Solvent Power Effect on Graessley's Time Constant in Concentrated Polystyrene Solutions

OTAKAR QUADRAT, JANA MIKEŠOVÁ, and EVA PROKOPOVÁ,
*Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia*

Synopsis

Results of our measurements of polystyrene solutions and those reported in the literature demonstrate the common dependence of Graessley's relaxation time on the product of concentration and molecular weight, irrespective of the solvent power and its viscosity, and of temperature. Such behavior is in agreement with the conclusions reached in our previous paper, namely, that the shear stress dependence of viscosity of this polymer in solvents differing considerably in viscosity and solvent power may be unified by plotting relative viscosity against the product of velocity gradient and Rouse's relaxation time.

INTRODUCTION

When interpreting the gradient dependence of viscosity (η) of concentrated polymer solutions by a theoretical function[1,2]

$$\eta/\eta_0 = f(\tau_0, \dot{\gamma}) \tag{1}$$

(where η_0 is the viscosity of solution at zero velocity gradient and $\dot{\gamma}$ is the velocity gradient), Graessley et al.[3] found that the time constant τ_0 (relaxation time) is proportional to the theoretical value ensuing from Rouse's theory of elasticity[4]

$$\tau_R = (6/\pi^2)\,(\eta_0 M_w/cRT) \tag{2}$$

(M_w is the weight average molecular weight, c is the polymer concentration, R is the gas constant, and T is temperature). They found that for polystyrene solutions in n-butylbenzene the plot τ_0/τ_R against the product of polymer concentration and molecular weight cM_w which is proportional to the number of entanglements per one polymer particle is universal for the given polymer–solvent system. It appeared that the τ_0/τ_R vs. cM_w dependence might be linearized by plotting the reciprocal value, τ_R/τ_0, and that an empirical relation

$$\tau_R/\tau_0 = k_1 + k_2 cM_w \tag{3}$$

is valid.

On the contrary, the results of investigations of the time constant in polymer solutions with various thermodynamic quality of solvent obtained up to now are not uniform. Rao and Gandhi[5] report that for six fractions

CCC 0021-8995/85/093585-04$04.00

of poly(methyl methacrylate) the dependence of τ_0/τ_R on cM_w have a maximum and that in a poor solvent (m-xylene) this ratio is twice as high as in a good one (chlorobenzene). Compared with these results, the values reported in a paper by Ballauff et al.[6] for one sample of polystyrene in *trans*-decalin (Θ-solvent) and in toluene (good solvent) differed much less.

The effect of temperature on τ_0/τ_R is also not clear. A rise in temperature from 30 to 35°C in poly(methyl methacrylate) solutions[5] in m-xylene led to a decrease in τ_0/τ_R to the level of values for chlorobenzene, which caused an improvement in the thermodynamic quality of the solvent. On the other hand, a decrease in τ_0/τ_R due to temperature observed in polystyrene solutions[6] was very small, and, more important still, it was approximately the same in both the good and the poor solvent.

To supplement results reported in the literature, we investigated three samples of polystyrene in decalin and cyclohexanone at several concentrations and tried to elucidate the differences just mentioned.

EXPERIMENTAL

Polystyrene samples were prepared by bulk polymerization with di-*tert*-butyl hyponitrite as initiator. Their molecular weight (1.9–2.1–3.8 × 10⁶ g mol⁻¹) was determined viscometrically in benzene solutions at 25°C using Meyerhoff's relation,[7] $[\eta] = 1.23 \times 10^{-4} M_w^{0.72}$. The intrinsic viscosity measurements were carried out in dilution viscometers of the Ubbelohde type at shear stress values at which the non-Newtonian flow could be neglected. No correction to the loss of kinetic energy and end effect was needed in view of long efflux times. The intrinsic viscosity was extrapolated graphically by employing Heller's method[8] from the plot $[(c/\eta_{sp}) + (c/\ln \eta_r)]/2$ vs. c for five concentrations.

All solvents, reagent grade purity, were redistilled before use. For decalin (a mixture of stereoisomers), $\Theta = 19°C$.[10]

The dependence of viscosity on the velocity gradient was measured using Weissenberg's rheogoniometer R-18 (cone-plate). No degradation of the polymer was observed. The viscosity η_0 and the time constant τ_0 were calculated by means of a microcomputer PDP 11/23 using our method[9] which consists of a comparison between the experimental and Graessley's dependence of viscosity by means of a linearized empirical equation.

RESULTS AND DISCUSSION

Measurements with our samples of polystyrene were carried out at three concentrations (from 0.02 to 0.10 g cm⁻³) and four temperatures (from 15 to 35°C). It was found that the τ_R/τ_0 values are indeed solvent-independent within the limits of experimental error and that these data along with those calculated from tabulated data reported in the literature[3,6] for polystyrene solutions in n-butylbenzene, *trans*-decalin, and toluene formed a common and universal dependence on cM_w (Fig. 1). The value of τ_R/τ_0 remained unaffected if the solvent power was changed by raising the temperature, or if the viscosity of the solvent (toluene, cyclohexanone) differed more than three times from each other.
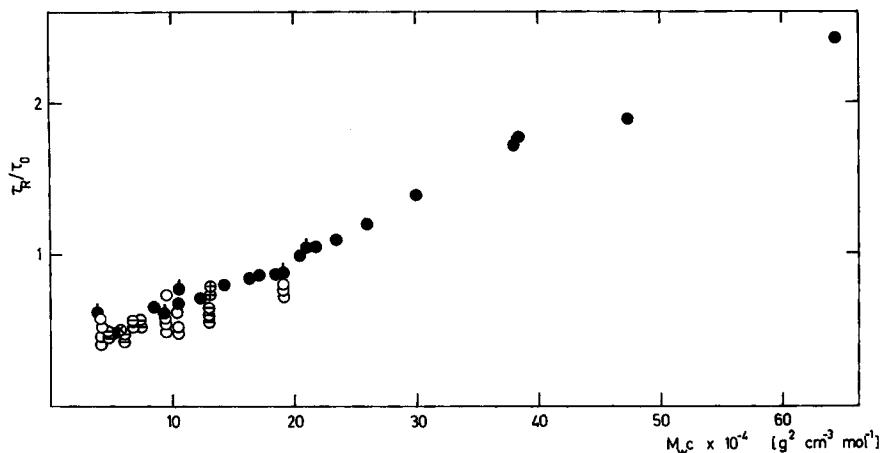
Fig. 1. Dependence of the ratio of relaxation times on the product of concentration and molecular weight. Solvents and temperatures: (●) cyclohexanone (25°C); (○) decalin (15–35°C); (⊖) trans-decalin[6] (16.6–49.7°C); (⊕) toluene[6] (17.6–45.2°C); (●) n-butylbenzene[3] (30–60°C); (⊗) cf. Ref. 7.

These results agree well with the conclusions of our previous paper[10] in which we reported that the η/η_0 vs. $\tau_R \dot{\gamma}/2$ plot is common for polystyrene solutions having the molecular weight 2.7×10^5 g mol^{-1} at the concentration 0.208 g cm^{-3} in 11 solvents with viscosity ranging between 0.637 and 62.6 mPa s, at the viscosity expansion coefficient α_η^3 (for infinity dilute solutions) in the range from 0.79 to 2.16. A comparison between this plot and Graessley's theoretical function gives $\log(\tau_0/\tau_R) = 0.3$ (i.e., $\tau_R/\tau_0 = 0.5$). This value plotted against $cM_w = 5.6 \times 10^4$ g^2 cm^{-3} mol^{-1} also fits the dependence shown in Figure 1.

The quantity $\tau_R \dot{\gamma}/2 = (3/\pi^2)(\eta_0 M_w \dot{\gamma}/cRT)$ used in Ref. 10 is analogous to the reduced shear stress $\beta = \eta_{sp}\eta_s M/cRT$ (η_{sp} is the specific viscosity and η_s is the viscosity of the solvent) which represents the reduced energy of the hydrodynamic field acting upon the macromolecule in dilute solutions. Since the relaxation time τ_0 may also be expressed through the reciprocal value of the critical velocity gradient $\dot{\gamma}_{cr}$ at which the non-Newtonian flow sets in, the ration of relaxation times τ_R/τ_0 corresponds to the critical value of the parameter β according to the relation

$$\tau_R/\tau_0 = \tau_R \dot{\gamma}_{cr} = (6/\pi^2)(\eta_0 M_w \dot{\gamma}_{cr}/cRT) \tag{4}$$

The universal τ_R/τ_0 vs. cM_w dependence means, therefore, that the non-Newtonian flow always sets in at a certain critical value of this quantity which is independent of the solvent and is characteristic only of the given density of macromolecular entanglements. This reduced value adequately reflects the effect of temperature and viscosity of the solvent. As to the solvent power, it is quite possible that the cause of the small effect of this factor on the critical reduced energy of the hydrodynamic field consists in the weak effect of the excluded volume in concentrated polymer solutions.[11]

The authors explain the dependence of τ_0/τ_R values for poly(methyl methacrylate) solutions[5] on the solvent power by relatively stronger intermo-

lecular attractive forces in the poor solvent. Results obtained for polystyrene solutions do not confirm this view, however. According to our experience, solutions of poly(methyl methacrylate) in poor solvents possess a strong effect of negative thixotropy. It seems quite probable that the results of measurements in m-xylene may have been affected just by this effect and that the higher values of τ_0/τ_R obtained for this solvent compared with chlorobenzene are a specific feature of this particular polymer.

References

1. W. W. Graessley, *J. Chem. Phys.*, **43**, 2696 (1965).
2. W. W. Graessley, *J. Chem. Phys.*, **47**, 1942 (1967).
3. W. W. Graessley, R. L. Hazleton, and L. R. Lindeman, *Trans. Soc. Rheol.*, **11**, 267 (1967).
4. P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).
5. V. G. Rao and K. S. Gandhi, *J. Appl. Polym. Sci.*, **19**, 1663 (1975).
6. M. Ballauff, H. Krämer, and B. A. Wolf, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1217 (1983).
7. G. Meyerhoff, *Z. Physik. Chem.* (Frankfurt), **4**, 335 (1955).
8. W. Heller, *J. Colloid Sci.*, **9**, 547 (1954).
9. O. Quadrat and E. Prokopová, *J. Appl. Polym. Sci.*, to appear.
10. Q. Quadrat, *Collect. Czech. Chem. Commun.*, **37**, 3239 (1972).
11. B. L. Hager and G. G. Berry, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 911 (1982).