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Flow Properties of Liquid Crystals of Polypeptides

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Viscosities and normal stresses in steady shear flow and viscoelastic properties under oscillatory motion were measured on concentrated solutions of poly-γ-ethyl-L-glutamate, its equimolar mixture with the D-isomer, and poly-γ-benzyl-L-glutamate, especially when in a liquid crystalline state. With increasing polymer concentration, the steady shear viscosity increased noticeably because interactions among the polymer molecules became strong. It, however, underwent a marked decrease when the solution became liquid crystalline. Under the action of shear stresses, long rod-like molecular clusters are produced in the solution, and oriented in the direction of the flow showing a strong Weisenberg effect. Even in an isotropic state, aggregation of the polypeptide molecules and their orientation under shear stresses were observed. When the shear rate increased, the steady shear viscosity decreased because of the orientation of the molecular clusters or of the aggregates in which their degradation was involved. Some differences in the flow properties were seen among the systems being observed.

INTRODUCTION

When liquid crystalline solutions of poly-γ-benzyl-L-glutamate (PBLG) are subjected to a static electric field as low as, say 84 V/cm, molecular clusters having huge permanent dipole moments are produced, and they orient quite well in the direction of the electric field[1,2]. The liquid crystalline solutions placed in an electric field show small-angle light scattering patterns typical of rod-like particles; their length is proposed to be about 25 μ.[3] NMR measurement of these solutions has suggested the presence of free solvent molecules which are not incorporated in the molecular clusters.[4] However, it should be noticed that the molecular clusters behave as if they are quite independent of each other in dilute liquid crystalline solutions (with concentrations still above Robinson's B-point[5]), and that in high electric fields intermediate regions among the molecular clusters become more or less indistinguishable, suggesting that a transition to a well oriented (and continuous) nematic structure has taken place.[3] Magnetic fields acting on the anisotropy of the magnetic susceptibility exert torques within the liquid crystalline phase of PBLG,[6] and produce molecular clusters that orient in the field direction.[7,8] This field effect is also observed in liquid crystalline solutions of poly-γ-ethyl-L-glutamate (PELG) and those of an equimolar mixture of PELG and its D-isomer (PEDG).[9] They occur whether the starting solution is cholesteric or not.

The rod-like molecular clusters are also produced in liquid crystalline solutions under shear stresses, and measurements of flow properties on these solutions have been proposed to supply useful information about the mechanism of the formation of the molecular clusters and about their shape and size.[10] Rheological studies on liquid crystals have been summarised by Porter and Johnson.[11] In this review, a few works on liquid crystalline phases of PBLG and PBDG[12-14] are cited and some distinct results are introduced. These results will be referred to later in the text. The purpose of this paper is to report new findings about the flow properties of concentrated solutions of polypeptides, especially in the liquid crystalline state, and to give some idea about the molecular clusters that are formed under the action of the shear stresses.

EXPERIMENTAL PROCEDURES

The polypeptides used were PELG, PEDG and PBLG. The PELG and PEDG were donated by Dr. S. Mori of Ajinomoto Co., Ltd., as ethyl acetate solutions with intrinsic viscosities 1.40 and 1.42, respectively, in dichloroacetic acid at 30 °C, and were used after being dried. If the mathematical equation for PBLG given by Doty et al[15] holds good in these polypeptides, their mean degree of polymerization (DP) turns out to be about 1500. The PBLGs were of mean DPs from 70 to 1460, and were prepared from the N-carboxy-α-amino acid anhydride of γ-benzyl-L-glutamate by Professor T. Hayakawa of this Faculty except for the DP 1460 specimen that was purchased from Pilot Chemicals Inc. (lot # G-141). PELG, an equimolar mixture of PELG and PEDG, or PBLG was dissolved in a solvent such as CH_2Br_2 or 1,4-dioxane that allows the formation of liquid crystals (and of α-helices), and was kept a few weeks in a sample tube at room temperature. Solutions with concentrations of 7 volume per cent or less were isotropic, those with concentrations 8.5 and 11.5 volume per cent were partly liquid crystalline, and those with concentrations 13 volume per cent or more were fully liquid crystalline; the liquid crystalline phase was nematic in CH_2Br_2 and cholesteric in 1,4-dioxane.

Using a multipurpose rheometer (a cone-and-plate rheogoniometer manufactured by Iwamoto Seisakusho Co., Ltd.), viscosities and normal stresses were measured at shear rates from 0.2 to 200 sec^{-1}, and dynamic properties at frequencies from 0.02 to 2 Hz. A three-dimensional structure (especially of cholesteric solutions) originally present in a sample tube was considered to be partly destroyed when the solution was introduced in the sample space of the rheometer. It was not possible to control the state of the solution to always get reproducible results. The temperature of the sample solutions was regulated at 22 °C in the closed chamber of the apparatus. No measurement at higher temperatures was carried out because the solutions were easily dried up. The increase of the solution temperature under shear stresses was less than 0.5 °C even at the highest shear rate, therefore, it was decided that temperature effects need not be taken into consideration in this study.

RESULTS AND DISCUSSION

Poly-γ-ethylglutamates

Viscosity versus shear rate plots of concentrated solutions of PELG and of the equimolar mixture of PELG and PEDG are shown in Figure 1. Without regard to the state of the initial solution, the viscosity decreases when the shear rate increases; Yang[12] observed similar results on isotropic *m*-cresol solutions

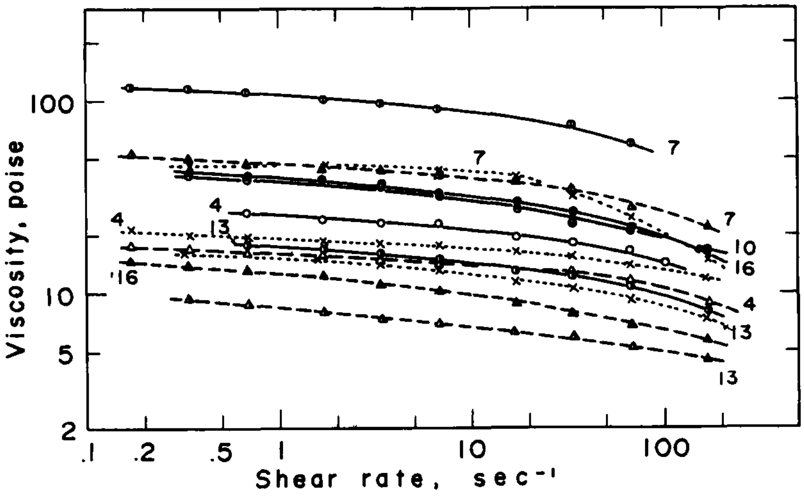

FIGURE 1 Apparent viscosity *vs.* shear rate relationship. Full lines, PELG in 1,4-dioxane; broken lines, PELG in CH_2Br_2; dotted lines, equimolar mixture of PELG and PEDG in CH_2Br_2. The numbers near the lines represent the polymer concentration in vol %.

of PBLG. According to Yang, the α-helix of the rod form remains stable even when subjected to a stress of 5×10^4 dynes/cm². In this study the maximum stress is about 1/10 of that value, and the rod form is stable. The decrease in the low shear rate region would mainly be caused by the destruction of the three-dimensional structure originally present in the initial solution. However, the decrease in the high shear rate region is mainly due to the orientation of molecular aggregates (or of molecular clusters) in the direction of the flow. Figure 2 shows how the reduced viscosity, η_{sp}/c, at a specific shear rate of 3.4 sec^{-1} and the dynamic elastic modulus, G', at a specific frequency of 0.33 Hz change when the polymer concentration increases. The reduced viscosity begins to increase noticeably at about 2 volume per cent, indicating marked interactions among the polymer molecules, and it has the maximum value at about 7 volume per cent. This concentration corresponds to Robinson's A-point at which a liquid crystalline phase begins to appear in solution. According to Flory[16] this is given approximately by the equation, $\phi^* = (8/p)\,(1 - 2/p)$ where ϕ^* is the critical concentration expressed in volume fraction and p is the axial ratio of the polymer molecule. This relationship holds good in the system of PBLG-*m*-cresol.[13] In this case p is calculated to be approximately 110, which seems reasonable for the DP 1500 specimen. The liquid crystalline phase is caused by restrictions on rotation, which in turn are caused by volume exclusion for the polymers (of high axial ratios), and is accompanied by the sharp decrease of

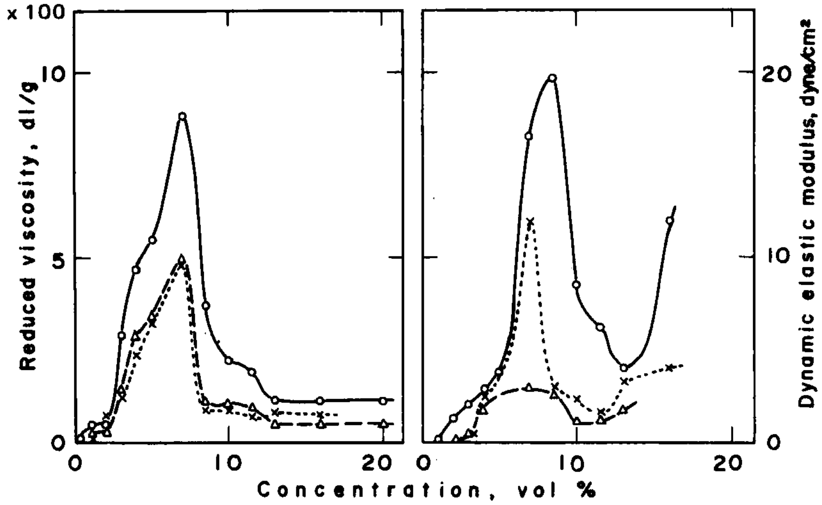

FIGURE 2 Reduced viscosity *vs.* polymer concentration and dynamic elastic modulus *vs.* polymer concentration relationships. Left: reduced viscosity measured at a shear rate of 3.4 sec^{-1}; right: dynamic elastic modulus measured at a frequency of 0.33 Hz. Lines, same as in Figure 1.

the reduced viscosity. The magnitude of the reduced viscosity has a small shoulder around 10-12 volume per cent where the isotropic and the birefringent phase coexist, decreases a little more and becomes almost constant after the polymer concentration is beyond 13 volume per cent; this concentration coincides with Robinson's B-point (above that the solution becomes fully liquid crystalline). These behaviors are quite similar to those of *m*-cresol solutions of PBLG as observed by Hermans.[13] In this connection, Robinson[14] has observed a viscosity reduction of 60% on increasing the concentration of PBLG from 19 to 30 weight per cent in 1,4-dioxane. Kuroiwa[17] has reported a similar behavior of concentrated aqueous solutions of non-ionic surface active agents. The feature of the concentration dependence of the dynamic elastic modulus is the same as that seen for the reduced viscosity, except for the sharp increase of the modulus after becoming fully liquid crystalline.

The dynamic elastic modulus and the dynamic loss modulus of the solutions are shown in Figure 3 with respect to frequency. If these moduli are compared at specific frequencies with the polymer concentration, the solution is seen to become slightly more elastic with increasing polymer concentration. Even in the liquid crystalline phase, its nature is that of a liquid rather than of a crystal. (The cholesteric solution will be highly elastic if the continuous structure is perfectly preserved.) With viscoelastic substances, the dynamic elastic modulus increases and the dynamic loss modulus decreases with increasing frequency. This tendency of the frequency dependence is naturally more noticeable in the isotropic solutions.

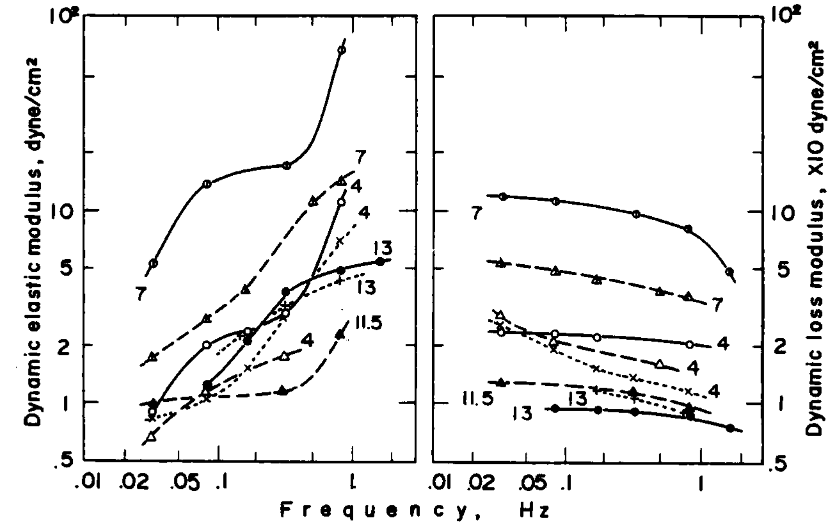

FIGURE 3 Dynamic properties *vs.* frequency relationships. Measured at a frequency of 0.33 Hz. The lines and the numbers, same as in Figure 1. Amplitude of the oscillatory motion of the plate of the rheometer was 0.93°.

In a previous paper[10] the author reported on the Weisenberg effect on concentrated solutions of PBLG. The extinction angle, χ, of the solution that is related to the orientation factor, F, was calculated by substituting the values of the total normal stress, f, and viscosity, η, of the solution into the equation[18],

$$\cot 2\chi = (f/\pi R^2)/\eta\lambda$$

where R and λ are the radius of the cone (and of the plate), 3 cm in this case, and the shear rate, respectively. Some of the results are shown in Figure 4 as a function of shear rate. The cone angle was 1,76°, and the cone was pushed up by 50 μ at the maximum stress of 100 g. Therefore, the shear rate became somewhat non-uniform and lowered, which should be taken into consideration. With increasing shear rate, the extinction angle decreases, starting from 45°; this change indicates the orientation of the rod-like particles present in solution. Using the results shown in Figure 4, the rotational diffusion constant, D_r, and F were read from the tables given by Scheraga et al.[19] The apparent length of the particle was calculated using the equation derived by Perrin,[20]

$$D_r = (3kT/16\pi\eta_0 a^3)(-1 + 2\ln(2a/b))$$

where k, T, and η_0 are the Boltzmann's constant, absolute temperature, and viscosity of the solvent, respectively. The particle was assumed to be a rotational ellipsoid with an axial ratio, $p(=a/b)$. The results are summarized in Table I. As this

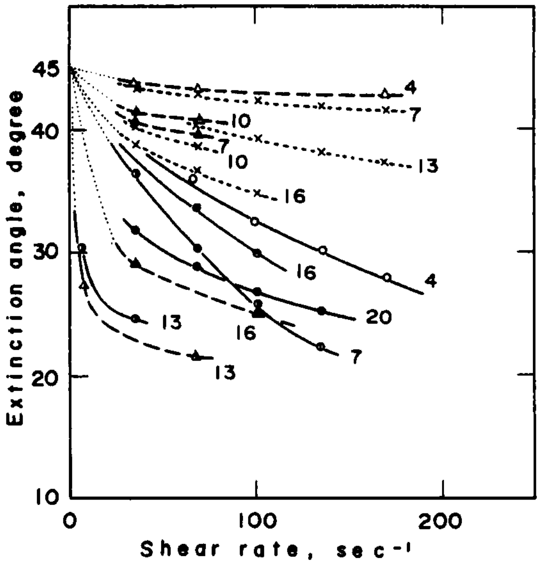

FIGURE 4 Extinction angle as a function of shear rate. The lines and the numbers, same as in Figure 1.

TABLE I

Apparent length of particles and their orientation factor

Solute	Solvent	4	7	10	13	16	20 vol%
PELG	CH_2Br_2	0.38	0.67	0.62	2.27	1.20	
		0.36	0.60	0.56	1.00	0.78	
		(0.02)	(0.07)	(0.05)	(0.35)	(0.28)	
	dioxane	0.65	0.75	0.96	1.88	0.70	1.00
		0.60	0.75	0.72	1.00	0.64	0.75
		(0.17)	(0.25)	(0.26)	(0.29)	(0.23)	(0.26)
Equimolar PELG + PEDG	CH_2Br_2		0.45	0.66	0.58	0.74	
			0.38	0.60	0.48	0.60	
			(0.03)	(0.09)	(0.10)	(0.15)	
PBLG	CH_2Br_2	1.40	1.34				
		0.73	0.91				
		(0.29)	(0.30)				
	dioxane	0.46	0.87	2.24	1.00		
		0.42	0.73	1.00	0.47		
		(0.07)	(0.18)	(0.39)	(0.04)		

The units are in micron. Upper, calculated at 10–20 sec^{-1}; lower, at 90–130 sec^{-1} (The values in the parentheses represent the orientation factors). The axial ratio of the particle was tentatively assumed to be 10. If it is assumed to be 5 or 100, the particle lengths are about 10% shorter or about 25% longer, respectively. The degree of polymerization for PBLG is 630. As for the decrease of the particle length in high-concentrated solutions, the following would be suspected: (1) the application of Perrin's equation was not adequate, and (2) the degradation of the molecular clusters occured prominently because of increased opportunity for collision among them.

equation is based on the assumption that the particles in solution do not interact with each other, there is left room for discussion in applying the equation to concentrated solutions with particles having dipole moments. However, the results will give a rough idea about the size of particles and their orientation. The apparent particle length may be seen to be larger than the particle length of the single polymer, 0.22μ even in the isotropic state. It may be seen that the particle length increases noticeably in the liquid crystalline state (especially when the polymer concentration is beyond the B-point). This indicates the formation of larger particles, that is, molecular clusters.

According to Wada's dielectric[21] and Watanabe's electric-birefringent[22] measurements, PBLG molecules aggregate side-by-side in 1,4-dioxane and head-to-tail in $CHCl_3$ or $C_2H_4Cl_2$ (this may be true also in CH_2Br_2) when in the isotropic state. This may be the case also in PELGs; however, a lengthwise aggregation would be present in addition to the side-by-side aggregation found in

1,4-dioxane. The difference in the type of molecular aggregation would probably also be true in liquid crystalline solutions. The polymer molecules present a parallel or nearly parallel orientation within the molecular cluster as Mark and Tobolsky[23] have pointed out. In this connection, stackings of the benzene groups among the neighboring polypeptide chains of PBLG have been proposed to appear in liquid crystalline solutions that have been measured for circular dichroism.[24] It may also be seen that the apparent particle lengths are shorter when estimated at a higher shear rate especially in liquid crystalline solutions. This would indicate the degradation of the molecular aggregates. In fact, the liquid crystalline solution does not orient well after it is subjected to the action of high shear stress for a long time.[9] The blend solutions do not show the large concentration dependence of the particle length. Still, the distinct electric-field or magnetic-field orientation takes place only when in the liquid crystalline state.[8,9] Thus, there are some differences in the flow property among the systems being observed. By the way, the cholesteric structure of the PELG-dioxane system (and of PBLG-dioxane system) appears only when the solution thickness is beyond 0.25 mm; molecular clusters are formed whether the initial solution is cholesteric or not, and their electric or magnetic properties do not seem to be different in the two cases.[3,8]

Poly-γ-benzyl-L-glutamate

Figure 5 shows the steady shear viscosity *vs.* shear rate relationship for PBLG. The viscosity decreases with increasing shear rate as in the case of PEGs. At high shear rates, this decrease is more noticeable in liquid crystalline solutions, and is due to the orientation (and the degradation) of the molecular clusters. Even at the highest shear rate, the shear stress was well below 5×10^4 dynes/cm^2. It has been suggested that[25] PBLG in *m*-cresol occurs as an α-helix in the anisotropic solutions, but as probably a 3.0_{10} helix characterized by a 2.0 Å per monomer unit repeat distance in the isotropic solutions. However, this is not the case in CH_2Br_2 or 1,4-dioxane. If the reduced viscosities are compared at specific shear rates with the polymer concentration, the same relationship as seen in PEGs may be obtained. This indicates that there is essentially no difference between the two systems of polypeptides. The A-point was 7 volume per cent, which is somewhat lower than the expected value for the DP 630 specimen whose axial ratio is estimated to be about 50. In Figure 6, the dynamic elastic modulus and dynamic loss modulus of the solutions are plotted against frequency. Here again the results obtained are similar to those observed in PEGs.

The extinction angle decreases with increasing shear rate as shown in Figure 7. When the shear rate was high, a tendancy to form a fiber appeared noticeably for the PBLG–CH_2Br_2 system especially when in the liquid crystalline phase; the real normal stress became impossible to measure. Calculated

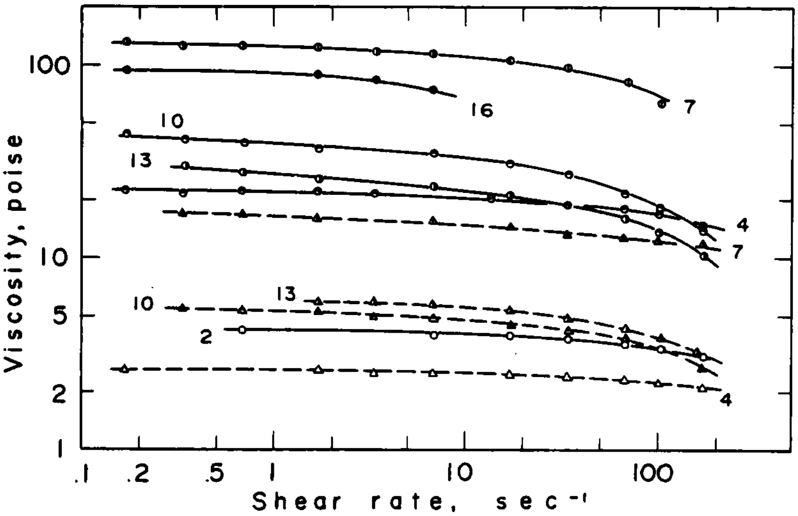

FIGURE 5 Apparent viscosity *vs.* shear rate relationship. Full lines, PBLG in dioxane; broken lines, PBLG in CH_2Br_2. The numbers near the lines represent the polymer concentration in vol%. Degree of polymerization was 630.

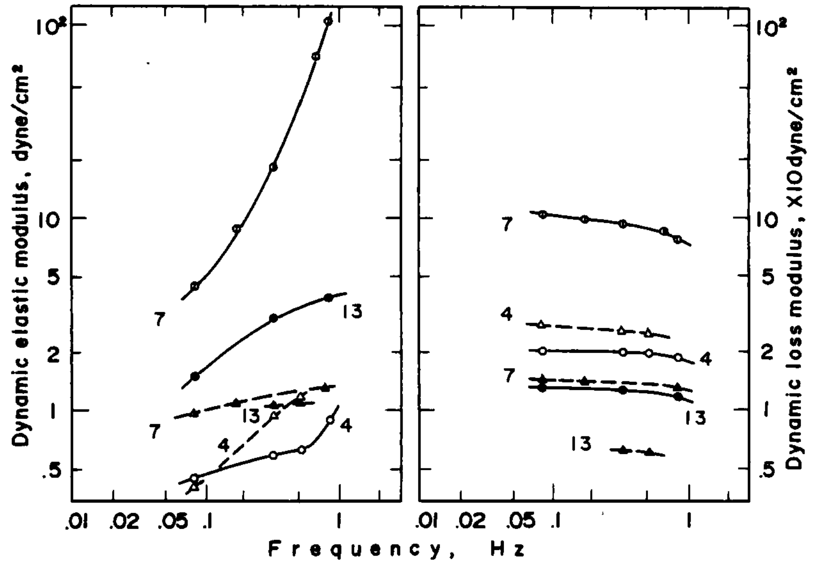

FIGURE 6 Dynamic properties *vs.* frequency relationships. The lines and the numbers, same as in Figure 5. Degree of polymerization was 630.

apparent particle lengths are shown in Table I. The mean length of the α-helical PBLG molecule of DP 630 is about 0.095 μ, and it may be seen that even in isotropic solutions the PBLG molecules aggregate to form long particles. The particle length is longer in CH_2Br_2 than in 1,4-dioxane which substantiates the idea of Wada and Watanabe. When the molecular clusters are formed, the particle length increases markedly. The calculated length, however, is shorter by far than the 25 μ length that has been proposed to explain the results of the small-angle light scattering measurement (see Ref. 3). This would be due mainly to the degradation of the molecular clusters under the action of shear stresses.

When the DP of PBLG increases, the reduced viscosity and the dynamic elastic modulus of the concentrated PBLG solutions change as shown in Figure 8. With increasing DP, both the reduced viscosity and the dynamic elastic modulus increase; the former more noticeably in the lower DP region and the latter more noticeably in the higher DP region. All the 4 volume per cent solutions were isotropic, but the 13 volume per cent solutions were anisotropic only when the DP was 630 or more. The maximum of the reduced viscosity seen in

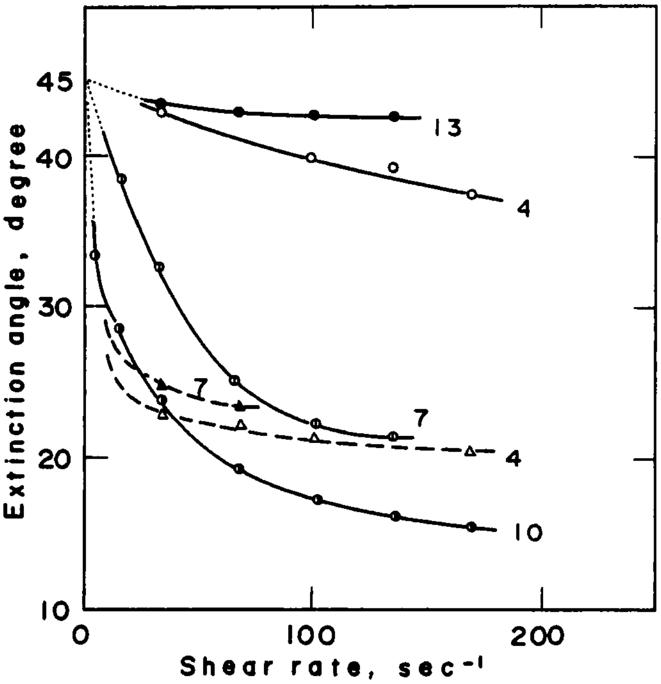

FIGURE 7 Extinction angle as a function of shear rate. The lines and the numbers, same as in Fifure 5. Degree of polymerization was 630.

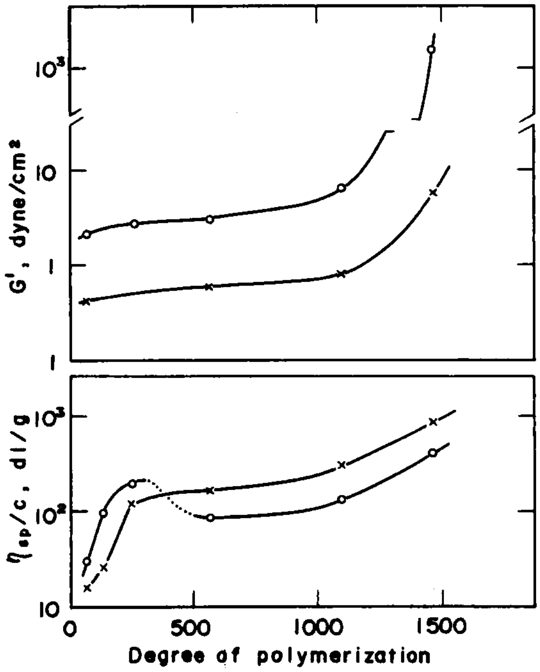

FIGURE 8 Reduced viscosity *vs.* degree of polymerization and dynamic elastic modulus *vs.* degree of polymerization relationships for PBLG in 1,4-dioxane. The viscosity was measured at a shear rate of 3.4 $\sec^{-1}$, and the elastic modulus, at a frequency of 0.33 Hz —o—, 13 vol%; —x—, 4 vol%.

the 13 volume per cent solutions is due to an isotropic–anisotropic transition. In the dynamic elastic modulus, this maximum is unexpectedly missing. The phase difference caused by variation of the viscosity and the elasticity are 87°, 77°, 73° and 21° for the DP 260, 630, 1100 and 1460 specimens, respectively, at 0.33 Hz for the 13 volume per cent solutions. The DP 1460 solution may be seen to be highly elastic and the others, to be rather viscous.

Acknowledgements

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