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Citation: *Journal of Rheology* (1978-present) **23**, 505 (1979); doi: 10.1122/1.549530

View online: <http://dx.doi.org/10.1122/1.549530>

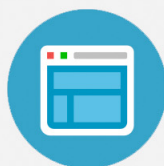
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Comparison of the Rheological Properties of Concentrated Solutions of a Rodlike and a Flexible Chain Polyamide*

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Synopsis

The steady state shear rheological properties of solutions of a rodlike polyamide, poly-*p*-phenyleneterephthalamide (PPT), in 100% sulfuric acid have been compared with those of solutions of a flexible chain polyamide, nylon 6,6, in the same solvent. For solutions of similar concentration (c) and molecular weight (M), it was found that the primary normal stress difference (N_1) and the viscosity (η), compared at the same shear rate ($\dot{\gamma}$), were an order of magnitude greater for solutions of PPT. It was believed that this behavior could be accounted for through the formation of an enhanced entanglement network in the PPT solutions. Plots of the zero shear viscosity (η_0) versus $c\bar{M}_w$, where \bar{M}_w is the weight average molecular weight, for both systems revealed that "bends" occurred in the data corresponding to a critical entanglement molecular weight (M_c) of 1180 for PPT (this corresponds to 30 main chain atoms (z)) and to 5260 ($z = 330$) for nylon 6,6. More significantly, η_0 was found to be proportional to $(c\bar{M}_w)^{6.8}$ for solutions of PPT and to $(c\bar{M}_w)^{3.4}$ for nylon 6,6 solutions. η versus $\dot{\gamma}$ curves were similar in shape for both systems and could be reduced to the same master curve with the only difference being that the relaxation times or shifting factors were considerably greater for the PPT solutions. This suggested that the process of destroying entanglements may be similar for both polymers.

The overlap parameter $c[\eta]$, where $[\eta]$ is the intrinsic viscosity, provided a much better correlation of η_0 data from the two sets of solutions than did the segment contact parameter $c\bar{M}_w$. This suggested that the structural variable controlling the onset of entanglements may be a parameter such as the radius of gyration. Because of the inability of rodlike molecules to coil around each other, further insight into the nature of entanglements is obtained.

*Presented at the 48th Meeting of The Society of Rheology, October 23–26, 1977, Madison, Wisconsin.

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Journal of Rheology, 23(4), 505–524 (1979) 0148-6055/79/0023-0505\$01.00

INTRODUCTION

The rheological properties of concentrated solutions and melts of flexible chain polymers point clearly to a universal physical interaction between chain molecules which are referred to as chain entanglements. For example, the dependence of the zero shear viscosity (η_0) on the 3.4 power of molecular weight (M), the change in the form of the steady state compliance (J_e^0) from M/cRT to $1/c^2RT$, where c is the concentration in g/ml, R is the gas law constant, and T is the temperature, and the appearance of a plateau in the relaxation modulus all depend on the Bueche segment contact parameter (cM), which is a measure of the number of intermolecular contacts per molecule.¹ The concept of a physical interaction rather than intermolecular attractive forces is well documented for nonpolar, non-crystallizable, flexible molecules.²

The exact nature of an entanglement, however, is not known. One view is that two chains are tightly kinked around each other by bending back on themselves in short-range contour. Another is that coupling involves looping of chains around each other in their long-range contour.^{3,4} Studies on the flow properties of relatively stiff and extended molecules such as cellulose derivatives,⁵ deoxyribonucleic acid,⁶ and a helical polyamino acid⁷ have shown these molecules to exhibit the effect of entanglement coupling even more prominently than do highly flexible polymers. These results have prompted Ferry and coworkers to conclude that the latter of the above two explanations is more plausible.⁸ However, these molecules are only semirigid and may still coil or loop around each other to some degree. As pointed out by Graessley in a recent review,² studies on the rheological properties of systems of rodlike molecules are not well documented. Further studies on systems of truly rodlike molecules are needed.

In the last few years a series of rigid, rodlike synthetic polymers such as poly-*p*-benzamide (PBA) and poly-*p*-phenyleneterephthalamide (PPT) have been synthesized and solution spun into fibers of ultra-high strength.^{9,10} These two polymers are believed to be highly rigid and extended for several reasons. First, Mark-Houwink exponents (α) as high as 1.7 have been reported.^{11,12} Second, solutions of these polymers exhibit liquid crystalline behavior at concentrations in agreement with the predictions of Flory's theory, which is based on the packing of rodlike molecules into solution.^{14,15} Finally, the structure and physical properties of fibers and films produced from these polymers suggest that the molecules are rodlike.^{16,17}

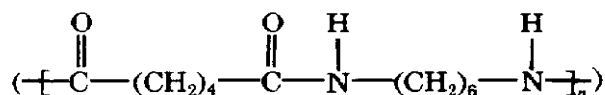
There have been only a few studies reported on the rheological properties of PBA and PPT and related rigid polymers.^{14,18,19} In one case, some interesting differences between the rheological properties of rigid and flexible chain polymers were noted. Papkov and co-workers¹⁴ reported for isotropic solutions of PBA in *N,N*-dimethyl acetamide that viscosity (η)–shear rate ($\dot{\gamma}$) curves plotted in reduced form as η/η_0 versus $\eta_0\dot{\gamma}$, where η_0 is the zero shear viscosity, which is the form predicted by Saito for rigid ellipsoids.²⁰ Furthermore, η_0 was observed to depend on $\bar{M}_w^{8.0}$ rather than $\bar{M}_w^{3.4}$, where \bar{M}_w is the weight average molecular weight. On the contrary, Berry¹⁸ observed for solutions of PPT and several other polymers thought to be only semirigid that the steady state rheological properties in general did not differ markedly from those of flexible molecules.

In this paper we studied the rheological properties of solutions of PPT in 100% H_2SO_4 measured in steady state shear. The concentration range was selected so that the solutions remained in the isotropic state. In order to compare the rheological properties of this rodlike molecule with those of a flexible molecule we also report data for solutions of nylon 6,6 in 100% H_2SO_4 . By selecting this system we are dealing with polyamides in both cases and the same complex solvent. Hence any differences observed in the two systems should be primarily the result of the polymer structure or its interaction with the solvent. The specific objectives of this work are (1) to determine the effect of chain stiffness on the rheological properties of polymer solutions; (2) to determine any rheological properties which are characteristic of rodlike molecules and which could be used to identify polymers with the potential for forming anisotropic solutions; and (3) to provide insight into the nature of chain entanglements.

EXPERIMENTAL

Polymers

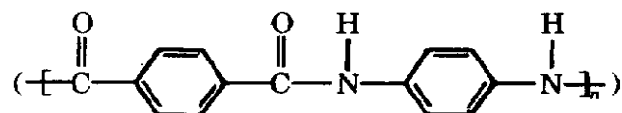
Nylon 6,6,



samples of various molecular weights were prepared by well-known solid state polymerization techniques. Molecular weight charac-

teristics were determined by means of gel permeation chromatography using hexafluoroisopropanol (HFIP) as the solvent. Values of \bar{M}_w and the ratio \bar{M}_w/\bar{M}_n , where \bar{M}_n is the number average molecular weight, are given in Table I.

PPT,



samples of various molecular weights were prepared as described elsewhere^{21,22} by reacting terephthaloyl chloride with 1,4-phenylenediamine in hexamethylphosphoramide. \bar{M}_w of these polymers was determined by light scattering from sulfuric acid solutions as described in another paper.¹² \bar{M}_w/\bar{M}_n was assumed to be about 2.0 since values of 1.8 were found for PBA, which is a similar polymer system.¹¹ A summary of the \bar{M}_w values is given in Table II.

Solutions

100% H_2SO_4 was used as a solvent for both polymers. Although this is a rather complex solvent because of its ability to dissociate into many complex ions,²³ it was selected because PPT is soluble only in strong acid solvents. PPT solutions of 0.004 g/ml to 0.16 g/ml were prepared (see Table II). For concentrations (c) above 0.16 g/ml the solutions became anisotropic for the highest-molecular-weight sample ($\bar{M}_w = 40,100$) and were not considered here. Nylon 6,6 solutions in the concentration range of 0.11–0.46 g/ml were prepared (see Table I). In order to observe any nonlinear rheological behavior for the nylon 6,6 solutions, the concentrations had to be considerably higher than for the PPT solutions.

Rheological Properties

Shear stress (τ) and primary normal stress (N_1) data were obtained under steady shear conditions at 24 and 60°C using the cone-and-plate geometry of the Rheometrics mechanical spectrometer (RMS). The plates were 5 cm in diameter and the cone angle was 0.04 rad. The torque and normal force measurements were reduced to the shear stress and primary normal stress difference, respectively, following well-known methods.²⁴

TABLE I
Rheological Parameters for Solutions of Nylon 6,6 in 100% H₂SO₄

[η] (dl/g)	\bar{M}_w	\bar{M}_w/\bar{M}_n	c (g/ml)	$c\bar{M}_w$	η_0	$J_e^0 \times 10^5$	J_{eR}	τ_0 (sec)	τ_R (sec)	T (°C)
0.64	14,500	2.01	0.117	1,697	8	—	—	—	—	24
0.98	25,100	2.14	0.117	2,940	20	0.68	0.26	<0.001	1.06×10^{-4}	24
1.06	35,200	2.01	0.117	4,120	34	1.26	0.34	0.001	2.5×10^{-4}	24
			0.240	7,180	180	1.11	0.53	0.002	7.6×10^{-4}	24
			0.406	16,200	3,180	0.68	0.73	0.015	0.006	
1.43	42,300	2.17	0.117	4,950	60	1.98	0.45	0.022	5.3×10^{-4}	24
			0.204	8,500	290	1.29	0.51	0.004	0.002	24
			0.460	19,500	5,760	0.63	0.56	0.031	0.013	24
1.86	54,300	2.52	0.204	11,100	660	2.43	0.75	0.010	0.004	24
			0.46	25,000	16,400	1.12	0.83	0.179	0.048	24
2.00	59,600	2.56	0.204	12,200	830	2.79	0.79	0.018	0.006	24
			0.46	27,400	20,700	1.19	0.76	0.165	0.066	24
2.09	63,000	2.56	0.240	15,300	1,020	2.50	0.67	0.019	0.008	24
			0.46	29,000	26,400	1.18	0.71	0.178	0.089	24
2.15	66,900	2.56	0.204	13,600	1,160	3.11	0.78	0.020	0.009	24
			0.46	30,800	20,700	1.19	0.76	0.400	0.074	24
2.35	73,200	2.56	0.117	8,560	300	1.23	0.70	0.005	0.005	24
			0.204	14,930	1,670	—	—	0.038	0.148	24
			0.46	46,850	64,000	—	—	0.588	0.565	24

TABLE II
Rheological Parameters for Solutions of PPT in 100% H₂SO₄

$[\eta]$ (dl/g)	\bar{M}_w	c (g/ml)	$c\bar{M}_w$	η_0 (P)	$J_e^0 \times 10^5$ (cm ² /dyn)	J_{eR}	τ_0 (sec)	τ_R (sec)	T (°C)
1.28	12,800	0.019	238	3	—	—	—	—	24
	12,800	0.117	1,500	80	—	—	0.010	0.002	24
2.07	20,200	0.117	2,422	1,430	2.77	1.32	0.032	0.010	24
2.68	23,700	0.019	440	20	—	—	—	—	24
3.43	27,600	0.117	3,230	5,200	2.90	0.96	0.106	0.033	24
4.35	32,000	0.077	2,464	270	2.50	0.50	0.006	0.003	24
	32,000	0.117	3,740	17,250	1.84	0.50	0.526	0.117	24
		0.160	5,120	47,500	1.69	0.50	0.580	0.235	24
9.4	40,100	0.038	1,484	650	5.85	0.45	0.022	0.017	24
		0.057	2,290	6,280	8.34	0.97	0.128	0.109	24
		0.077	3,088	30,500	2.56	0.40	0.330	0.393	24
		0.097	3,890	82,000	2.56	0.51	1.136	0.835	24
	32,000	0.077	2,460	110	2.48	0.55	0.004	0.001	60
		0.117	3,740	22,600	2.76	0.93	0.073	0.014	60
		0.160	5,120	159,000	2.32	1.07	0.339	0.069	60
	40,100	0.004	170	2	—	—	—	—	60
		0.038	1,520	120	7.78	0.68	0.015	0.003	60
		0.077	3,090	4,600	5.40	0.96	0.119	0.052	60
		0.117	4,690	156,000	3.51	0.95	0.617	0.232	60
		0.160	6,420	192,000	2.87	1.06	4.808	0.800	60

RESULTS AND DISCUSSION

Comparison of Rheological Properties

The steady state shear rheological properties of nylon 6,6 and PPT solutions having the same polymer concentration and similar \bar{M}_w are compared in Figs. 1 and 2. The zero shear viscosity (η_0) values of the PPT solutions are at least one order of magnitude higher than values of the nylon 6,6 solutions of similar c and \bar{M}_w . The onset of non-Newtonian behavior occurs at a $\dot{\gamma}$ about one decade lower for the PPT solutions. Likewise N_1 values measured at similar $\dot{\gamma}$ are about one order of magnitude higher for the PPT solutions.

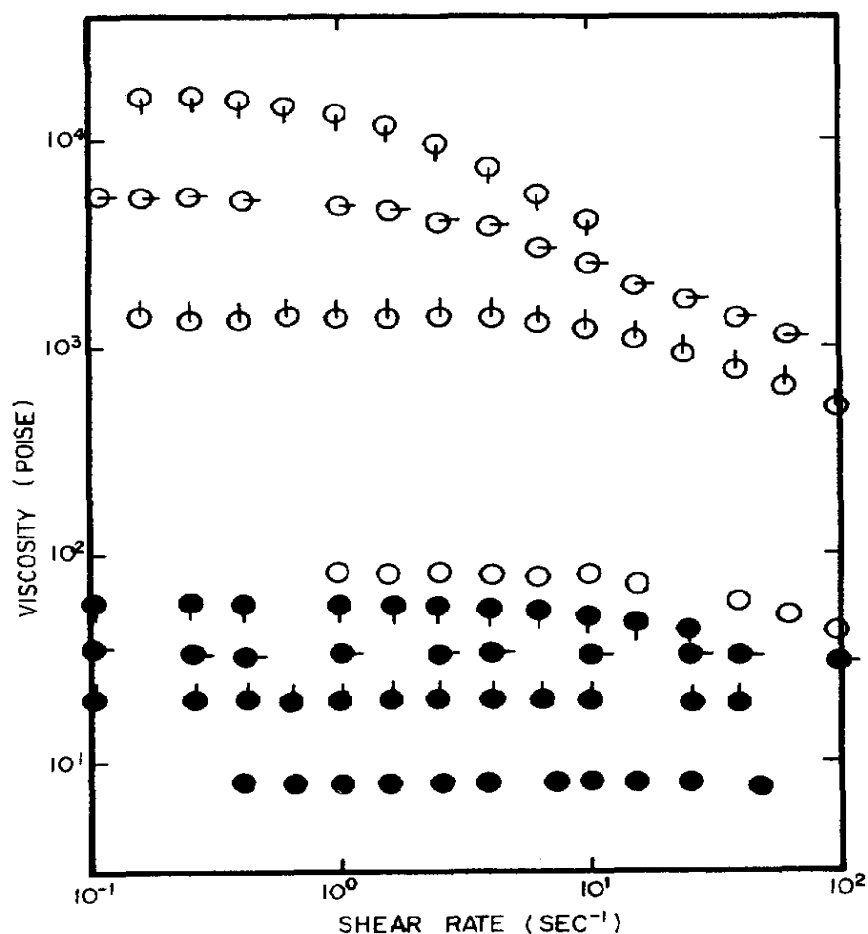


Fig. 1. Comparison of viscosity-vs-shear rate curves for solutions of nylon 6,6 and PPT in 100% H_2SO_4 both at a concentration of 0.117 g/ml and of similar molecular weights. For nylon 6,6: (\bullet) $\bar{M}_w = 14,500$, (\blacklozenge) $\bar{M}_w = 25,100$, (\blacktriangleright) $\bar{M}_w = 35,200$, (\blacklozenge) $\bar{M}_w = 42,300$. For PPT, (\circ) $\bar{M}_w = 12,800$, (\circ) $\bar{M}_w = 20,200$, (\circ) $\bar{M}_w = 27,600$, (\circ) $\bar{M}_w = 32,000$.

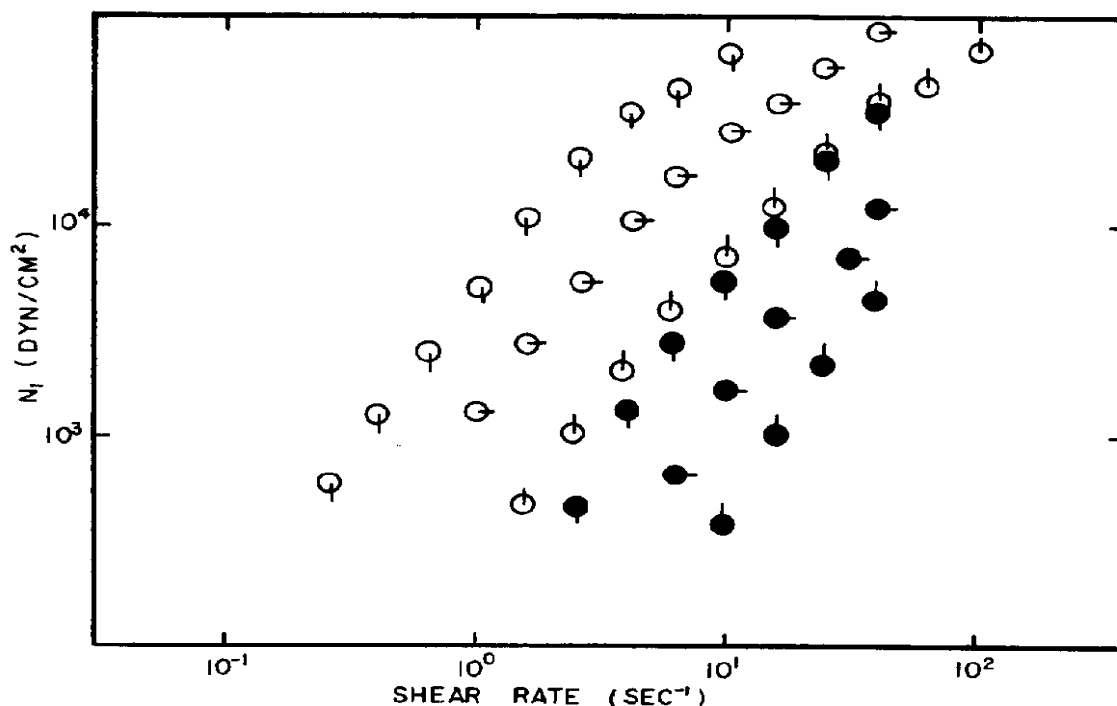


Fig. 2. The primary normal stress difference versus shear rate for solutions of nylon 6,6 and PPT in 100% H₂SO₄ both at a concentration of 0.11 g/ml and of similar molecular weights. The symbols are the same as in Fig. 1.

The manner in which chain stiffness contributes to the observed rheological properties of the PPT solutions is not clear. If we are dealing with dilute solutions, then the observed behavior could be accounted for (e.g., compare the predictions of the rigid and flexible dumbbell models²⁵). We are, however, dealing with conditions in which considerable coil overlap occurs. According to Frisch and Simha,²⁶ the product of c and the intrinsic viscosity $[\eta]$ is a measure of the degree of coil overlap in a solution. The onset of coil overlap begins near $c[\eta] = 1$ and free draining behavior starts near $c[\eta] = 10$.² For the nylon 6,6 solutions, $8 < c[\eta] < 17$, while for the PPT solutions $16 < c[\eta] < 47$. On the other hand, the number of intermolecular contacts as measured by the Bueche parameter $c\bar{M}_w$ lie in the same range for both solutions, i.e., $1500 < c\bar{M}_w < 5000$. Thus, in order to account for the differences in the rheological properties of the flexible and rigid polymers it becomes necessary to understand the nature of intermolecular contacts or "entanglements," what parameters control the onset of these entanglements, and whether there is any similarity in the nature of entanglements for rigid and flexible molecules.

Evidence for Entanglements

The most characteristic behavior cited as evidence for the onset of an entanglement network for concentrated polymer solutions is the rather abrupt change in the dependence of η_0 on $(c\bar{M}_w)$ to $(cM_w)^{3,4}$. In Fig. 3, $\ln \eta_0$ is plotted against $\ln c\bar{M}_w$ for both polymer solutions. Within each system the parameter $c\bar{M}_w$ provides a reasonable superposition of data obtained from solutions of varying c and \bar{M}_w . Bends occur in both sets of data, indicating the onset of an entanglement network. The critical value $(c\bar{M}_w)_c$ for PPT is about 1700 while for nylon 6,6 it is about 6000. We note also that this value for PPT is independent of temperature as data measured at 60°C yield $(cM)_c = 1800$. From these values of $(c\bar{M}_w)_c$ and using

$$(c\bar{M}_w)_c = \rho M_c, \quad (1)$$

where M_c is the critical molecular weight required for the formation of an entanglement network in undiluted polymer, it is estimated that $M_c = 1180$ ($\rho = 1.44 \text{ g/cm}^3$) for PPT and 5260 for nylon 6,6. For PPT this corresponds to 30 main chain atoms and to 326 for nylon 6,6, which is in the range of 300–700 main chain atoms observed for other flexible polymer systems for the onset of an entanglement network.²⁷ Furthermore, above $(c\bar{M}_w)_c$ η_0 becomes proportional to $(c\bar{M}_w)^{3,43}$ for nylon 6,6 solutions and to $(c\bar{M}_w)^{6,8}$ for PPT solutions. Thus, it appears that in stiff chain systems the entanglement network is enhanced.

In the next sections we attempt to determine whether the effects of an enhanced network are reflected in the $\dot{\gamma}$ dependence of η , the relaxation times, and the fluid elasticity.

Viscosity—Shear Rate Behavior

The shape of η versus $\dot{\gamma}$ curves is similar for many flexible chain polymers and when the curves are shifted parallel to the coordinate axes, they are found to fall on a single master curve.² One interpretation of this behavior is that the process of breaking up intermolecular interactions in a constant shear field is similar for many polymer systems.

We next compare the η versus $\dot{\gamma}$ behavior of PPT and nylon 6,6 solutions. Because the shape of the master curve depends on the molecular weight distribution, we have selected a theoretical master curve proposed by Graessley²⁸ for polymers with $\bar{M}_w/\bar{M}_n = 2$ with

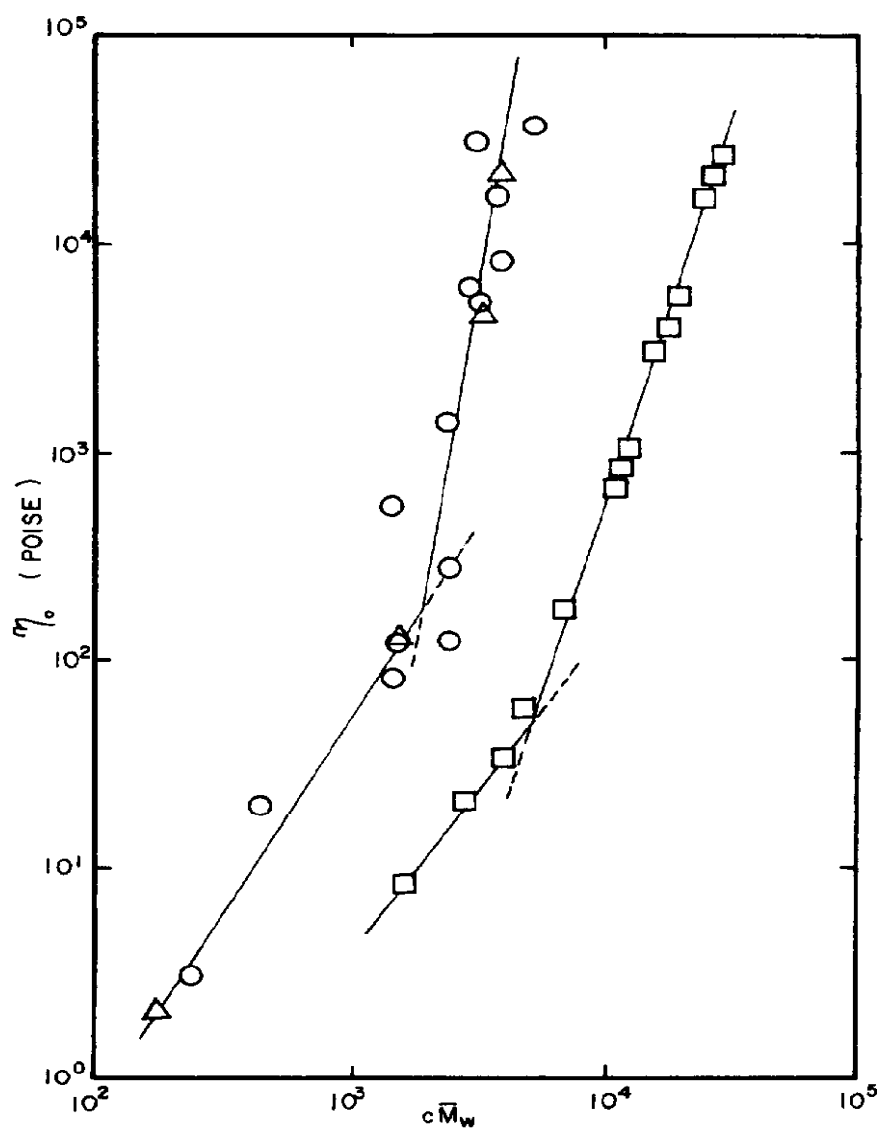


Fig. 3. Zero shear viscosity (η_0) versus the segment contact parameter ($c\bar{M}_w$) for solutions of nylon 6,6 (O) and PPT (\square) in 100% H_2SO_4 at 24°C. Data taken from Tables I and II and consist of different concentrations and molecular weights. (Δ) η_0 measured at 60°C and shifted vertically to show that ($c\bar{M}_w$) is independent of temperature.

which to compare our data. Although there are several questions about the origin and derivation of Graessley's theory, it has proven successful in several instances^{29,30} and for this reason will be used here. Representative η versus $\dot{\gamma}$ data for nylon 6,6 solutions presented in Fig. 4 are shown shifted for best fit with the master curve in Fig. 5.

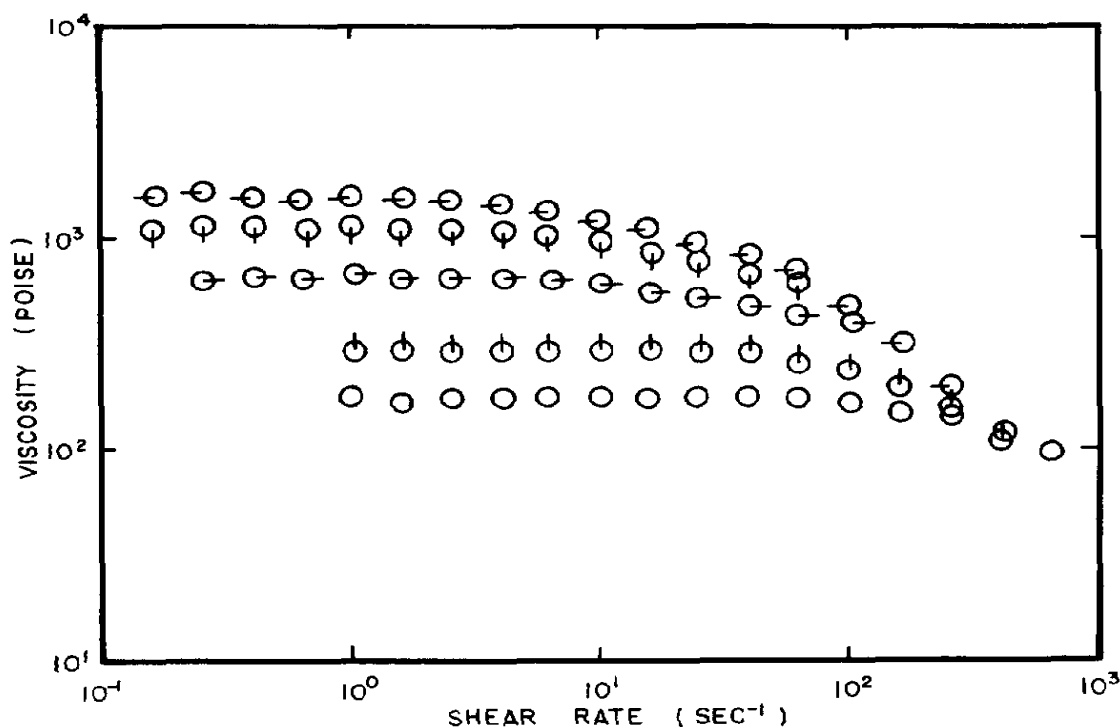


Fig. 4. Shear rate dependence of viscosity as a function of molecular weight for nylon 6,6/100% H_2SO_4 solutions. The data were obtained on samples all of the same concentration of 0.204 g/ml and at a temperature of 24°C . (\circ) $\bar{M}_w = 35,200$, (\circ) $\bar{M}_w = 42,300$, (\circ) $\bar{M}_w = 54,300$, (\circ) $\bar{M}_w = 66,900$, (\circ) $\bar{M}_w = 73,200$.

Likewise the η versus $\dot{\gamma}$ data for PPT solutions shown in Fig. 1 are shifted for best fit with the master curve and results are shown in Fig. 6. For both systems excellent agreement with the Graessley master curve was observed not only for the representative data shown above, but for other solutions of differing c and \bar{M}_w . The main difference was that the shifting factor or the relaxation time (τ_p) was considerably larger for the PPT solutions (see Tables I and II). Apparently, the enhanced network of the PPT solutions does not affect the shear rate dependence of η . In fact, these results suggest there may be some similarity in the breakup of entanglements for rigid and flexible molecules.

Comparison of Experimental and Rouse Relaxation Times

Graessley and Segal²⁹ reported for highly entangled solutions of polystyrene that experimental relaxation times (τ_0) obtained by shifting η versus $\dot{\gamma}$ data to a theoretical master curve were no longer

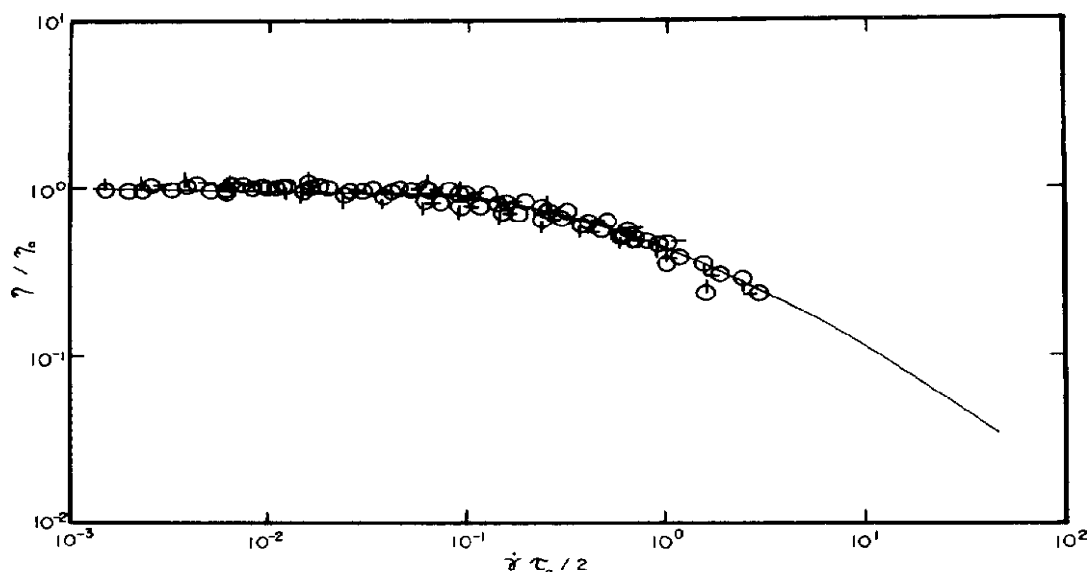


Fig. 5. Data of Fig. 4 shifted for best fit with Graessley's theoretical master curve for polymers with $\bar{M}_w/\bar{M}_n = 2$. Symbols are the same as in Fig. 4. Solid line represents theory.

simply related to the Rouse relaxation time τ_R but residual variations were noted which depended on ϕM in a form shown below:

$$\tau_0/\tau_R = \alpha_1/(1 + \beta_1\phi M), \quad (2)$$

where α_1 and β_1 are constants and ϕ is the volume fraction of polymer. Following the same procedure, values of τ_0 were obtained for both PPT and nylon 6,6 solutions and are summarized in Tables I and II. Values of τ_0/τ_R are plotted versus $\phi\bar{M}_w$ in Fig. 7 for both systems, where $\phi\bar{M}_w$ is proportional to the entanglement density.⁹ Although there is considerable scatter in the data, there is no tendency for τ_0/τ_R to depend on $\phi\bar{M}_w$ for PPT solutions. Only at large values of $\phi\bar{M}_w$ is there any indication that τ_0/τ_R depends on $\phi\bar{M}_w$ for nylon 6,6 solutions.

The fact that τ_0 is in general simply related to τ_R for both systems is rather puzzling. We are dealing with solutions for which values of $c\bar{M}_w$ are considerably greater than those of $(c\bar{M}_w)_c$. Furthermore, since η_0 is so strongly dependent on $c\bar{M}_w$ for PPT solutions, one might expect values of τ_0 to no longer be simply related to τ_R . It may be that although we are above $(c\bar{M}_w)_c$, a residual dependence on $c\bar{M}_w$ may only arise for polymers of very high molecular weight. Graessley and Segal were dealing with very-high-molecular-weight polystyrenes, some of which had values of \bar{M}_w as high as 3,370,000.

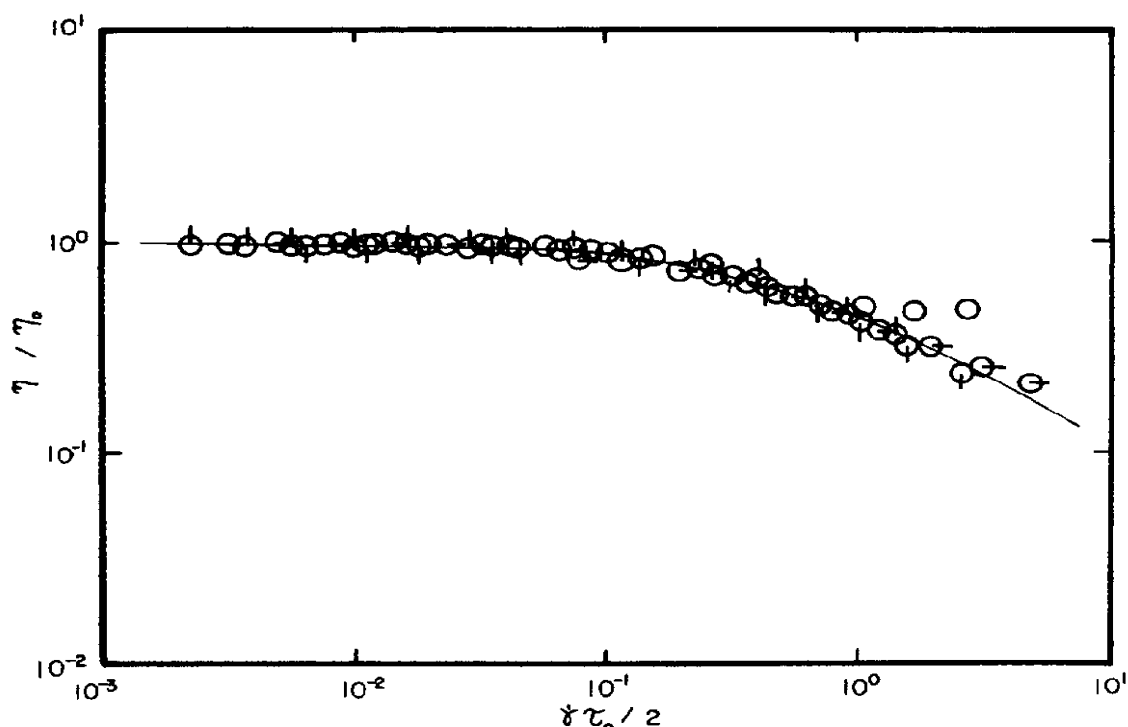


Fig. 6. Viscosity data of Fig. 1 for PPT solutions shifted for best fit with Graessley's master curve for polymers with $\bar{M}_w/\bar{M}_n = 2$. Symbols are the same as in Fig. 1. Solid line represents theory.

Elastic Properties

Finally, the onset of an entanglement network should be reflected in the elastic properties of the solutions. The steady state compliance (J_e^0) is used as a measure of fluid elasticity, since it is related to the recoverable shear strain γ_r and the shear stress (τ) by the following relation³¹:

$$\gamma_r = J_e^0 \tau. \quad (3)$$

Values of J_e^0 were obtained by plotting N_1/η^2 versus $\dot{\gamma}^2$ and using the following relation:

$$J_e^0 = \frac{1}{2} \min_{\dot{\gamma} \rightarrow 0} \frac{d \ln(N_1/\eta^2)}{d \ln \dot{\gamma}^2}. \quad (4)$$

Such plots consistently gave straight lines over a fairly large $\dot{\gamma}$ range, as illustrated in Fig. 8. The linearity of such plots is a consequence of Hooke's law in shear.³²

As suggested by dilute solution molecular theories, J_e^0 is analyzed in reduced form for polydisperse systems as follows:

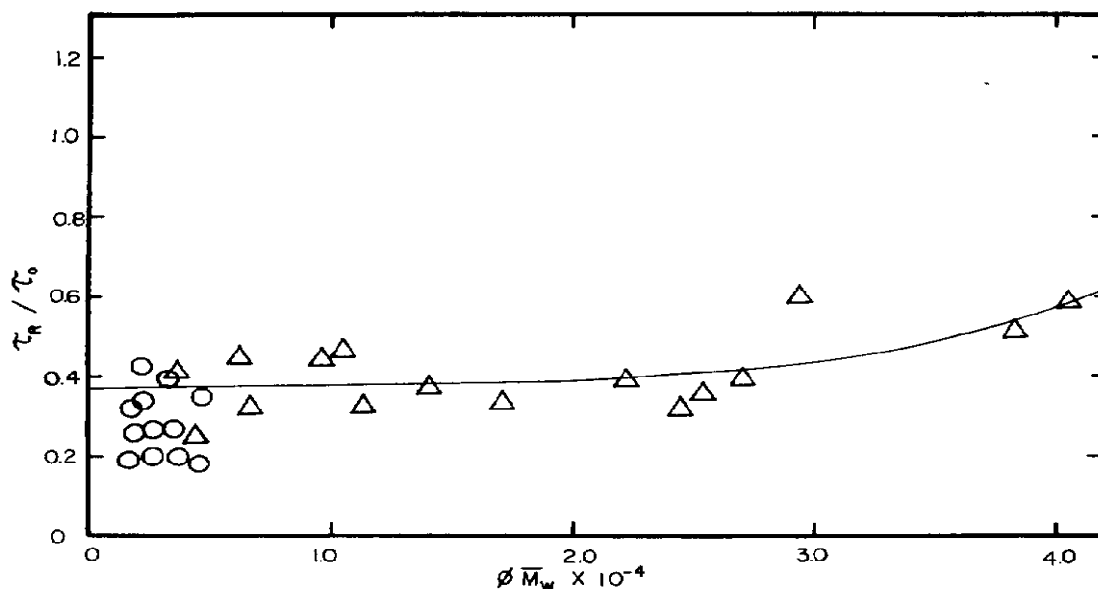


Fig. 7. Viscosity time constant ratio versus the product of the volume fraction and \bar{M}_w : (O) PPT data from Table II; (Δ) nylon 6,6 data from Table I.

$$J_{eR} = \frac{J_e^0 c R T \bar{M}_w^2}{M_w \bar{M}_z \bar{M}_{z+1}} \quad (5)$$

For $\bar{M}_w/\bar{M}_n = 2$, $\bar{M}_z \bar{M}_{z+1}/\bar{M}_w^2 = 3$. Values of J_e^0 and J_{eR} are given in Tables I and II and plotted in Fig. 9 for both systems as a function of $c\bar{M}_w$. For nylon 6,6 solutions, J_{eR} rises from a value of about 0.2 to values of about 0.7–0.8. The dependence of J_{eR} on $c\bar{M}_w$ at low values of $c\bar{M}_w$ presumably reflects the change from Zimm to Rouse-like behavior. The values of 0.7–0.8 are somewhat higher than the value of 0.4 predicted by the Rouse theory, but are definitely independent of $c\bar{M}_w$. The higher values of J_{eR} can probably be accounted for by the difficulties encountered in determining J_e^0 and the polydispersity of the samples. On the other hand, for PPT J_{eR} varies from 0.4 to 1.3, but no dependence on $c\bar{M}_w$ is observed for either low or high values of $c\bar{M}_w$. However, this is to be expected for low values of $c\bar{M}_w$ since dilute solution theories for rigid macromolecules predict J_{eR} to be 0.6.²⁵

Again, although we are well above $(c\bar{M}_w)_c$, and apparently an entanglement network exists, J_e^0 is still of the form M/cRT rather than $1/c^2RT$. The only explanation for this is that the change in behavior of J_e^0 occurs at values of $c\bar{M}_w$ approximately 3–4 times $(c\bar{M}_w)_c$,² and we are only approaching these values with our data.

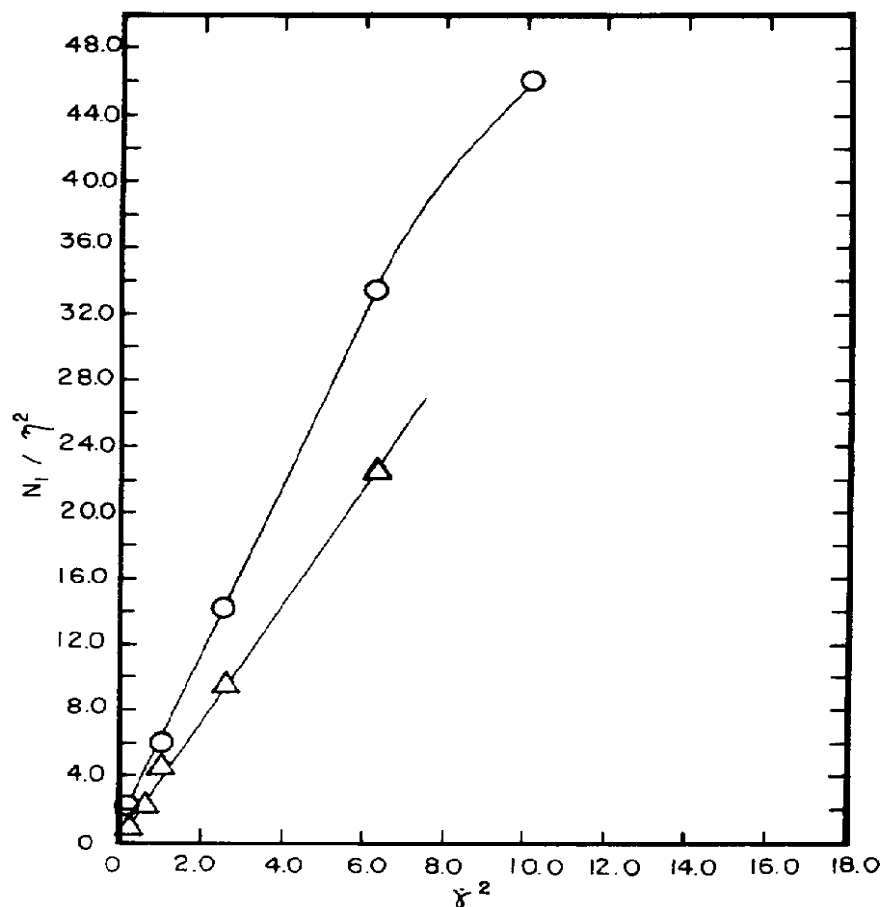


Fig. 8. The ratio of primary normal stress difference to the square of viscosity (N_1/η^2) versus $\dot{\gamma}^2$ for solutions of PPT in 100% H_2SO_4 . Concentration; 0.117 g/ml; T , 24°C. (Δ) $\bar{M}_w = 32,000$; (\circ) $\bar{M}_w = 20,700$.

FURTHER DISCUSSION

The contact parameter (cM) has been found to produce a better superposition of η_0 data within the same flexible chain polymer system than does the overlap parameter, $c[\eta]$.² This result has prompted Graessley to conclude that this was evidence for interactions which arise from ropelike coupling of chains.² However, if this is the case, then one wonders why cM does not reduce η_0 values obtained from both flexible and rigid polymers to a common curve. Corrections for differences in the segmental friction factor (ζ), plus replacement of M with z , the number of main chain atoms, provide a better reduction of data for flexible chain polymers. With these corrections taken into account, Fox and Allen²⁷ found for a number of flexible chain poly-

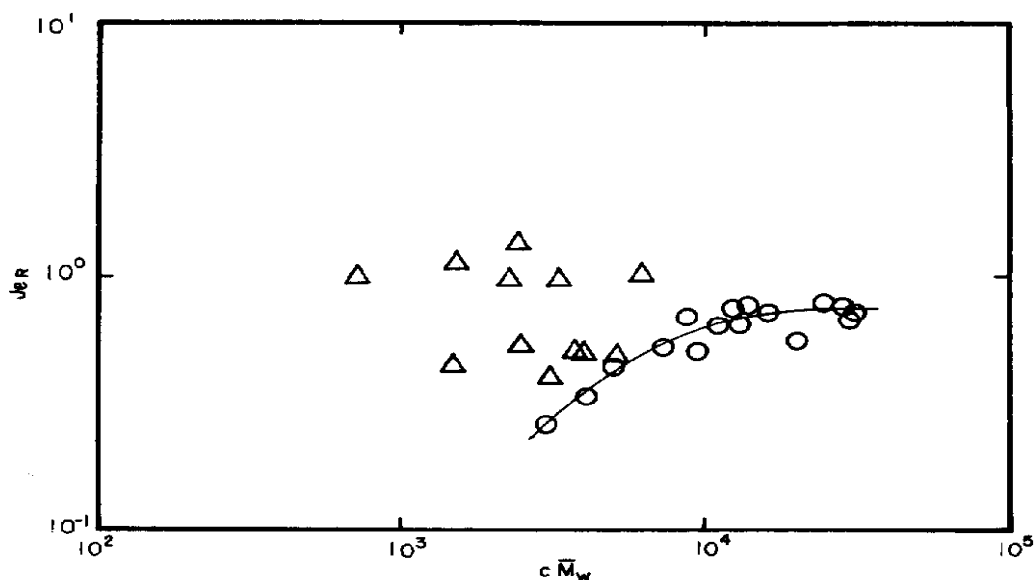


Fig. 9. Reduced compliance versus $c\bar{M}_w$. (Δ) PPT/100% H_2SO_4 , and (\circ) nylon 6,6/100% H_2SO_4 . All data were obtained at 24°C and are presented in Tables I and II.

mers that the critical number of main chain atoms (z_c) for the onset of an entanglement network was between 300 and 700. Yet there is still considerable scatter in the values of z_c . The idea of using cM or even cz still neglects the importance of polymer structure and configuration. It would seem that the onset of physical contacts between molecules would certainly depend on the hydrodynamic volume swept out by a given molecule and hence on the radius of gyration $\langle S^2 \rangle^{1/2}$ of a molecule. Furthermore, it would seem that the number of physical contacts would also be related to $\langle S^2 \rangle^{1/2}$ since the larger the hydrodynamic volume swept out by a molecule, the more chances for collision with neighboring molecules. It would seem that a parameter which reflects the shape of a molecule could possibly account for differences in η_0 data for flexible and rigid chain polymers.

With these thoughts in mind we used $c[\eta]$ as the reducing parameter, with results presented in Fig. 10, rather than $c\bar{M}_w$, which had been used in Fig. 3. Values of $[\eta]$ for PPT in 100% H_2SO_4 were determined by well-known methods and results are given elsewhere.¹² For nylon 6,6 solutions, values of $[\eta]$ were estimated using the following relation given by Burke and Orofino³³:

$$[\eta] = 11.5 \times 10^{-4} M_v^{0.67} \quad (6)$$

for solutions of nylon 6,6 in 96% H_2SO_4 . $c[\eta]$ provides a much better

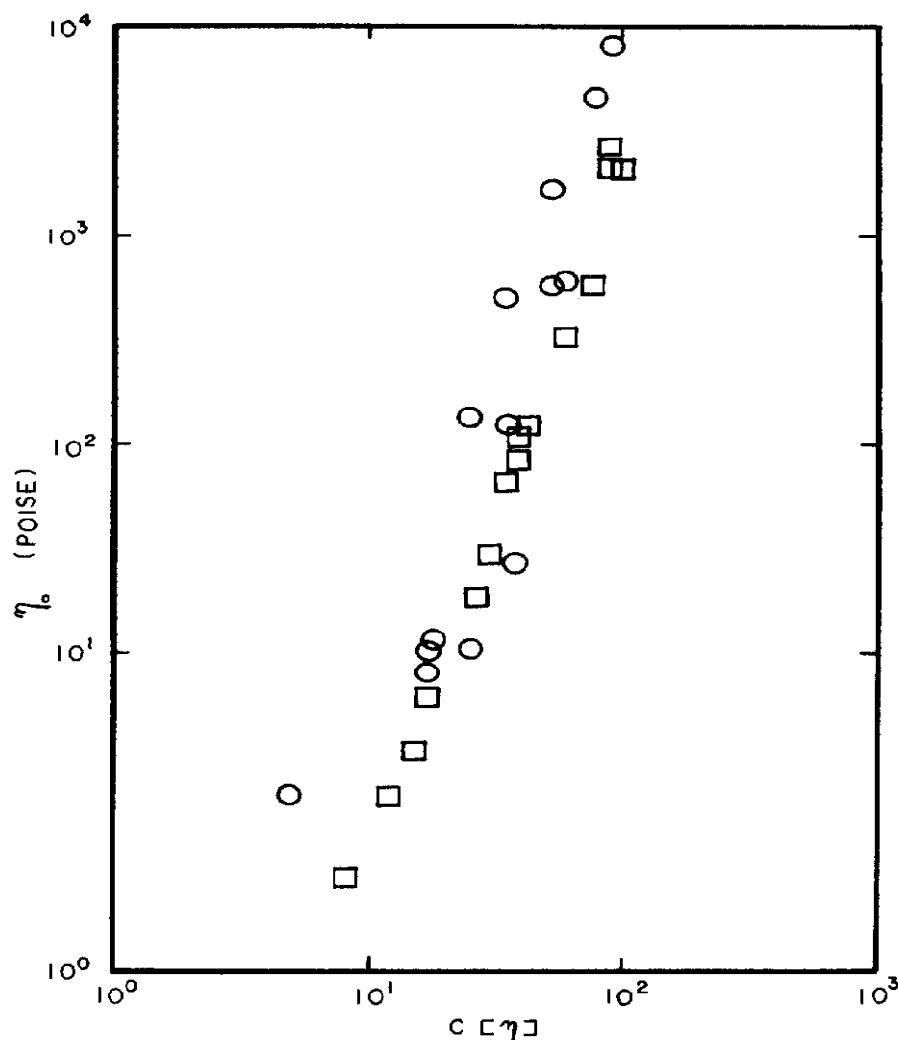


Fig. 10. Zero shear viscosity versus the overlap parameter ($c[\eta]$) for solutions of nylon 6,6 (\square) and PPT (\circ) in 100% H_2SO_4 at 24°C.

superposition of η_0 data onto a single plot. Although $c[\eta]$ does not account completely for differences in η_0 data for the flexible and rigid chain polymers, it at least suggests the importance of selecting a parameter which reflects the configuration of polymer molecules.

Fox and Allen²⁷ first recognized the importance of chain structure and configuration in accounting for differences in M_c values for different polymer systems. Following Bueche's theory for short chains¹ they proposed an empirical law:

$$\eta_0 = \frac{N_0}{6} \left[\frac{\langle S_0^2 \rangle_{AV}}{M} \frac{Z_c}{v} \right] \left(\frac{Z_w}{Z_c} \right)^\alpha \zeta, \quad (7)$$

where $\langle S_0^2 \rangle_{AV}$ is the unperturbed mean square radius of gyration, N_0 is Avogadro's number, v is the specific volume, ζ is the segmental friction factor, and $\alpha = 3.4$ for $Z_w \geq Z_c$ or $\alpha = 1.0$ for $Z_w \leq Z_c$. Designating

$$\chi = \frac{\langle S_0^2 \rangle_{AV}}{M} \left(\frac{Z_w}{v} \right)$$

and

$$\chi_c = \frac{\langle S_0^2 \rangle_{AV}}{M} \left(\frac{Z_c}{v} \right),$$

Eq. (7) can be written as

$$\eta_0 = \frac{1}{6} N_0 \chi_c \left(\frac{\chi}{\chi_c} \right)^\alpha \zeta, \quad (8)$$

where $\alpha = 3.4$ for $\chi \geq \chi_c$ and $\alpha = 1$ for $\chi \leq \chi_c$. Based on data for a number of flexible chain polymers, they observed a value of $\chi_c = 4.7 \times 10^{-15} \pm 20\%$ and proposed that χ_c is approximately a universal constant for flexible chain polymers. Berry and Fox³⁴ further confirmed this value χ_c with additional data obtained from other flexible chain polymers.

Values of χ_c were calculated for both PPT and nylon 6,6 to determine whether this concept could be extended to rigid macromolecules. Using $M_c = 5260$ from the data in Fig. 1, $Z' = 14$, where Z' is the number of chain atoms per repeat unit, $\zeta = 1.14 \text{ g/cm}^3$ and $\langle S_0^2 \rangle_{AV}/M = 96 \times 10^{-10} \text{ cm mol}^{1/2} \text{ g}^{-1/2}$,³⁵ we estimated χ_c to be 5.70×10^{-15} for nylon 6,6. This is in reasonable agreement with the universal value of χ_c and is similar to the value reported for nylon 6 ($\chi_c = 5.0 \times 10^{-15}$).³⁴

Calculating χ_c for PPT is a more difficult task since values of $\langle S_0^2 \rangle_{AV}/M$ are not defined for rodlike molecules. In place of $\langle S_0^2 \rangle_{AV}/M$ we used the value of $\langle S^2 \rangle$ at M_c estimated from data of Arpin and Strazielle¹³ for values of \bar{M}_w up to 40,100. From their data,

$$\langle S^2 \rangle / M_w = 1.93 \times 10^{-2} \bar{M}_w^{0.514}, \quad (9)$$

with $\langle S \rangle / \bar{M}_w$ having dimensions of $\text{cm}^2 \text{ g/g mole}$. With $M_c = 1180$, $\langle S^2 \rangle / M_c$ becomes $7.31 \times 10^{-17} \text{ cm}^2 \text{ g/g mol}$. The phenylene rings were considered to be long bonds, as is generally accepted,³⁴ and thus counted as only one chain atom. With $Z' = 6$, $M_c = 1180$, $\zeta = 1.44$

g/cm^3 and $\langle S^2 \rangle / M_c = 7.31 \times 10^{-17}$, χ_c was estimated to be 3.13×10^{-15} . Although this value is some 33% lower than the universal value, it is in agreement with the range of values reported for flexible chain polymers.³⁴

CONCLUSIONS

The following conclusions can be drawn from this study:

1. The effect of chain stiffness on the rheological properties of concentrated polymer solutions is to promote the onset of intermolecular interactions or entanglements at much lower values of c , M_w , and z than for flexible chain polymers.

2. The dependence of η_0 on $(cM_w)^{6.8}$ distinguishes solutions of PPT from solutions of linear flexible chain polymers, and hence this may be indicative of polymer systems with the potential to exhibit liquid crystalline behavior.

3. The structural variable controlling the onset of entanglement effects seems to be a parameter which reflects the shape and configuration of the molecule such as the radius of gyration.

4. "Entanglements," at least in the case of rigid molecules, may not require any notion of molecular looping or bending at all. Just the action of one molecule encountering a neighboring molecule during the deformation process and thereby limiting the number of paths available to this molecule may serve as an entanglement.

It would seem that further studies of the rodlike systems under dynamic or transient flow conditions (i.e. start of shear flow) or in extensional flow would be well worthwhile in that they would provide further insight into the nature of entanglements for rodlike molecules that cannot be obtained under steady flow conditions.

We are grateful to the Monsanto Company for permission to publish this work and to Dr. J. H. Saunders for his support and interest. We also appreciate the assistance of J. A. Burroughs and J. K. Smith in the preparation of samples and rheological characterization of the polymer solutions.

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Received September 27, 1978

Accepted as revised January 11, 1979