and lower slopes of the flow curves, Fig. 5, and also causes reduction of intermolecular repulsion. As the more expanded chains overlap more extensively and can be more easily organized in the shear field, $\tau^{\text{II}}_{\text{min}}$ should increase, when decreasing the degree of ionization. On the other hand, lower intermolecular repulsion should lead to lower values $\tau^{\text{II}}_{\text{min}}$ owing to higher ability of PHPAA to associate. As $\tau^{\text{II}}_{\text{min}}$ decreases monotonously with decreasing degrees of ionization, we can conclude that reduction of intermolecular repulsions prevails over the simultaneous decrease in coil dimensions.

Mechanism of polymer association in the shear field

At critical shear stress, the association process sets in and the time changes of stresses are recorded. Due to shearing at constant shear velocity, the shape of these dependences reflects both association of macromolecules and disintegration of the associates. We assume that negative thixotropy of the type I, Fig. 2, reflects formation of relatively small associates such as doublets, triplets, etc. of macromolecules. Shear forces acting on the associates grow with their dimensions and hence, after a sufficient time of shearing, a steady-state distribution of the multiplets is reached as proposed in the theory of thickening phenomena in dilute polymer solutions [12, 13].

With increasing glycerol content, viscosity of the solvent increases, Table I. which brings about prolonged lifetime of associates in a more viscous solvent [12]. Thus, a greater number of intermolecular junctions can be formed in the shear field. After some time of shearing, this may lead to the formation of a network structure extending over the whole volume of the sample. As a result of this process, shear stress and normal stress steeply increase and negative thixotropy of the type II is observed, Fig. 3a. Further shearing of such network structures brings about its disintegration and polymer degradation [14] which is reflected in both shear and normal stress decrease. As the normal stress is sensitive to the presence of networks, it decreases even though shear stress does not exhibit any decrease. It can be supposed that the increase in shear stress to the secondary maximum might arise from the formation of new associates by shearing the rest of network structure and disintegration of the associates in the shear field which proceeds until structures that cannot be destroyed at a given shear velocity remain in the solution.

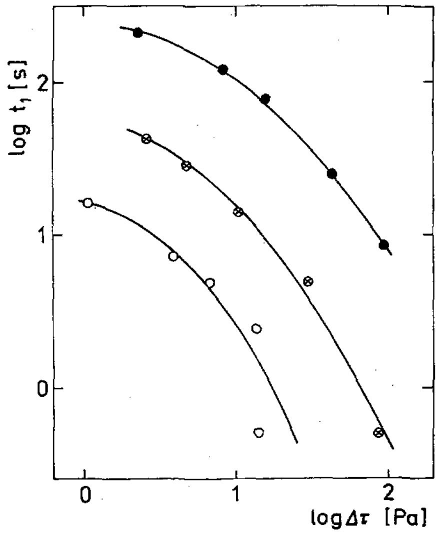
Fig. 6 Dependences of minimum shear stress $\tau^{\text{II}}_{\text{min}}$ on degree of ionization α. PHPAA concentration 1440 ppm, 85% aqueous glycerol



The influence of glycerol content on induction periods

To compare the influence of glycerol content on the induction period, plot t_1 vs. shear stress increment $\Delta\tau = \tau_0 - \tau^{\text{II}}_{\text{min}}$ should be the most suitable [7]. It is apparent, Fig. 7, that the shapes of these dependences for different composition of the solvent are similar, but the individual curves shift to higher values of induction periods with increasing glycerol content. Assuming type II of negative thixotropy to be a process of shear-induced crosslinking of primary chains [10] and postulating that induction period corresponds to a certain critical number

Fig. 7 Dependence of induction periods t_1 on the increment of shear stress $\Delta\tau = \tau_0 - \tau^{\text{II}}_{\text{min}}$ in aqueous glycerol (wt.%): 50 - (○), 75 - (⊗) and 90 - (●). PHPAA concentration 1500 ppm



of crosslinks formed in the system, it was derived [7] :

$$t_1 \cdot A = K \cdot [F(\Delta\tau)]^{-1} , \tag{1}$$

where frequency factor A for was expressed as a sum of two terms corresponding to collisions of polymer coils caused by thermal motion and describing collisions caused by flow. $F(\Delta\tau)$ is a universal function of the shear stress increment and K is a constant at a given molecular weight of polymer and its concentration. Since the 1500 ppm PHPAA concentration is more than ten times higher than c^*, polymer coils cannot move independently and such expression for collision frequency cannot be used. Let us suppose that in an undiluted polymer solution of a more uniform distribution of a polymer material than in dilute solution, the collision frequency is in the first approximation determined by thermal motion of polymer segments of activated macromolecules which should be inversely proportional to solvent viscosity η_s. Consequently, the plot of t_1/η_s vs. $\Delta\tau$ at constant molecular weight of the polymer and constant temperature should be universal irrespective of solvent viscosity. It is apparent, Fig. 8, that this plot is common for the data obtained at different compositions of solvents. Thus, reduced thermal motion of polymer segments in more viscous solvent might prolong induction periods in mixtures with a higher glycerol content.

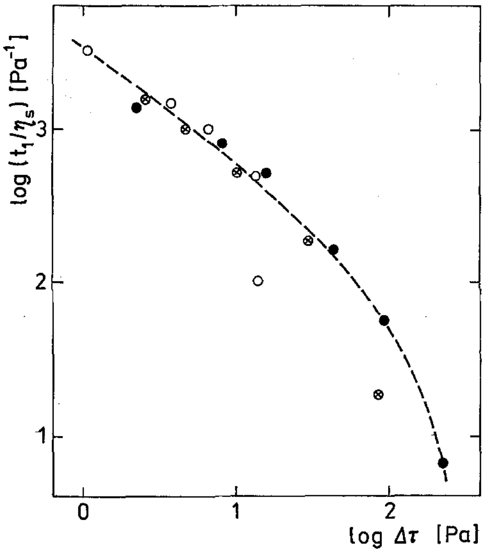


Fig. 8 Plot of the t_1/η_s ratio on the shear stress increment $\Delta\tau = \tau_0 - \tau^{\mathrm{II}}_{\min}$. η_s is solvent viscosity. For the meaning of points see Fig. 7

Conclusion

Negative thixotropy seems to reflect a special type of the association process of macromolecules induced by shear field. Despite the fact that the effect has been studied experimentally in a great number of systems, its origin still remains unclear. It is obvious that rheological measurements are applicable only for indication of the effect; elucidation of the effect, however, requires other methods that would make possible a direct observation of structural changes of the system. For such investigation a slowly relaxing negative thixotropic systems will be required. The results of this study suggest that aqueous glycerol solutions of partially hydrolyzed polyacrylamide could meet such requirements.

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