

## Solvent Effect on the Time Constant of Concentrated Polymer Solutions

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### Synopsis

The time constant,  $\tau$ , signifying the onset of non-Newtonian behavior of polymer solutions is known to be a function of mass concentration,  $C$ , molecular weight,  $M$ , temperature,  $T$ , and zero shear viscosity,  $\eta_0$ . Williams' theory predicts that the time constant is also affected by the solvent character. To study the predicted effect, the time constants of poly(methyl methacrylate) solutions in chlorobenzene (good solvent) and *m*-xylene (poor solvent) were experimentally determined. It was found that the ratio of the time constant to the Rouse relaxation time was a function of the combined variable  $CM$ . For all values of  $CM$ , both the time constant and the ratio of the time constant to the Rouse relaxation time were larger in a poor solvent than in a good solvent. This behavior may be attributed to the relatively stronger attractive interpolymer molecular forces present in solutions in poor solvents. As the temperature is raised the poor solvent becomes better and the ratio of the time constant to the Rouse relaxation time is found to become independent of solvent character.

### INTRODUCTION

Polymer melts and solutions are non-Newtonian in nature and their viscosity,  $\eta$ , depends upon the shear rate,  $\dot{\gamma}$ . It is generally observed that at low shear rates the viscosity is independent of shear rate and the low shear rate limit of the viscosity is referred to as the zero shear viscosity,  $\eta_0$ . As the shear rate is increased beyond a certain critical value,  $\dot{\gamma}_c$ , the viscosity is observed to decrease continually. It is customary to define a time constant,  $\tau$ , as being inversely proportional to the critical shear rate,  $\dot{\gamma}_c$ , the constant of proportionality being a number somewhere between 1 and 2. Besides marking the onset of non-Newtonian behavior, the time constant has correlative significance with regard to the functional dependence of viscosity of solutions of monodisperse polymers on shear rate as well, since it has been observed that plots of  $\log(\eta/\eta_0)$  against  $\log(\tau\dot{\gamma})$  produce a master curve unifying the effects of temperature, concentration, and molecular weight. It is clear that the time constant depends upon the concentration, molecular weight, and temperature as well as many other variables.

Although the molecular mechanisms behind non-Newtonian behavior are not well understood, several useful empirical observations have been made. For example, the time constant was found to be numerically approximately equal to the first relaxation time appearing in the molecular theories of Rouse<sup>1</sup> and

Bueche.<sup>2</sup> These theories, applicable to dilute solutions, predict that the relaxation time is given by

$$\tau_{\text{Rouse}} = \frac{6}{\pi^2} \frac{(\eta_0 + \eta_s)}{CRT} M \quad (1)$$

$$\tau_{\text{Bueche}} = 2\tau_{\text{Rouse}} \quad (2)$$

where  $\eta_s$  is the viscosity of the solvent,  $C$  is the mass concentration of the polymer,  $M$  is the molecular weight,  $T$  is the absolute temperature, and  $R$  is the gas constant. Experimental evidence<sup>3</sup> confirms that  $\tau$  is proportional to  $(\eta_0 - \eta_s)M/CT$  for dilute solutions. However, the work of DeWitt et al.<sup>4</sup> and Graessley et al.<sup>5</sup> on concentrated solutions showed that the expressions of Rouse and Bueche fail to predict the dependence of the time constant on concentration and molecular weight correctly. DeWitt et al.,<sup>4</sup> who studied the effect of concentration only, observed that  $1/\tau = (AC/\eta_0) + (BC^2/\eta_0)$  where  $A$  and  $B$  are constants. Graessley and co-workers<sup>5</sup> showed that  $1/\tau = E(CT/\eta_0M) + G(C^2T/\eta_0)$ , where  $E$  and  $G$  are constants. Considering the fact that for concentrated solutions  $\eta_0$  is usually much larger than  $\eta_s$ , the above observations indicate that Rouse-like behavior is obtained only in the limit of low concentrations. At higher concentrations the term proportional to the square of the concentration dominates and  $\tau$  is proportional to  $\eta_0/C^2T$  and independent of molecular weight.

Williams<sup>6,7</sup> proposed a theory for concentrated solutions which predicts that

$$\tau \propto \frac{\eta_0 - \eta_s}{C^2T} \frac{1}{F} \quad (3)$$

where  $F$  is a function of concentration calculable from the thermodynamic properties of the polymer solution. Since  $F$  was expected to be a weak function of concentration<sup>6,7</sup> and since  $\eta_0 \gg \eta_s$  for concentrated solutions, Williams' theory predicts that  $\tau$  is proportional to  $\eta_0/C^2T$ , in agreement with previous data.<sup>4,5</sup> Since the thermodynamic properties of a polymer solution are a function of the solvent character, Williams' theory predicts that  $\tau$  is a function of the solvent character. No work exists to confirm or reject the predicted solvent effect and this is the aim of the present paper.

## EXPERIMENTAL WORK

Commercially available poly(methyl methacrylate) (PMMA) was fractionated into six samples by the triangular precipitation method<sup>8</sup> to minimize the effect of molecular weight distribution, and acetone and hexane were chosen as the solvent-nonsolvent pair. Chlorobenzene (CB) was selected as the good solvent and *m*-xylene (X), a near theta solvent around 25°C, as the poor solvent. Further, these solvents had low vapor pressures (<15 mm Hg) around room temperature and posed no problems due to evaporation during viscometric measurements. Laboratory reagent grade solvents were used without any further purification. Intrinsic viscosities of the polymer samples were measured in toluene at 25°C and the molecular weights of the fractionated samples were calculated using the correlation<sup>9</sup>

$$[\eta]_0 = 7.1 \times 10^{-5} M^{0.73} \quad (4)$$

TABLE I  
Characteristics of the Samples

Sample	$[\eta]_0$ , dl/g	$M \times 10^{-5}$
A	3.21	23.85
B	2.11	13.4
C	1.40	7.66
D	1.04	5.09
E	0.76	3.28

where  $[\eta]_0$  is the zero shear limit of intrinsic viscosity. The molecular weights as well as the intrinsic viscosities are tabulated in Table I.

RHEOTEST II coaxial cylinders viscometer, supplied by Prüfgeräte-werk Medingen, East Germany, was used to measure the viscosity of the solutions. In the system used, the ratio of the radii of the inner and outer cylinders was equal to 0.98 and hence no corrections for shear rate variation in the flow field were made. At all rotational speeds employed, the Reynolds number was well below the critical value needed for secondary flow transition to occur.

Solutions of the polymer samples were prepared in the concentration range  $1.9 \times 10^{-2}$  to  $18 \times 10^{-2}$  g/ml. Shear rate in the apparatus could be varied from 0.17 to 1310  $\text{sec}^{-1}$  and shear stresses could be measured in the range of 16 to 5600 dynes/cm<sup>2</sup>. Data were obtained, within the above limitations, on each solution until a clear non-Newtonian trend was observed. Data on the samples C, D, and E were taken at 30°C in both solvents, while data on the sample A were taken at 35°C in *m*-xylene and at 25°C in chlorobenzene. The reasons for the different temperatures employed while obtaining data on the sample A are discussed later.

## RESULTS AND DISCUSSION

The flow curves of the solutions of the samples of PMMA in chlorobenzene and *m*-xylene are shown in Figures 1-9. The data show that at all concentrations studied the zero shear relative viscosity,  $\eta_0/\eta_s$ , in the poor solvent is greater

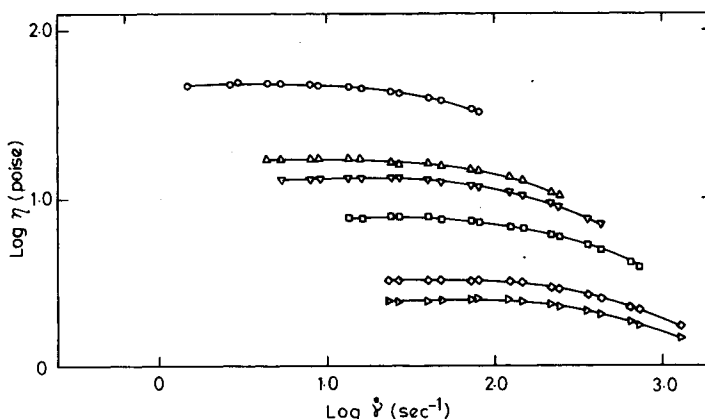


Fig. 1. Viscosity versus shear rate for PMMA in chlorobenzene ( $M = 766,000$ ) at 30°C: (○) 0.1377 g/ml, (Δ) 0.1188 g/ml, (∇) 0.1114 g/ml, (□) 0.0906 g/ml, (◇) 0.074 g/ml, (▷) 0.0636 g/ml.

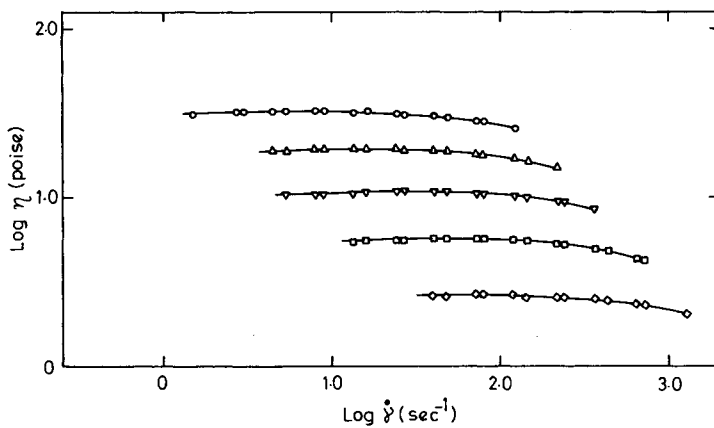


Fig. 2. Viscosity versus shear rate for PMMA in chlorobenzene ( $M = 509,000$ ) at  $30^{\circ}\text{C}$ :  
 (○) 0.1773 g/ml, (Δ) 0.1685 g/ml, (▽) 0.1456 g/ml, (□) 0.1164 g/ml, (◇) 0.0911 g/ml.

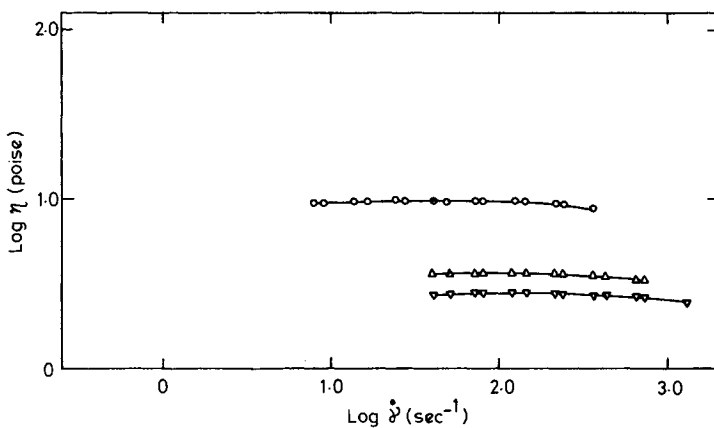


Fig. 3. Viscosity versus shear rate for PMMA in chlorobenzene ( $M = 328,000$ ) at  $30^{\circ}\text{C}$ :  
 (○) 0.18 g/ml, (Δ) 0.147 g/ml, (▽) 0.1362 g/ml.

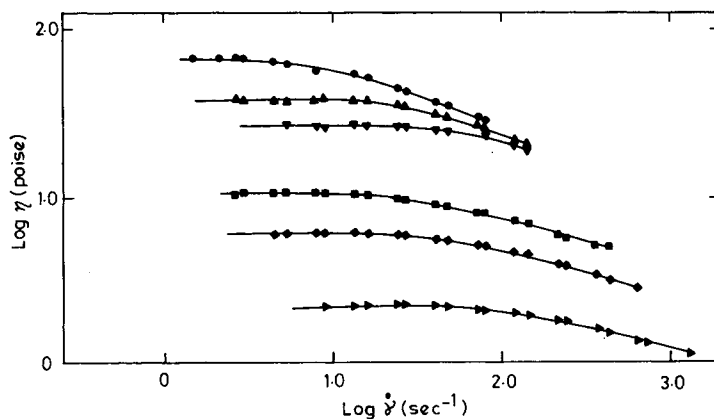


Fig. 4. Viscosity versus shear rate for PMMA in *m*-xylene ( $M = 766,000$ ) at  $30^{\circ}\text{C}$ : (●) 0.0885 g/ml, (▲) 0.0801 g/ml, (▼) 0.0726 g/ml, (■) 0.0568 g/ml, (◆) 0.0532 g/ml, (▶) 0.048 g/ml.

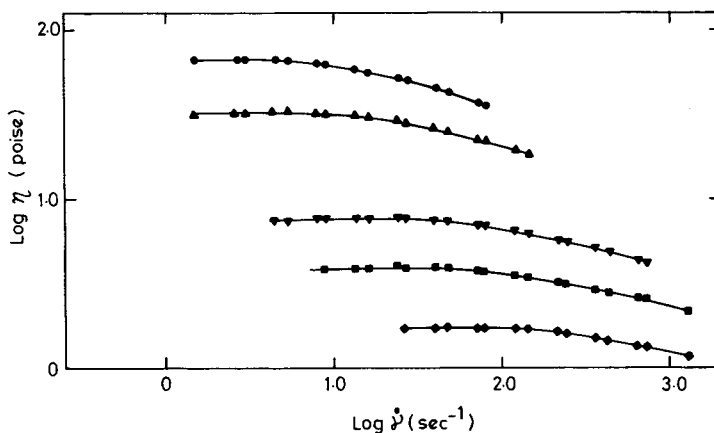


Fig. 5. Viscosity versus shear rate for PMMA in *m*-xylene ( $M = 509,000$ ) at  $30^{\circ}\text{C}$ : (●) 0.1083 g/ml, (▲) 0.0977 g/ml, (▼) 0.0761 g/ml, (■) 0.0691 g/ml, (◆) 0.0584 g/ml

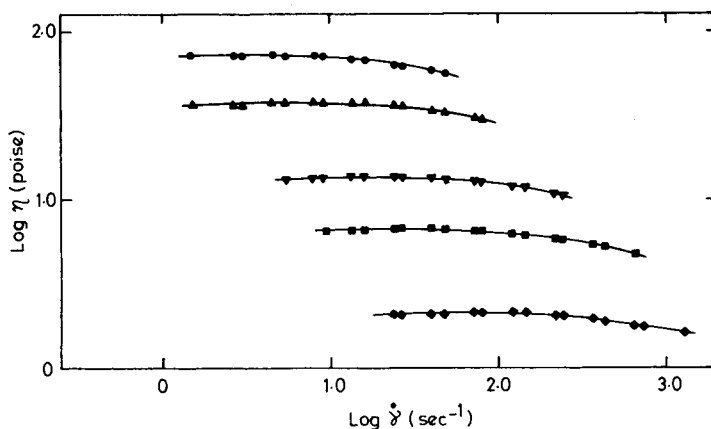


Fig. 6. Viscosity versus shear rate for PMMA in *m*-xylene ( $M = 328,000$ ) at  $30^{\circ}\text{C}$ : (●) 0.1372 g/ml, (▲) 0.1268 g/ml, (▼) 0.1053 g/ml, (■) 0.095 g/ml, (◆) 0.0784 g/ml.

than in the good solvent. Similar observations have been made by others.<sup>10,11</sup> Figure 10 gives a comparison of our data with the data available in the literature. Since in dilute solutions the relative viscosity should be larger in a good solvent than in a poor solvent, it can be concluded that the observed behavior is typical of concentrated solutions at all the concentrations investigated.

#### Evaluation of the Time Constant

The data of all samples were replotted in the form of  $\log(\eta/\eta_0)$  against  $\log \dot{\gamma}$ . The method of superposition as employed by Graessley<sup>5</sup> was used to determine the time constant. For each molecular weight a curve corresponding to a particular concentration was chosen as the reference curve. The plots of  $\log(\eta/\eta_0)$  versus  $\log \dot{\gamma}$  for the same molecular weight but at other concentrations were shifted by an appropriate amount along the  $\log \dot{\gamma}$  axis onto the reference curve to achieve satisfactory superposition. Then the curves obtained for different molecular weights were again shifted along the  $\log \dot{\gamma}$  axis onto a reference curve chosen from among them. The superposed data are shown along with the

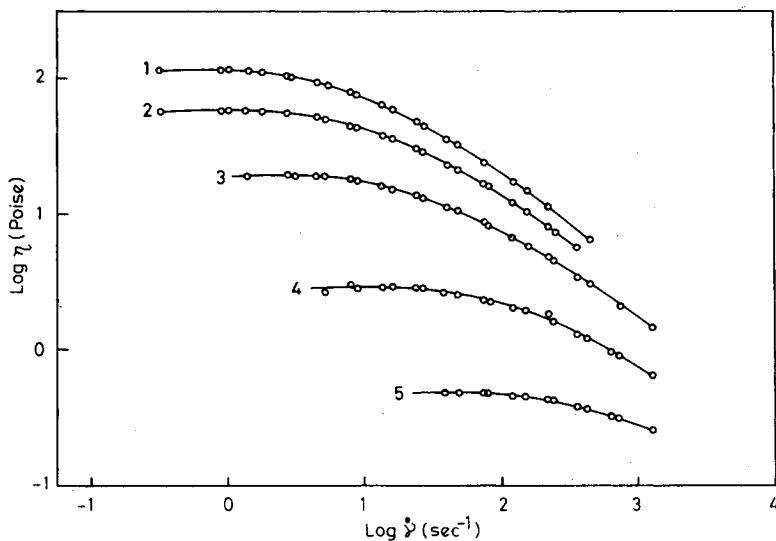


Fig. 7. Viscosity versus shear rate for PMMA in chlorobenzene ( $M = 2,385,000$ ) at  $25^{\circ}\text{C}$ : (1) 0.0839 g/ml, (2) 0.072 g/ml, (3) 0.0566 g/ml, (4) 0.0356 g/ml, (5) 0.0191 g/ml.

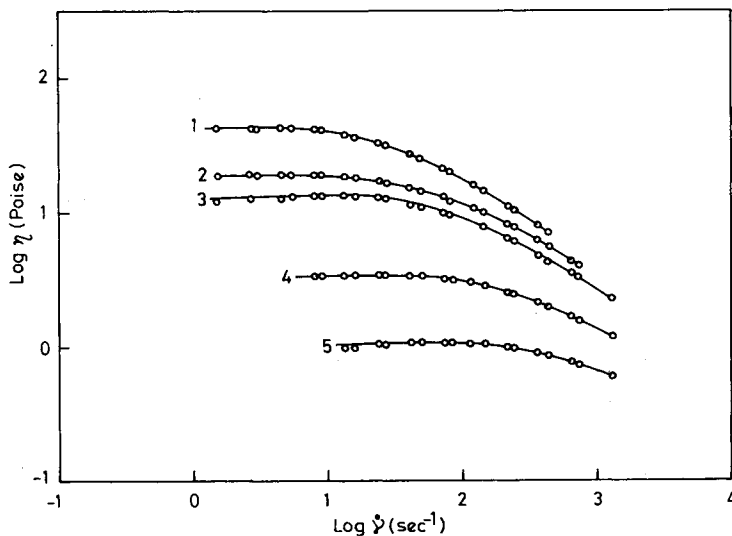


Fig. 8. Viscosity versus shear rate for PMMA in chlorobenzene ( $M = 1,340,000$ ) at  $25^{\circ}\text{C}$ : (1) 0.11 g/ml, (2) 0.0865 g/ml, (3) 0.078 g/ml, (4) 0.0574 g/ml, (5) 0.0398 g/ml.

theoretical curve of Graessley<sup>12</sup> in Figure 11. While small differences exist between individual curves, the superposition is seen to be quite satisfactory. The superposed master curve was compared with the theoretical curve of Graessley<sup>12</sup> and the time constant was easily computed by a direct comparison of the  $\log \dot{\gamma}$  axis of the experimental data with the  $\log (\tau\dot{\gamma})$  axis of the theoretical curve. In a comparison of the master curve with the theoretical curve agreement at low shear rates was given importance, with stress on the usefulness of the time constant in indicating the onset of non-Newtonian behavior. Achieving average agreement with the theoretical curve over the entire range of shear rate

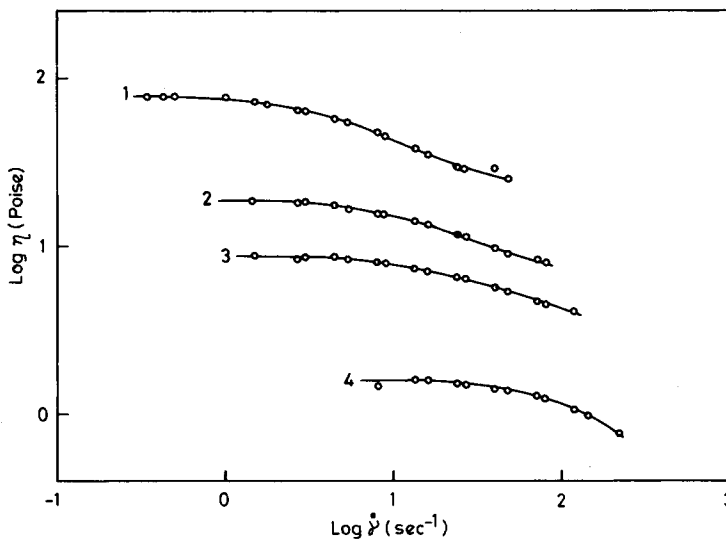


Fig. 9. Viscosity versus shear rate for PMMA in *m*-xylene ( $M = 2,385,000$ ) at  $35^{\circ}\text{C}$ : (1) 0.0492 g/ml, (2) 0.0365 g/ml, (3) 0.0312 g/ml, (4) 0.0219 g/ml.

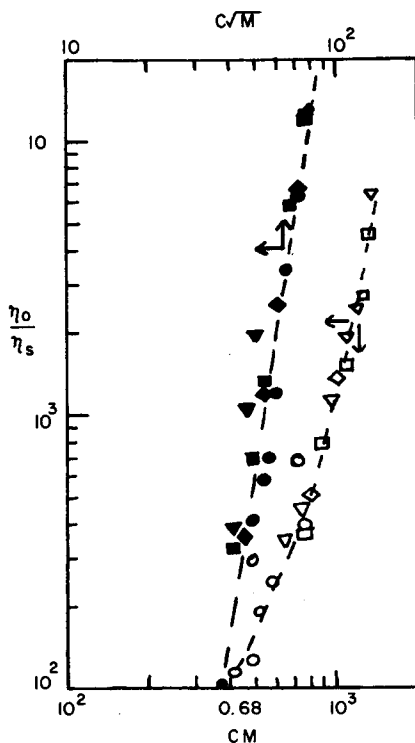


Fig. 10. Comparison of viscosity data for PMMA solutions with literature data: ( $\circ$  and  $\bullet$ ) data of Gandhi and Williams,<sup>11</sup> ( $\nabla$  and  $\blacktriangledown$ ) 766,000, ( $\square$  and  $\blacksquare$ ) 509,000, ( $\diamond$  and  $\blacklozenge$ ) 328,000. The filled points correspond to *m*-xylene and unfilled points to chlorobenzene.

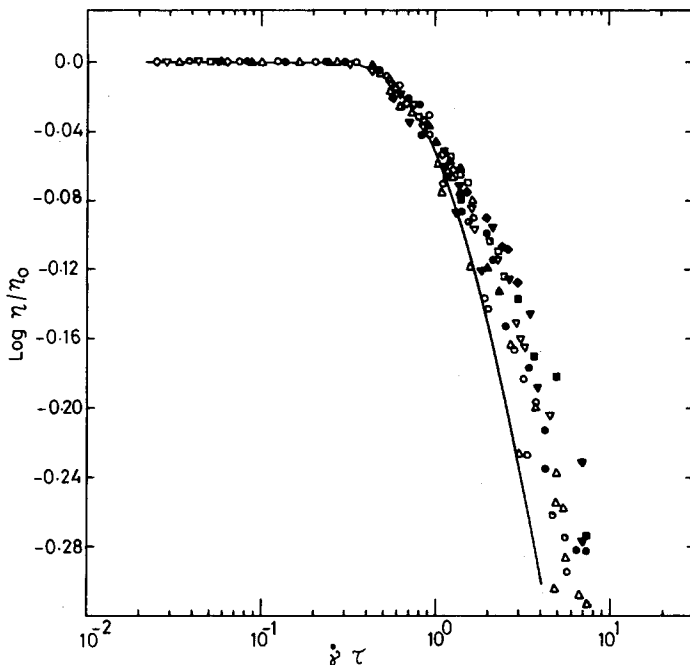


Fig. 11. Composite master curve for PMMA solutions for different molecular weights: (○ and ●) 2,385,000, (△ and ▲) 1,340,000, (▽ and ▼) 766,000, (□ and ■) 509,000, (◇ and ◆) 328,000. Filled points correspond to *m*-xylene and unfilled points to chlorobenzene.

would only alter the absolute value of the time constant and not the relative values of the time constant. (To make this point explicit, we denote the measured time constant  $\tau_{\text{obs}}$ .) This would not affect the evaluation of the solvent effect, which is the main objective of the present work. For each of the curves,  $\tau_{\text{Rouse}}$  was also calculated for comparison. The results are presented in Table II.

The dissimilarity between the data and Graessley's curve at high shear rates has also been observed by Amari and Nakamura.<sup>13</sup> Experimental evidence<sup>14-16</sup> indicates that, in comparison with monodisperse samples, polydisperse samples deviate from Newtonian behavior at relatively lower shear rates and exhibit a more gradual rate of decrease of viscosity with increasing shear rate. Comparison of the present experimental data with the theoretical curve indicates the existence of both the discrepancies mentioned above with respect to the theoretical curve; this may be due to a small residual distribution of molecular weights in the samples.

The ratio  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  for all samples was plotted as a function of concentration for different molecular weights in Figure 12. It shows that for a given molecular weight the ratio of the relaxation times increases at low concentrations and decreases at higher concentrations. The observed maximum in  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  is to be expected and will be discussed later. Observation of the data also shows that if only a partial range of concentrations is investigated, either the increasing or the decreasing behavior only is observed. Typically for low molecular weights,  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  increases with concentration, and for high molecular weights  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  decreases with increasing concentration. Such behavior indicates



that  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  is a combined function of both concentration and molecular weight. Data of Graessley et al.<sup>5</sup> show that in the range of concentrations investigated by them  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  decreases with increasing concentrations, although at low concentrations the ratio appears to have reached a maximum.

TABLE II  
Time Constants of the Samples Studied

$M \times 10^{-5}$	Temp., °C	$C \times 10^{+2}$ , g/cc	$\eta_0$ , poise	$\tau_{\text{obs}} \times 10^3$ , sec	$\tau_{\text{Rouse}} \times 10^3$ , sec
Chlorobenzene					
7.66	30	13.77	48.1	40.4	6.5
		11.88	17.4	18.1	2.7
		11.14	13.4	14.2	2.2
		9.6	7.9	10.5	1.5
		7.46	3.3	5.3	0.8
5.09	30	6.36	2.5	3.6	0.7
		17.73	32.5	17.0	2.3
		16.85	19.3	10.5	1.4
		14.56	10.8	6.3	0.9
		11.64	5.6	3.9	0.6
3.28	30	9.11	2.7	1.9	0.36
		18.0	9.9	3.1	0.43
		14.7	3.6	1.3	0.20
		13.62	2.8	0.93	0.16
<i>m</i> -Xylene					
7.66	30	8.85	69.1	162	14.4
		5.68	10.7	40.4	3.5
		5.32	6.0	23.4	2.1
		4.8	2.2	9.5	0.86
5.09	30	10.83	67.4	91.3	7.6
		9.77	32.8	50.8	4.1
		7.61	7.7	13.8	1.2
		6.91	3.9	7.6	0.7
3.28	30	5.84	1.7	3.2	0.36
		13.72	72.7	50.8	4.2
		12.68	37.7	26.9	2.4
		10.53	13.8	11.7	1.0
		9.50	6.7	6.0	0.56
		7.84	2.1	2.3	0.21
Chlorobenzene					
23.85	25	8.39	116	350	81
		7.20	55.5	206	45.2
		5.66	19.3	82.4	20.0
		3.56	2.9	25.9	4.8
		1.91	0.47	4.4	1.4
13.4	25	11.0	42.8	66.6	12.9
		8.65	19.4	38.9	7.4
		7.8	13.4	30.9	5.7
		5.74	3.5	11.3	2.0
		3.98	1.09	4.1	0.9
<i>m</i> -Xylene					
23.85	35	4.92	77.5	467	89.5
		5.65	18.5	160	28.8
		3.12	8.5	92.1	15.5
		2.14	1.6	28	4.2

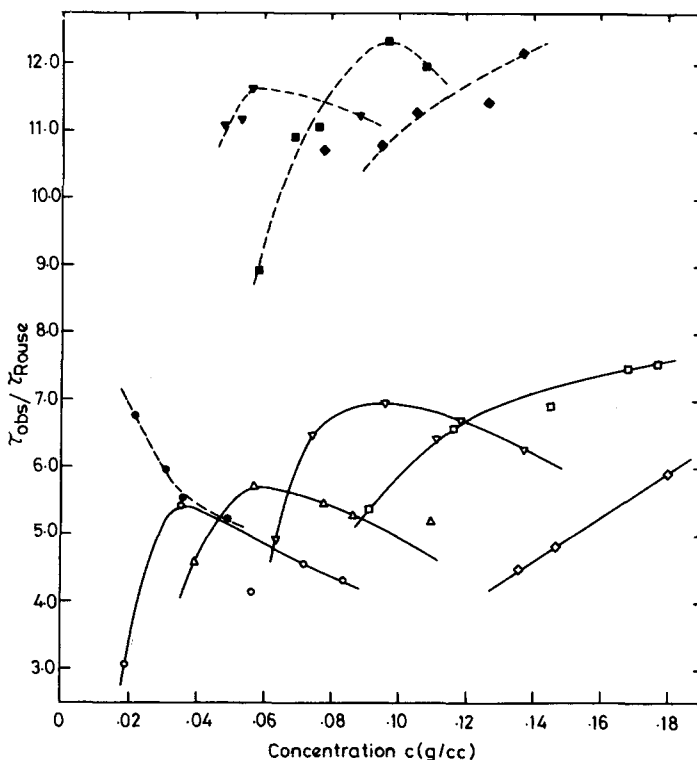


Fig. 12. Ratio of experimental and Rouse relaxation time versus concentrations and molecular weight to 30°C for different molecular weights: (○ and ●) 2,385,000, (△ and ▲) 1,340,000, (▽ and ▼) 766,000, (□ and ■) 509,000, (◇ and ◆) 328,000. Filled points correspond to *m*-xylene and unfilled points to chlorobenzene.

### Reduction of Variables

As suggested by the previous data<sup>5</sup>, as well as by Williams' theory,<sup>6,7</sup> a plot of  $\tau_{obs}/\tau_{Rouse}$  against  $CM$  is shown for samples C, D, and E in Figure 13. It can be seen that the combined variable,  $CM$ , is reasonably successful in unifying the data. The range of  $CM$  values investigated for good solvent as well as for the poor solvent clearly show that  $\tau_{obs}/\tau_{Rouse}$  exhibits a maximum. Graessley et al.<sup>5</sup> found that at high values of  $CM$ ,  $\tau_{obs}/\tau_{Rouse}$  varies approximately as  $1/CM$ . However, the present data do not go to high enough values of  $CM$  to compare with this observation.

In view of the previous data<sup>5</sup> as well as the present data it is clear that as  $CM$  decreases from high values,  $\tau_{obs}/\tau_{Rouse}$  increases and reaches a value much greater than unity. However, as  $CM \rightarrow 0$ ,  $\tau_{obs}/\tau_{Rouse}$  should equal 2 if Bueche's theory holds or attain a value between 0.7 and 1, depending on the solvent character.<sup>3</sup> Thus it is to be expected that as  $CM$  is decreased further, the ratio of relaxation times which has far exceeded unity should decrease and ultimately reach the dilute solution limit. Hence a maximum in  $\tau_{obs}/\tau_{Rouse}$  as  $CM$  is varied is to be expected.

### Discussion of Solvent Effect

Plots of  $\tau_{obs}/\tau_{Rouse}$  versus  $CM$  presented in Figure 13 show that the data in good and poor solvents are roughly parallel except that the slope of the poor

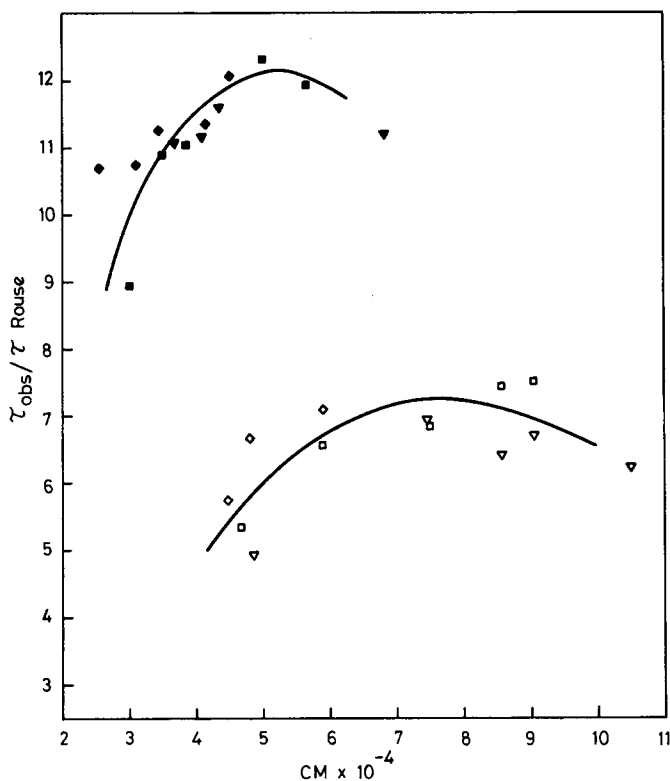


Fig. 13. Relaxation time ratio versus the product of concentration and molecular weight for different molecular weights: ( $\nabla$  and  $\blacktriangledown$ ) 766,000, ( $\square$  and  $\blacksquare$ ) 509,000, ( $\diamond$  and  $\blacklozenge$ ) 328,000. Filled points correspond to *m*-xylene and unfilled points to chlorobenzene.

solvent line at low concentrations is greater than the corresponding good solvent line. For this reason, it is possible to say that the data presented in Figure 13 are not inconsistent with the expected theoretical behavior of  $(\tau/\tau_R)_{good} > (\tau/\tau_R)_{poor}$  as  $CM \rightarrow 0$ . Existing data on non-Newtonian intrinsic viscosity are not clear on this aspect. Data obtained by Pasaglia et al.<sup>17</sup> on polystyrene solutions in toluene (good solvent) and cyclohexane-carbon tetrachloride mixtures (theta solvent) show that  $\tau_{obs}$  is proportional to the solvent viscosity only. Since as  $CM \rightarrow 0$

$$\tau_{Rouse} = \frac{6 [\eta]_0 \eta_s M}{\pi^2 RT} \quad (5)$$

for the data of Pasaglia et al.<sup>17</sup> it would mean that  $\tau_{obs}/\tau_{Rouse}$  is inversely proportional to  $[\eta]_0$ . Therefore, in this data, as  $CM \rightarrow 0$  the good solvent curve should attain a lower limiting value of  $\tau_{obs}/\tau_{Rouse}$  in comparison with the poor solvent curve. However data of Kotaka et al.<sup>18</sup> on polystyrene solutions in benzene, 1-chlorobutane (good solvents), *t*-decalin and cyclohexane (theta solvents) seem to indicate that  $\tau_{obs}/\tau_{Rouse}$  is unaffected by the solvent character in the infinite dilution limit. Further, according to the theory proposed by Fixman,<sup>19</sup> onset of non-Newtonian behavior in intrinsic viscosity occurs at lower values of  $(\tau_{Rouse}\dot{\gamma})$  in a good solvent than in a poor solvent. This implies that  $\tau_{obs}/\tau_{Rouse}$  in a good solvent is greater than in a poor solvent. More precise

data at lower values of  $CM$  are needed to resolve the behavior in the limit of infinite dilution.

Plots of  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  against  $CM$  indicate that at a given value of  $CM$ , the ratio of the relaxation times in a good solvent is less than in a poor solvent. Examination of data presented in Table II shows that at a given value of  $CM$ ,  $\tau_{\text{obs}}$  in a poor solvent is also greater than in a good solvent. Comparison of the data presented in Table II on a given molecular weight sample at approximately the same concentration in the good and poor solvent again shows that both  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  values as well as  $\tau_{\text{obs}}$  values are greater in a poor solvent than in a good solvent. Non-Newtonian behavior originates from several factors including the deforming force exerted by the shear field on the coil, resistance offered by the coil, and the altered rate of entanglement formation. In essence, the finite speed with which the polymer molecules adjust themselves to the high rate of deformation (or shear rate) is the source of non-Newtonian behavior. Hence the time constant in a solution of larger viscosity should be larger since all modes of motion of a polymer molecule will be slower. However, if this were the only reason,  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$ , which is proportional to  $\tau_{\text{obs}}/\eta_0$ , should be unaffected by the solvent character. Hence there must exist another mechanism for the observed slower response of polymer in a poor solvent. The source of the additional retarding force is the intermolecular interactions between neighboring polymer molecules. The segmental motion of a polymer molecule is hindered by the hydrodynamic resistance of the surrounding solution (being proportional to the viscosity of the solution) as well as by the force exerted on the molecule by the immediately neighboring molecules. In a poor solvent the polymer-polymer contacts are energetically more favorable than polymer-solvent contacts. The situation is exactly the opposite in a good solvent. Hence in a poor solvent there will be a relatively stronger attractive force between polymer molecules than in good solvent. Thus the relatively stronger attractive force will impede the motion of polymer molecules to a greater extent in a poor solvent than in a good solvent. The result is a larger time constant in a poor solvent.

As the temperature of the solution in a poor solvent is increased beyond the "theta" temperature, the "goodness" of the solvent increases and hence the solution should behave more like a solution in a good solvent. As a test of the above explanation of the solvent effect on the time constant, data were obtained on sample A in *m*-xylene at 35°C, about 10°C above the theta temperature, and on samples A and B in chlorobenzene at 25°C. For these solutions  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  is plotted against  $CM$  in Figure 14, which shows the absence of the solvent effect. (This can be concluded definitely since the effect of temperature by itself on the ratio of relaxation times was shown by Graessley et al.<sup>5</sup> to be insignificant.) Examples of such behavior where poor solvent transforms itself into a good solvent when temperature is increased have also been shown by Simha and Chan.<sup>20</sup>

Our data support the prediction of Williams' theory and show the explicit effect of solvent nature. The function  $F$  appearing in eq. (3) is given by

$$F = \frac{1}{V_s} \frac{d^2\epsilon}{dv_p^2} \quad (6)$$

where  $\epsilon$  is the Helmholtz free energy density of mixing,  $V_s$  is the partial molar volume of the solvent, and  $v_p$  is the volume fraction (obviously related to  $C$ ) of the polymer in the solution. Since  $\epsilon$  is related to the interpolymer molecular po-

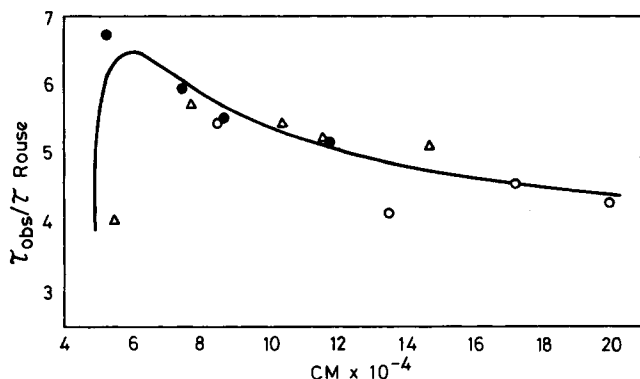


Fig. 14. Relaxation time ratio versus the product of concentration and molecular weight for different molecular weights: (○ and ●) 2,385,000, (△ and ▲) 1,340,000. Filled points correspond to *m*-xylene at 35°C and unfilled points to chlorobenzene at 25°C.

tential of average force, our interpretation of the solvent effect as being due to interpolymer interactions is in qualitative agreement with Williams' theory. Extensive thermodynamic data must be obtained, which is outside the scope of the present work, before quantitative verification of Williams' theory is possible.

### CONCLUSIONS

The ratio of time constant to Rouse relaxation time was found to be a function of the product of mass concentration and molecular weight. At high concentrations  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  was found to decrease with increasing values of  $CM$ . At intermediate concentrations the behavior is reversed and  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  decreases with decreasing values of  $CM$ . The time constant of a polymer solution is affected considerably by the nature of the solvent. The ratio  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  at a given value of  $CM$  is greater in a poor solvent than in a good solvent. The absolute value of  $\tau_{\text{obs}}$  in a poor solvent can be much greater than in a good solvent since  $\tau_{\text{Rouse}}$  is proportional to  $\eta_0$  and  $\eta_0$  in a poor solvent is much greater than in a good solvent. The larger time constants in a poor solvent may be attributed to the relatively stronger interpolymer molecular forces present in a poor solvent. As the goodness of the solvent is increased by increasing the temperature, the explicit solvent effect vanishes and  $\tau_{\text{obs}}/\tau_{\text{Rouse}}$  becomes independent of solvent character.

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