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Role of Solvent Nature on Rheological Properties of Nylon 6,6 Solutions

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Synopsis

The rheological properties of concentrated solutions of nylon 6,6 of various molecular weights in various solvents have been determined in steady shear flow. Four solvents including 90% formic acid, *m*-cresol, 97% H_2SO_4, and 100% H_2SO_4 were selected based on their effect on the ionic nature of nylon 6,6 in dilute solutions. The magnitude of the rheological properties of concentrated solutions depended on the solvent when compared at the same shear rate ($\dot{\gamma}$) and segment contact parameter ($c\overline{M}_w$, where c is the concentration and $\overline{M}_w$ is the weight average molecular weight). However, as observed by others, the critical value of $c\overline{M}_w$ for the onset of entanglements was independent of the solvent. The contact parameter was effective in reducing values of η_0 versus $c\overline{M}_w$ to a single curve for three of the solvents but values of η_0 for formic acid solutions were consistently two orders of magnitude lower than for the other solutions. Values of the equilibrium compliance, J_e^0, were highest for the formic acid solutions. However values of the reduced compliance (J_{eR}) for all four solutions were around 0.4 which is in reasonable agreement with the Rouse theory. The onset of non-Newtonian viscosity depended on the solvent but the shape of the flow curves was similar for all polymer/solvent systems. It is concluded that the solvent viscosity may contribute more to the rheological properties of concentrated solutions than the solvent's influence on the ionic nature of polymer chains.

INTRODUCTION

The rheological properties of concentrated solutions and melts of flexible chain polymers point clearly to a universal physical interaction between 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 $1/cRT$ to $1/c^2RT$, where c is the concentration in g/mL, R is the gas constant, and T is the temperature, and the appearance of a plateau in the relaxation modulus all depend on

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the Bueche segment contact parameter (cM), which is a measure of the number intermolecular contacts per molecule.[1] The concept of a physical interaction rather than intermolecular attractive forces is well documented for nonpolar, noncrystallizable, flexible chain molecules.[2]

On the other hand, in the last few years several studies have been reported which emphasize the role of the "goodness" of a solvent and polar side groups.[3–9] In general, it is observed that the zero shear viscosity (η_0) increases faster with concentration for poor solvent systems than for good solvents. Eventually η_0 for the poor solvent systems becomes greater than for the good solvents. This behavior seems to be enhanced for polar polymers. Furthermore, it has been observed that the critical concentration (C_{crit}) for the onset of intermolecular interactions for a given molecular weight decreases in poor solvents[3,4] and the effect is enhanced for polar polymers.[5–9] However, the critical molecular weight (M) for the onset of intermolecular interactions for a given concentration is the same for all qualities of solvents.[5–9] Similar effects are observed for other material functions such as the primary normal stress in the limit of zero shear rate $\psi_1(0)$.

Our objective in this paper is to investigate the effect of solvent on not only the low shear rate material functions but on the onset of shear thinning behavior of the viscosity, the magnitude of the longest relaxation time, and the shear dependence of the primary normal stress difference (N_1). Nylon 6,6 of various molecular weights (M) is used in this study. Four solvents are selected including 90% formic acid, m-cresol, 97% H_2SO_4, and 100% H_2SO_4. As discussed later these were selected according to their effect on the ionic nature of the polymer and their apparent thermodynamic goodness.

EXPERIMENTAL

Polymers: Nylon 6,6 of various molecular weights was prepared by well known solid state, polymerization techniques.[10] Molecular weight characteristics were determined by means of gel permeation chromatography using hexafluroisopropanol as the solvent. Values of the weight average molecular weight ($\overline{M}_w$) ranged from 35,200 to 73,200 for samples used in this study and more complete details of the polymer characteristics are presented in Table I.

Solvents: Four solvents were selected for this study based on their

TABLE I

Molecular Weight Characteristics of Nylon 6,6 Samples

Sample No.	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$[\eta]^a$ (dL/g)
1	35,200	2.01	1.06
2	38,800	2.02	1.09
3	42,300	2.17	1.43
4	54,300	2.52	1.86
5	59,600	2.56	2.00
6	63,000	2.56	2.09
7	66,900	2.56	2.19
8	73,200	2.56	2.35

[a] Determined in hexafluroisopropanol.

ability to ionize the amide groups. The solvents included 90% formic acid ($\eta_s = 1.804$ cp, $\rho = 0.882$ g/mL), *m*-cresol ($\eta_s = 20.8$ cp, $\rho = 1.0346$ g/mL), 97% sulfuric acid ($\eta_s = 25.4$ cp, $\rho = 1.834$ g/mL), and 100% sulfuric acid ($\eta_s = 25.4$ cp, $\rho = 1.874$ g/mL). The Mark-Houwink exponents (α) for nylon 6,6 in formic acid, *m*-cresol, 97% H_2SO_4, and 100% H_2SO_4 are 0.79, 0.61, 0.67, and 0.8, respectively.[10,11] Further discussion on the nature of the solvents and their effect on the ionization of polyamides is presented in a later section.

Rheological properties: All rheological properties of concentrated solutions were determined in steady shear at 25°C using a Rheometrics Mechanical Spectrometer (RMS). Both the shear stress (σ) and the primary normal stress difference (N_1) were obtained at 25°C using a cone-and-plate attachment (0.04 rad cone, 50 mm diam). The repeatability of all measurements was extremely good with variations in N_1 being less than ±5%.

Solutions: Solutions were prepared at three concentration levels of 10, 20, and 30% by weight in both sulfuric acid solvents but only at levels of 10 and 20% in formic acid and *m*-cresol because of limited solubility.

Dilute solution properties were obtained at 25°C using cannon-fenske viscometers. Viscometer sizes were selected to maintain drop times above 100 s in order to justify the neglect of kinetic energy corrections.

Highly viscous solutions were prepared by allowing the nylon 6,6 pellets to soak in the solvent for a week and then dissolution was completed by mixing in a low shear Helicone Mixer (model 2CV).

RESULTS AND DISCUSSION

The flow behavior of solutions of nylon 6,6 in the dilute solution range ($c < 1$ g/dL) is highly dependent on the solvent.[12] This is illustrated by representative data in Fig. 1 for various solutions of nylon 6,6 of $\overline{M}_w = 73{,}200$. For 90% formic acid solutions values of the reduced viscosity (η_r) decrease nonlinearly with decreasing concentration whereas in *m*-cresol, η_r decreases linearly with decreasing concentration. For 100% H_2SO_4 solutions, the η_r vs c curve is highly nonlinear with η_r decreasing rapidly with decreasing concentration. For 97% H_2SO_4 solutions, the η_r vs c curve appears to be linear and similar to that of *m*-cresol solutions. We also note that the extrapolated values of η_r to zero concentration to obtain the intrinsic viscosity, $[\eta]$, are dependent on the solvent.

Explanations of these results have been offered for nylon 6 in the same solvents[12] and can be expected to be valid for nylon 6,6 solutions. Schaefgen and Trivisonno[12] proposed the following mechanisms to account for the concentration dependence of η_r for nylon 6 in various

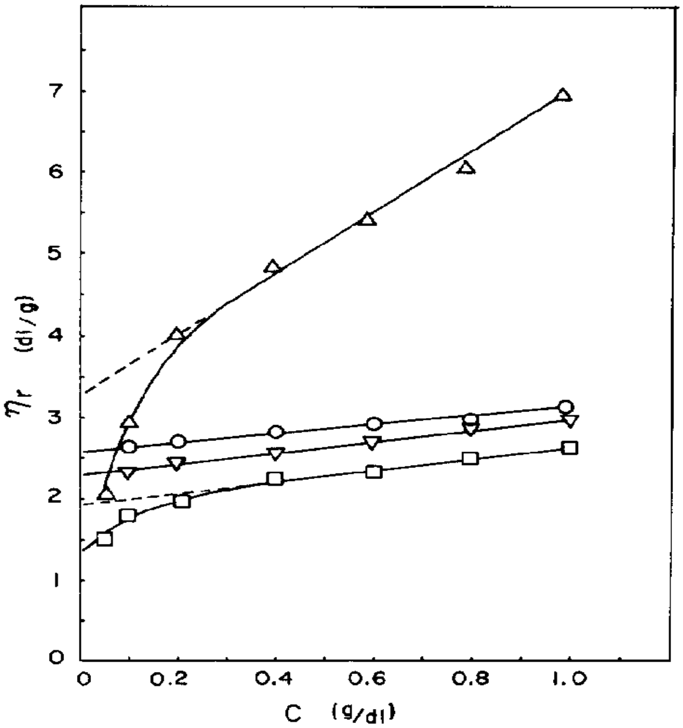

Fig. 1. Reduced viscosity versus concentration for nylon 6,6 in four solvents at 25°C: △, 100% H_2SO_4; ○, *m*-cresol; ▽, 97% H_2SO_4; □, 90% formic acid.

solvents: In 90% formic acid, the polyamide chains are highly ionized which causes the chain segments to repel each other. As the polymer concentration decreases there is a sufficient concentration of counter-ions from the interaction of water with formic acid to shield some of the ionized amide groups. This shielding allows the chains to partially collapse and competes with the expansion of the chains caused by the ionized amide groups to affect chain conformation. The behavior of nylon 6,6 in 100% H_2SO_4 is similar to that exhibited by other polyelectrolytes in the presence of counter-ions. 100% H_2SO_4 self-ionizes to yield a small amount of bisulfate ion[13] which serves to shield the ionized amide linkages. This allows the chains which are expanded by the ionized amide groups to collapse. As C decreases there is an increased concentration of bisulfate ions to shield the ionized groups, and this leads to even further collapsing of the chains. In 97% H_2SO_4 the concentration of bisulfate ions is very large because of the reaction of H_2SO_4 with H_2O. These ions are at sufficient levels at all polymer concentrations to shield the ionized groups. Hence there appears to be no polyelectrolytic behavior.

Because of the complex behavior of nylon 6,6 in the dilute solution range, it is natural to ask whether the solvent has any significant effect on the rheological properties of concentrated solutions. Based on the goodness of the solvents as determined by the Mark–Houwink exponents (these exponents are 0.79, 0.61, 0.67, and 0.80 for nylon 6,6 in formic acid, m-cresol, 97% H_2SO_4, and 100% H_2SO_4, respectively,[10,11] we would expect the viscosity of concentrated solutions of nylon 6,6 in formic acid and 100% H_2SO_4 to be lower than that for solutions involving *m*-cresol and 97% H_2SO_4. We now turn our attention to the effect of the solvent on the magnitude of viscosity and the primary normal stress difference for concentrated solutions.

STEADY SHEAR PROPERTIES

Representative data for the four solutions compared at a contact parameter of about 14,000 are presented in Fig. 2. In general we observe that there is no difference in the viscosity and primary normal stress (N_1) data at the same value of the contact parameter ($c\overline{M}_w$) for 97% and 100% H_2SO_4. The viscosity data for the sulfuric acid solutions is slightly higher than that for *m*-cresol but values of N_1 are nearly identical. On the other hand, values of η and N_1 for solutions of formic acid are nearly two orders of magnitude lower than those

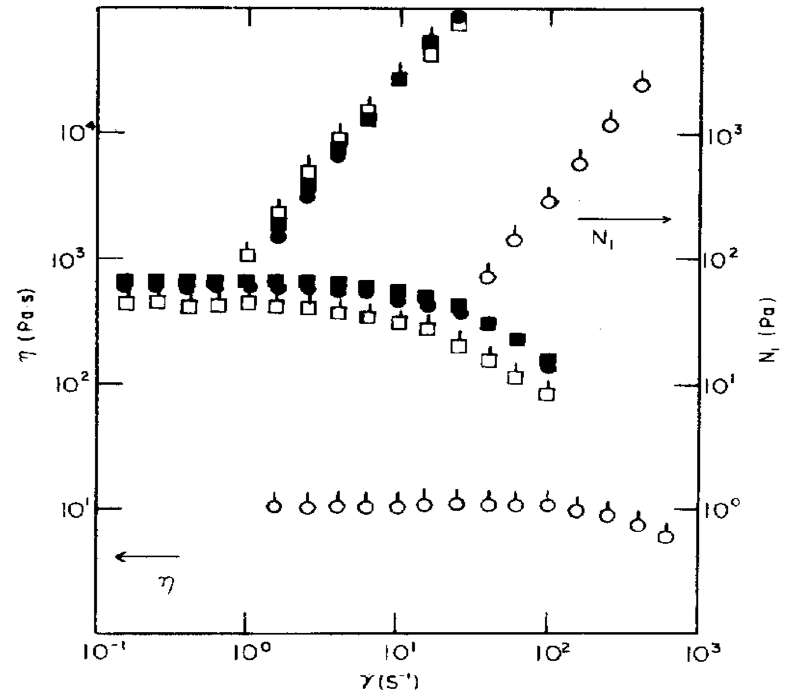

Fig. 2. Viscosity and primary normal stress difference versus shear rate for solutions of nylon 6,6 in various solvents for the same contact parameter ($c\overline{M} \simeq 14{,}000$): ⚲, 90% formic acid; □, *m*-cresol; ■, 97% H_2SO_4; ●, 100% H_2SO_4.

obtained from the other solutions. Even if the viscosity were presented in reduced form by dividing η by the solvent viscosity (η_s), the viscosity data for the sulfuric acid and *m*-cresol solutions would still be an order of magnitude higher than that for solutions of formic acid. No significant polymer degradation occurred as long as data were obtained within two weeks of preparing the solutions. One proposed explanation for the difference in the magnitude of the rheological properties for other polar polymers is the enhancement of entanglements in certain solvents.[5–9] The enhancement of entanglements in our case could arise through strong attractive forces of the ionized chains. In the next sections we present further results which should help us understand whether there is any role played by the solvent in affecting intermolecular contacts. We next look at the molecular weight dependence of the zero shear viscosity (η_0) and the primary normal stress difference in the limit of zero shear rate $\psi_1(0)$.

TABLE II
Entanglement Parameters for Nylon 6,6 in Various Solvents

Solvent	c (g/mL)	a^*	$b^\dagger$	$(\overline{M}_w)_{\text{crit}}$
m-cresol	0.21	3.37	7.44	6000
	$0.10^\ddagger$	2.35	7.76	
90% formic acid	0.24	3.51	8.11	6600
90% H_2SO_4	0.17	3.37	7.41	6000
96% H_2SO_4	0.33	3.70	7.95	
100% H_2SO_4	0.17	3.18	6.51	6600
	0.33	4.15	8.62	

* $\eta_0 \propto \overline{M}_w{}^a$

† $\psi_1(0) \propto \overline{M}_w{}^b$

‡ data obtained from solutions for which $c\overline{M}_w < (c\overline{M}_w)_{\text{crit}}$

ZERO SHEAR RATE BEHAVIOR

Plots of η_0 versus $\overline{M}_w$ are known to show an abrupt change in slope when a critical value of $\overline{M}_w$ is reached. This change in slope is associated with the onset of an entanglement network. When $\overline{M}_w$ is greater than the critical value for entanglements, $(M_w)_{\text{crit}}$, then η_0 depends on $\overline{M}_w$ raised to powers between 3.1 and 4.0.[14] From plots of η_0 versus $c\overline{M}_w$ for each solvent we have found that the critical molecular weight, $(\overline{M}_w)_{\text{crit}}$, is to within experimental error the same ($\simeq$6000) as observed in Table II. This is illustrated further in Fig. 3 where η_0 is plotted versus $c\overline{M}_w$ for each solution. Although $(\overline{M}_w)_{\text{crit}}$ is independent of the solvent, the power dependence of η_0 on $\overline{M}_w$ seems to depend slightly on the solvent and the concentration (see Table II). In particular we observe in Table II that values of the exponent can be as high as 4.15 in 100% H_2SO_4.

Returning to Fig. 3 in which η_0 is plotted versus $c\overline{M}_w$, we see that data for solutions of nylon 6,6 in m-cresol and 97% and 100% H_2SO_4 superimpose fairly well on one curve. However, data for formic acid lie on a separate curve which is significantly lower than the composite curve for the other solvents. Even dividing values of η_0 by η_s will not reduce the data to a single plot.

It is conceivable that in sulfuric acid the counter-ions could serve as temporary crosslinks between two ionized amide groups. Once entanglements have formed, then the ionic nature of the chains may lead to an enhancement of the entanglements. However, this cannot account for the differences in viscosity completely, since values of η

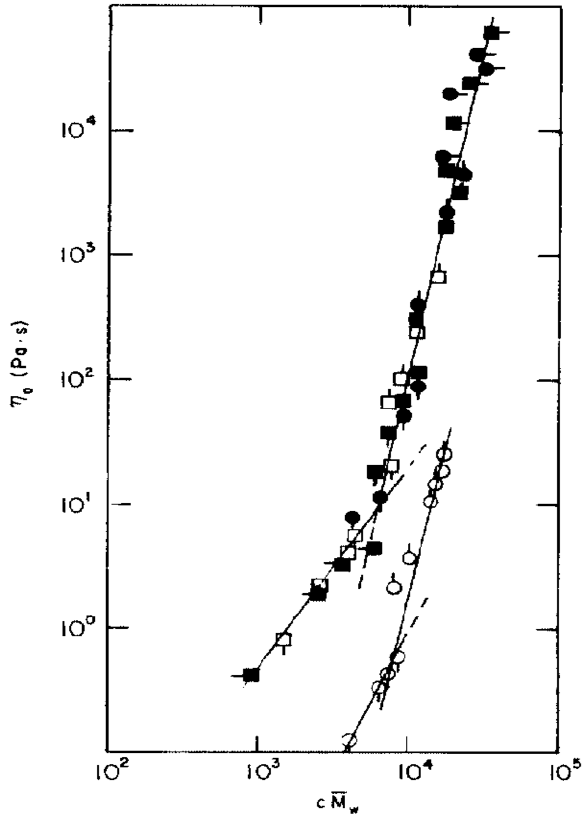

Fig. 3. Zero shear viscosity versus the contact parameter ($c\overline{M}_w$) for nylon 6,6 in various solvents: ȯ, 90% formic acid (20 wt %); ọ, 90% formic acid (10 wt %); □, *m*-cresol (20 wt %); □, 97% H_2SO_4 (30 wt %); ■, 97% H_2SO_4 (20 wt %); ●, 100% H_2SO_4 (30 wt %); ●, 100% H_2SO_4 (20 wt %).

in *m*-cresol are not much different from those in solutions of sulfuric acid. So the difference in data may somehow be more related to the solvent viscosity.

Values of the primary normal stress difference in the limit of zero shear rate, $\psi_1(0)$, are plotted versus $c\overline{M}_w$ in Fig. 4. Because of the limited range of molecular weights and concentration these data are confined to a narrow region which makes the plot itself of limited value. However, actual data are available in Tables III–VI which can be used to calculate the slopes. Just as for η_0 data, we see that values of $\psi_1(0)$ fall on a single curve for all solvents except for formic acid. Values of $\psi_1(0)$, however, all seem to depend on $\overline{M}_w$ raised to a similar power (see Table II). So although the magnitude of $\psi_1(0)$ depends on the solvent for a given value of $c\overline{M}_w$, the dependence of $\psi_1(0)$ on $\overline{M}_w$ is apparently independent of the solvent.

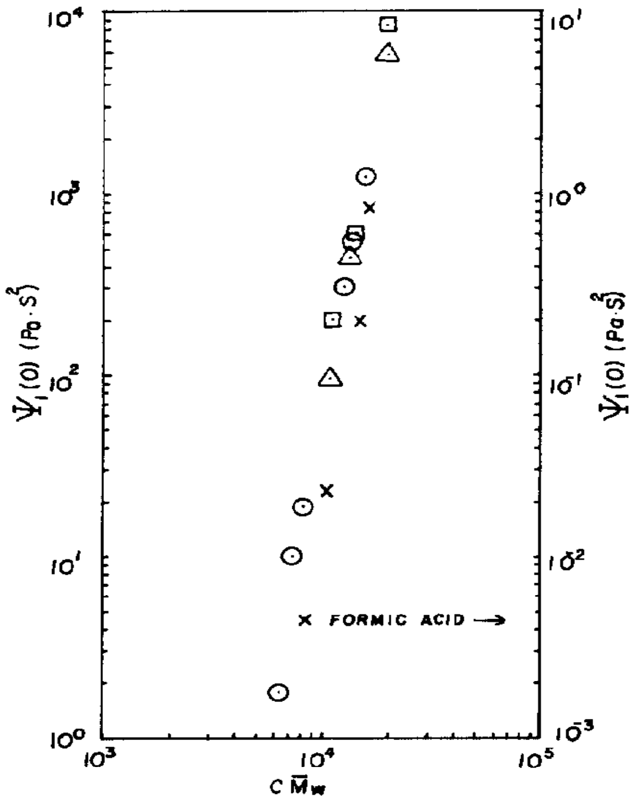

Fig. 4. Primary normal stress difference coefficient in limit of zero shear rate versus the contact parameter for nylon 6,6 in various solvents: ×, 90% formic acid; ○, *m*-cresol; □, 97% H_2SO_4; △, 100% H_2SO_4.

SHEAR DEPENDENCE OF VISCOSITY

We have observed that the solvent has a significant effect on the magnitude of η and N_1. However, the question arises as to whether the shear dependence of η and the onset of non-Newtonian behavior are affected by the nature of the solvent. The viscosity data in Fig. 2 are plotted in reduced form (i.e., η/η_0 versus $\dot{\gamma}\ \tau_0/2$, where τ_0 is the relaxation time) in Fig. 5. The data are compared with Graessley's master curve[15] for a molecular weight distribution of $\overline{M}_w/\overline{M}_n = 2$, where $\overline{M}_n$ is the number average molecular weight. This master curve fits the data rather well with the worst agreement coming from the formic acid solutions. In general, the solvent did not seem to affect the shape of the viscosity versus shear rate curves.

A noticeable difference, however, was observed in the relaxation time, τ_0, or the shear rate for the onset of non-Newtonian behavior

TABLE III

Rheological Parameters for Solutions of Nylon 6,6 in 90% Formic Acid

$\overline{M}_w$	c (g/mL)	η_0 (Pa·S)	τ_0 (s)	τ_R (s)	$J_e^0 \times 10^4$ (m^2/N)	J_{eR}
35200	0.2406	2.2	0.00010	7.74×10^{-5}	0.47	0.264
38800	0.2426	2.3	0.00025	8.92×10^{-5}	0.96	0.489
42300	0.2406	3.7	0.00025	1.56×10^{-4}	0.74	0.346
54300	0.2486	10.0	0.00080	5.43×10^{-4}	1.16	0.423
59600	0.2416	10.5	0.00125	6.25×10^{-4}	1.12	0.372
63000	0.2406	15.0	0.00138	9.45×10^{-4}	1.88	0.549
66900	0.2406	19.0	0.00200	1.27×10^{-3}	1.31	0.386
73200	0.2406	26.0	0.00250	1.90×10^{-3}	1.58	0.427

($\dot{\gamma}_0$) as the solvent was changed. The relaxation time was obtained by graphically shifting η vs $\dot{\gamma}$ data to fit the master curve of Graessley. A summary of values of τ_0 is given in Tables III–VI for a representative set of data (20% by weight of nylon 6,6 in each of the solvents). In general, we find that at the same values of $c\overline{M}_w$, values of τ_0 are similar for m-cresol and sulfuric acid solutions whereas a significant difference exists between these values of τ_0 and those for formic acid solutions. Values of the Rouse relaxation time

$$\tau_R = \frac{6\eta_0 M}{\pi^2 cRT} \tag{1}$$

were also calculated and compared favorably well with those determined experimentally (see Tables III–VI). The agreement between values of τ_0 and τ_R for all four solvents suggests that the solvent af-

TABLE IV

Rheological Parameters for Solutions of Nylon 6,6 in M-Cresol

$\overline{M}_w$	c (g/mL)	η_0 (Pa·S)	τ_0 (s)	τ_R (s)	$J_e^0 \times 10^4$ (m^2/N)	J_{eR}
35200	0.2107	66	0.0045	2.7×10^{-3}	1.10	1.543
38800	0.2107	60	0.0058	2.71×10^{-3}	0.96	0.432
42300	0.2107	100	0.0055	4.9×10^{-3}	1.22	0.501
54300	0.2107	240	0.0220	1.5×10^{-2}	1.54	0.488
59600	0.2107	310	0.0270	2.148×10^{-2}	1.56	0.455
63000	0.2107	440	0.0450	3.22×10^{-2}	1.99	0.540
66900	0.2107	425	0.0400	3.306×10^{-2}	2.29	0.595
73200	0.2107	670	0.0770	5.7×10^{-2}	2.14	0.508

TABLE V

Rheological Parameters for Solutions of Nylon 6,6 in 97% H_2SO_4

$\overline{M}_w$	c (g/mL)	η_0 (Pa·S)	τ_0 (s)	τ_R (s)	$J_e^0 \times 10^4$ (m²/N)	J_{eR}
35200	0.3238	395	0.0117	0.01040	0.58	0.44
38800	0.3278	380	0.0080	0.01105	0.69	0.48
42300	0.3278	625	0.0200	0.01983	0.71	0.45
54300	0.3278	2220	0.0770	0.09040	0.21	0.10
59600	0.3278	2480	0.1110	0.11080	0.66	0.29
63000	0.3278	2640	0.1000	0.12470	0.53	0.23
66900	0.3278	2670	0.1430	0.13390	0.68	0.27
73200	0.3278	4500	0.1660	0.24710	—	—

fects τ_0 only through the magnitude of η_0. It is suggested by an empirical law proposed by Fox and Allen[16]

$$\eta_0 = \frac{N_0}{6}\left[\frac{\langle S_0^2\rangle_{AV}}{M}\frac{z_c}{\nu}\right]\left[\frac{z_w}{z_c}\right]^{\alpha}\zeta \tag{2}$$

where $\langle S_0^2\rangle_{AV}$ is the unperturbed mean square radius of gyration, N_0 is Avogadro's number, ν is the specific volume, of the polymer ζ is the segmental friction factor, $\alpha = 3.4$, and z_w and z_c are the number of main chain atoms and the critical number of main chain atoms for the onset of entanglements, respectively, that the difference in η_0 values in the different solvents comes from differences in the specific volume and the segmental friction factor. Hence, the difference in the onset of non-Newtonian behavior for the different solvents may be accounted for primarily through their effect on η_0.

TABLE VI

Rheological Parameters for Solutions of Nylon 6,6 in 100% H_2SO_4

$\overline{M}_w$	c (g/mL)	η_0 (Pa·S)	τ_0 (s)	τ_R (s)	$J_e^0 \times 10^4$ (m²/N)	J_{eR}
35200	0.3278	318	0.0182	8.366×10^{-3}	0.48	0.37
38800	0.3278	270	0.0200	7.83×10^{-3}	0.73	0.54
42300	0.3278	576	0.0282	0.0182	0.63	0.41
54300	0.3278	1640	0.0870	0.0667	0.96	0.48
59600	0.3278	2070	0.1250	0.0925	1.19	0.54
63000	0.3278	2640	0.1170	0.1247	1.17	0.50
66900	0.3278	3100	0.1110	0.1555	1.21	0.49
73200	0.3278	6400	0.1660	0.3513	—	—

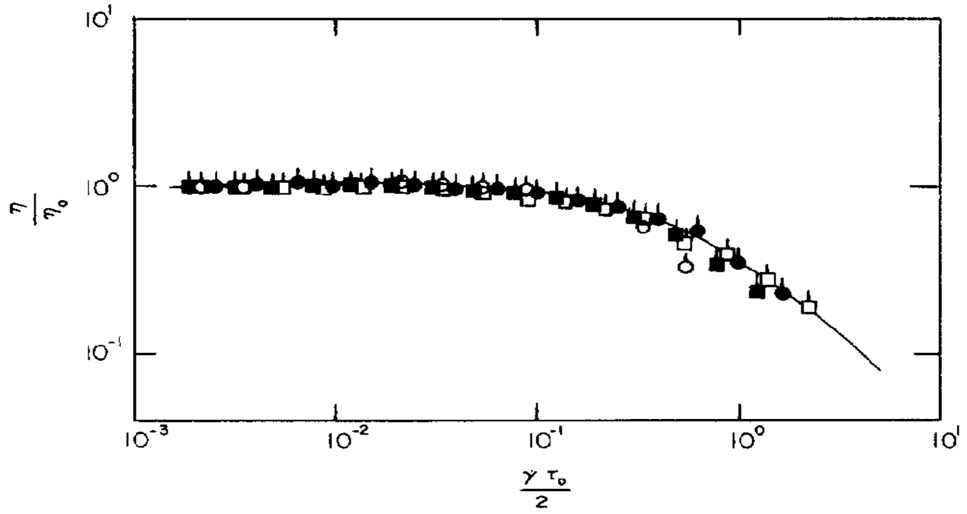

Fig. 5. Comparison of viscosity data with Graessley's master curve: ○, 90% formic acid; □, *m*-cresol; ■, 97% H_2SO_4; ●, 100% H_2SO_4.

ELASTIC PROPERTIES

Finally, the onset of an entanglement network should be reflected in the elastic properties of the solutions.[17] The equilibrium compliance (J_e^0) has been used as a measure of fluid elasticity, since it is related to the recoverable shear strain γ_r and the shear stress by the following relation[18]:

$$\gamma_r = J_e^0 \, \sigma. \tag{3}$$

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

$$J_e^0 = 1/2 \lim_{\dot{\gamma} \to 0} \frac{d(N_1/\eta^2)}{d\,\dot{\gamma}^2}\,. \tag{4}$$

Such plots consistently gave straight lines over a fairly large $\dot{\gamma}$ range. Representative data is presented in Tables III–VI for the four solvents. For similar values of the contact parameter we observe that values of J_e^0 are slightly higher in formic acid than in the other solvents (e.g., for a value of $C\overline{M}_w \simeq 14{,}000$, J_e^0 is 2.29×10^{-6}, 1.16×10^{-6}, 0.71×10^{-6}, and 0.63×10^{-6} m^2/N in *m*-cresol, formic acid, 97% H_2SO_4, and 100% H_2SO_4, respectively). Thus, although the absolute values of viscosity and N_1 are considerably lower for formic acid solutions, the elasticity of the solutions as determined by values of J_e^0 is somewhat higher than values for the sulfuric acid solutions.

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

$$J_{eR} = \frac{J_e^0\, cRT\, \overline{M}_w{}^2}{\overline{M}_w \overline{M}_z \overline{M}_{z+1}}. \tag{5}$$

For $\overline{M}_w/\overline{M}_n = 2, \overline{M}_z\overline{M}_{z+1}/\overline{M}_w{}^2 = 3$. Values of J_{eR} are presented for representative solutions in Tables III–VI. For combinations of concentration and molecular weight greater than $(c\overline{M}_w)_{\text{crit}}$, values of J_{eR} lie in a range between 0.35 and 0.59 for formic acid, which is in reasonable agreement with the value of 0.4 predicted by the Rouse theory. Similar results are obtained for the other three solutions except in 97% H_2SO_4 where values of J_{eR} fall below 0.4.

CONCLUSIONS

The solvent seems to have a strong effect on the magnitude of rheological properties. However, because of the similarity in the results obtained from *m*-cresol in which nylon 6,6 chains are not highly ionized with those of nylon 6,6 in sulfuric acid where the chains are highly ionized, it is not possible to conclude that intermolecular interactions are greater for polar molecules. Likewise, even in formic acid the chains are highly ionized, yet the magnitude of the rheological properties of the solutions are significantly lower than for the other solutions. White and coworkers have also observed this same phenomenon for solutions of nylon 6,6 in 96% H_2SO_4 and 90% formic acid.[19] Based on the results reported in this paper, we conclude that the viscosity of the solvent still makes a significant contribution to the rheological properties of concentrated solutions. This contribution probably arises from the effect of this parameter on the segmental friction factor. The polar nature of the polymer/solvent system and the goodness of the solvent seem to have less of an effect than the solvent viscosity for the solutions studied here. Whatever the mechanism is responsible for the observed results, the difference in rheological properties can be accounted for rather well through the effects of the solvent on the magnitude of the zero shear viscosity.

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