Original Contributions

Negative thixotropy of solutions of partially hydrolyzed polyacrylamide. Part I: The influence of shear rate on time changes of flow characteristics

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Abstract: A strongly negative thixotropic behavior of solutions of partially hydrolyzed polyacrylamide in a glycerol-water mixture has been observed at high dilution. Using a Couette viscometer, time changes of viscosity at various shear rates were studied in detail.

Key words: Negative thixotropy; solutions of partially hydrolyzed polyacrylamide

Introduction

It has been reported [1, 2] that the viscosity-shear rate measurement of solutions of partially hydrolyzed polyacrylamide in a glycerol-water mixture is accompanied by shear thickening. We found that, under specific conditions, the viscosity of such polymer systems increases continuously during the measurement at constant shear rate. The effect is obviously negative thixotropy (antithixotropy), resulting from a specific ability of the system to form (probably by means of physical bonds) supermolecular structures in the flow field. In previous papers [3–10], we have described similar effects in poly(methyl methacrylate) solutions.

Despite a detailed investigation of negative thixotropic behavior, its mechanism is not yet clear. It seems that solutions of partially hydrolyzed polyacrylamide are a very interesting material for this purpose, because the effect sets in at a very low polymer concentration, and relaxation of the negative thixotropic structure proceeds very slowly. The objective of this study is a verification of the existence of the effect of negative thixotropy in this system at various shear rates.

Experimental

Polymer

Polyacrylamide, partially hydrolyzed (31.2% of NH₂ functional groups substituted by the carboxyl groups) was provided by BASF as sample No 2005/20 (below, only PHPAA). The molecular weight determined by low-angle light scattering in 0.1 M aqueous NaCl solutions was $7 \times 10^6$.

Preparation of solutions

A weighed quantity of the polymer was dissolved in distilled water (conductivity 3.8 $\mu$S/cm), and glycerol was added so that its total concentration was 75 vol.%. The polymer concentration in such solution was 0.03 g/ml.

Viscometry

To measure the time dependence of viscosity, a Couette rotational viscometer Rheotest 2 (Type RV Prüfgeräte-Werk Medingen, Dresden, FRG) was used with a S1 rotor of 39.2 mm diameter and a 0.8 mm gap, connected with a registration millivoltmeter (Standard-Kompensationsschreiber G1B1, Zeiss, Jena, FRG). The apparatus made possible continuous registration of the dependence of shear stress of viscosity on the time of measurement at 24 values of the velocity gradient, ranging from 1.5 to 1312 s$^{-1}$. 
Dynamic measurements were performed using a Bohlin VOR rheometer at shear strains in the range 0.010–0.022. The reduced viscosity-polymer concentration dependence was measured in a capillary dilution viscometer of the Ubelohde type at shear rates about 9–25 s\(^{-1}\). Correction for the loss of kinetic energy and the end effect was negligible. All measurements were performed at 25 °C.

**Results**

Unlike solutions of poly(methyl methacrylate) of similar molecular weight, where the viscosity increased only after a certain induction period [5–10], in PHPAA solutions the viscosity rise set in practically immediately. The slope of the increase in viscosity and the shape of its time functions depended on the velocity gradient used (Fig. 1). At the gradient \(\dot{\gamma} = 40.4 \text{ s}^{-1}\) the total increase in viscosity was very small, at 24.3 s\(^{-1}\) it did not appear at all. With increasing velocity gradient the initial viscosity displayed a pseudoplastic decrease and its time dependence during the measurement rose more quickly.

The general character of viscosity-time dependences of both systems was also different. While in the case of poly(methyl methacrylate) solutions after the induction period the viscosity increased steeply to an extremely high value corresponding to the formation of a gel, in PHPAA solutions the slope of the viscosity-time dependences continuously decreased from the very beginning until constant viscosity was reached after a certain time. We believe that such differences in behavior may be a consequence of the quite different concentrations of the two polymers.

At higher velocity gradients a different behavior could be observed. After some time of shearing the slope of the viscosity-time dependences rose more slowly (at \(\dot{\gamma} = 364.5 \text{ s}^{-1}\)); its increase nearly stopped (at \(\dot{\gamma} = 656 \text{ s}^{-1}\), or it even decreased after only several seconds of flow (at \(\dot{\gamma} = 1312 \text{ s}^{-1}\)). Such course with a maximum can be explained by the competition between the formation of a supermolecular structure on the one hand, and of its disintegration and degradation on the other, as the destruction of macromolecules due to extremely high shear forces arising during shearing of negative thixotropic structures at high flow rates sets in very easily [10].

**Discussion**

It is assumed that the negative thixotropy of polymer solutions is caused by intermolecular association of macromolecules in the flow field leading to a supermolecular structure. According to the dynamic measurements, such structure had a distinctly higher elasticity than the original solution (Fig. 2). To produce this effect, two requirements should be satisfied. First, the polymer system must

![Fig. 1](image1.png)  
**Fig. 1.** The time dependence of viscosity \(\eta\) of PHPAA solutions during shearing at different constant shear rates

![Fig. 2](image2.png)  
**Fig. 2.** Frequency dependences of the storage modulus \(G'\) (solid line) and the loss modulus \(G''\) (broken line) before (solid line) and after shearing (broken line) at the shear rate 387 s\(^{-1}\)