*Macromolecules* **1981**, *14*, 352-354

# Shear Rate Dependent Viscosities of PPO–PS Polymer Blend–Solvent Systems

**B. Chitrangad* and S. Middleman**[†]

*Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003.* *Received May 29, 1980*

ABSTRACT: The rheology of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-polystyrene (PS) blends was studied in various solvents in order to understand the effect of the nature of interactions on shear viscosities and structure of the system. PPO was found to exist in aggregated form in PPO–PS blend–solvent systems. Rather strong shear rate dependency in viscosities of PPO–PS blend solutions, in the region of 90% PPO content, was explained in terms of the changes brought about in packing structure of the system from increasing the proportion of the other constituent component, polystyrene.

## Introduction

A combination of polymers is increasingly found to meet the specific property requirements of new end uses. Very few polymers are known to be compatible with each other in nature. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) form a pair of such polymers found to be compatible in melts.[1,2] The solution rheology of these polymers was studied in different solvents to gain an understanding of the nature of their compatibility and dispersion in the presence of solvents. A number of polymer concentrations were chosen for the study. The relative proportion of the two polymers was varied in solution with the total polymer concentration kept constant at a chosen value. Pairs of other polymer–solvent systems with thermodynamic parameters similar to those of the PPO–solvent systems were studied to confirm the evidence that PPO aggregated in the solvents studied.

## Experimental Section

**Materials.** The PPO used in the study was manufactured and kindly supplied by General Electric Co. The viscosity-average molecular weights ($\bar{M}_v$) for the PPO samples were measured[3] as $5.5 \times 10^3$ and $1.4 \times 10^4$ with a polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of about 2. The $\bar{M}_w$ and $\bar{M}_n$ were $2.96 \times 10^5$ and $1.45 \times 10^5$ for PS, $8.0 \times 10^4$ and $3.9 \times 10^4$ for poly(vinyl chloride) (PVC), and $2.5 \times 10^4$ and $1.25 \times 10^4$ for poly($\epsilon$-caprolactone) (PCL).

**Measurement Method.** The steady-state shear viscosities were measured by any one or a combination of glass capillary viscometers, a Drage concentric cylinder rotational rheometer, a Weissenberg rheogoniometer, and an air-pressurized capillary viscometer. In the case of a gas-operated capillary viscometer, steady-state viscosities were determined from a combination of capillaries of varying lengths but of the same diameter.

## Results and Discussion

Relative viscosities ($\eta_r$) for PS and PPO solutions are plotted in Figures 1 and 2. Curve A in Figures 1–3 represents the correlation found for polyisobutylene (PIB) in various solvents.[4] Although the present results show a trend similar to the observations for low-$T_g$ polymer–solvent systems, they are not quantitatively described by curve A, which correlates $\eta_r$ with either the volume fraction parameter, $c[\eta]$, or a measure of entanglement density, $cM^{5/8}$.

Some PPO solutions were not clear after preparation. The presence of PPO in the dissolved form was confirmed by the fact that the temperature coefficient of viscosity showed no unusual variation. In addition, the viscosities of PPO solutions were identical when the solutions were prepared and measurements were conducted at room temperature or when the solutions were clarified at higher temperatures and the measurements were conducted at 25 °C.

The presence of 5–10% crystallinity itself in PPO is ruled out as the cause of the deviation observed in zero shear viscosities from correlation curve A. Curve A represents results for low-$T_g$ polymers without crystallinity. PCL, which has crystallinity comparable to the amount found in PPO, was studied in two solvents. The results for PCL in toluene and 2-butanone at 25 °C are shown in Figure 3. These results closely correspond to the correlation A previously observed for linear polymer–solvent systems and thus rule out the presence of crystallinity as the cause of deviation.

The relative viscosities of very dilute PPO solutions, needed to determine intrinsic viscosities, depended on the molecular weight of the test sample and its concentration. The relative viscosities were found to be independent of molecular weights in the range of intermediate polymer concentrations. As Figure 4 shows, the relative viscosities measured were a function only of polymer concentration and thus were described well by an Einstein type of expression. Figure 5 shows the separation in the curve of Figure 4 brought about by differences in the intrinsic viscosity, $[\eta]$, for PPO samples of two different molecular weights. Since for concentrations above about 1 g/dL of PPO in solution the relative viscosities depend only on concentration, it appears that intermolecular association exists in the higher concentration region. Then an Einstein type of expression would successfully correlate the relative viscosities to polymer concentration. Therefore, it is concluded that PPO exists in aggregated form in the solutions.

The data of Figure 2 further support the concept of aggregation in these polymer–solvent systems. The small separation between curve A and the correlation for viscosity of PS solutions is caused by the fact that curve A is based on the viscosity-average molecular weight while the data for PS only are plotted based on weight-average molecular weight.

But the large horizontal separation between curve A and the correlation for relative viscosities of PPO solutions may be attributable to the fact that the effective molecular weight of PPO was not used to calculate the parameter $cM^{5/8}$. Thus the shift factor necessary to transpose the PPO curve horizontally, so as to superimpose it on curve A, may be used as a measure of the degree of aggregation present in the system. Molecular association and aggregation may exist in the case of other polymer–solvent systems which have similar physical properties and thermodynamic parameters (such as $T_g$, crystallinity, poly-

---

* To whom correspondence should be addressed at the Department of Chemical Engineering, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3.

[†] Now at the Department of Applied Mechanics and Engineering Sciences, University of California, San Diego, La Jolla, Calif. 92093.

0024-9297/81/2214-0352$01.25/0

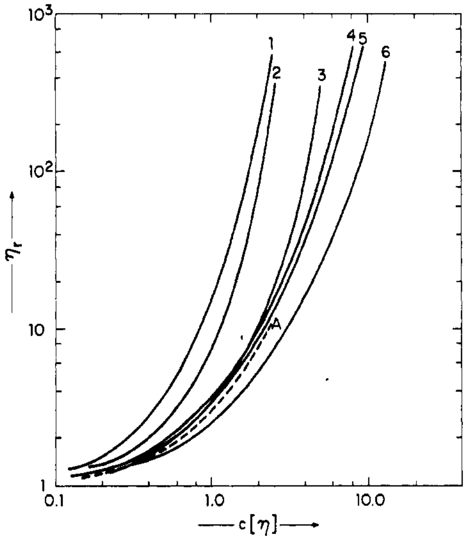

**Figure 1.** Relative viscosity as a function of polymer volume fraction parameter, $c[\eta]$: (1) PPO-benzene; (2) PPO-toluene; (3) PPO-chlorobenzene; (4) PS-benzene; (5) PS-toluene; (6) PS-chlorobenzene. $\bar{M}_v = 1.4 \times 10^4$, $T = 25$ °C.

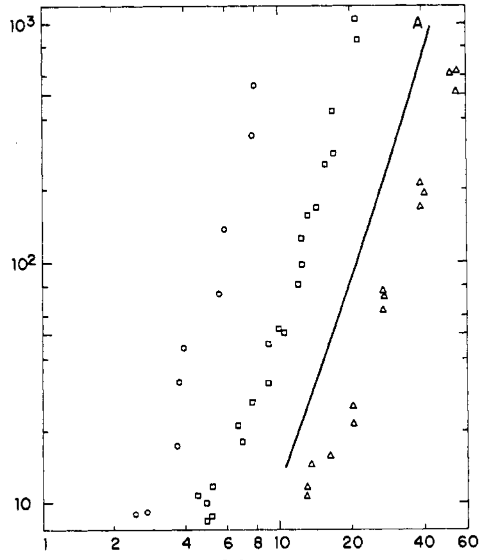

**Figure 2.** Relative viscosity as a function of $c\bar{M}_v^{5/8}$ for polymer–solvent systems: (○) PPO; (□) PVC; (△) PS.

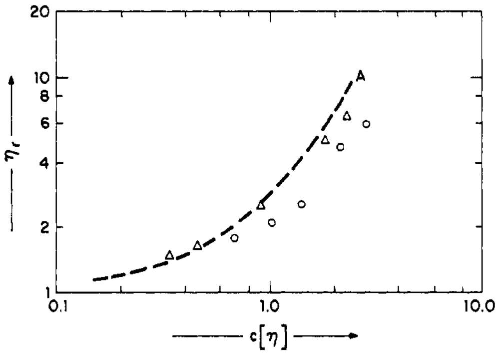

**Figure 3.** Relative viscosity of PCL solutions as a function of $c[\eta]$: (△) PCL-2-butanone; (○) PCL–toluene.

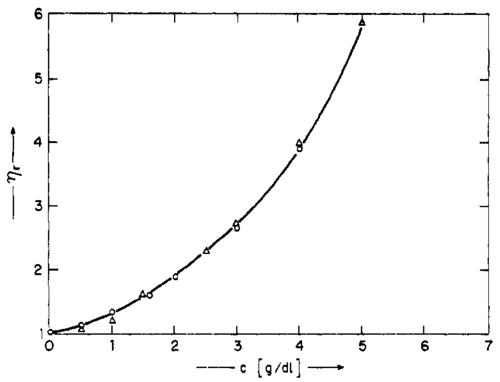

**Figure 4.** Concentration dependence of relative viscosity for PPO in toluene: (△) $\bar{M}_v = 5500$; (○) $\bar{M}_v = 14400$.

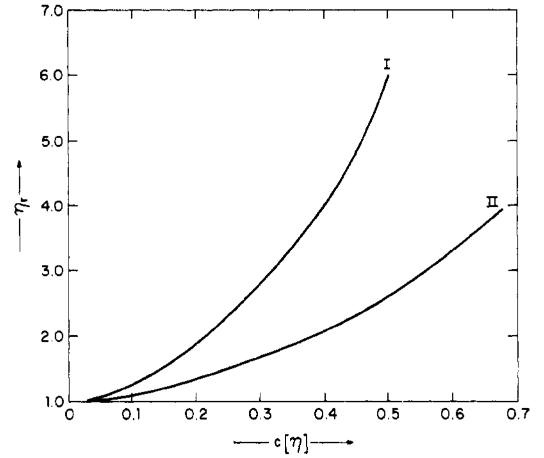

**Figure 5.** Relative viscosity of PPO–toluene solutions as a function of $c[\eta]$: (I) $\bar{M}_v = 5500$; (II) $\bar{M}_v = 14400$.

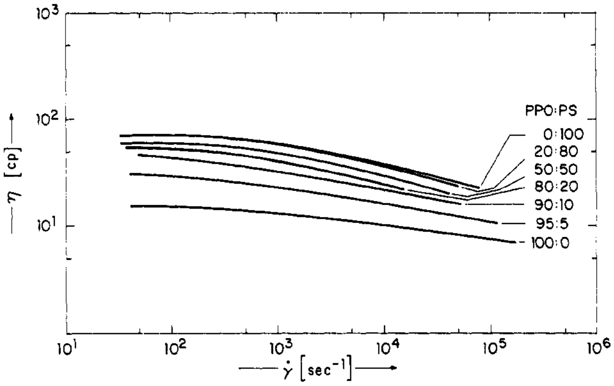

**Figure 6.** Shear rate dependency of viscosity for 12% polymer blend solutions with varying proportions of PPO. $T = 25$ °C.

mer–solvent interaction parameters, etc.).

PVC in tributyl phosphate was studied to confirm the evidence of molecular aggregation. PVC–tributyl phosphate at 55 °C presents a system with physical properties and thermodynamic parameters similar to the values observed for the above-mentioned PPO–solvent systems. Figure 2 shows the data for PVC–tributyl phosphate system. Data for PVC in toluene[5] are indistinguishable from the correlation for PVC–tributyl phosphate shown in Figure 2. Thus, as observed for PPO, PVC also shows the tendency for molecular aggregation, although to a lesser degree. The degree of aggregation depends on the physical properties and interaction parameters of the polymer–solvent system under study. To the extent of the accuracy of the experiments, physical properties of the polymer were found to predominantly influence the degree of aggregation.

Shear rate dependence of the viscosity of the solutions of PPO–PS blends at different polymer concentrations was studied. The study was carried out to observe any change in behavior of the shear rate dependency of blend–solvent systems with the change in blend compositions. Figure 6 shows characteristic shear rate behavior for solutions of PPO–PS blends. The figure shows rheological behavior for solutions of a fixed total polymer concentration of 12% but with varying proportions of the two polymers as indicated by the individual curves. The highest and lowest curves represent the behavior observed for homopolymers PS and PPO in solution. The changes in shear rate dependent viscosities do not correspond linearly with the changes in proportion of the polymers in the blend. The variation in polymer blend solution behavior becomes particularly sensitive to the amount of PPO as the proportion falls below 90% PPO. This is observed to be true for the whole range of rate of shear covered in the study, which is from 50 $s^{-1}$ to about $3 \times 10^5$ $s^{-1}$.

The changes brought about in the packing structure of the blend–solvent system may explain the enhanced sensitivity of shear viscosity to the changes in relative proportion of the two polymers. Solutions of PPO–PS blends in toluene are used to illustrate this point.

Most efficiently packed spheres, touching one another, occupy a volume fraction of 0.74. $c[\eta]$ is a measure of the volume fraction occupied by the polymer molecules. Therefore, we can use this quantity to approximate the relative volume fraction occupied by the two homopolymer components in solution. The intrinsic viscosities, $[\eta]$, for PPO and PS in toluene were measured to be 0.17 and 0.45 dL/g, respectively, at 25 °C. These measured intrinsic viscosities yield a value of 88% PPO required to correspond to an occupied volume fraction of 0.74 for PPO in the blend solution. Thus, a close-knit continuous structure of PPO aggregates is formed for 88% and more PPO proportion. But for PPO proportions of lower than 88%, PS molecules are increasingly able to occupy the exclusive next-neighbor positions of a continuous PPO structure. The PPO molecules are more rigid than PS molecules. Therefore the comparatively flexible PS molecules are able to alter the characteristics of the continuous PPO system quite drastically. With an increase of PS proportion, the system approaches a condition where PPO entities are suspended essentially in a continuum of PS solution. This satisfactorily explains the observed behavior of solutions of PPO–PS blends.

In conclusion, though PPO–PS blends form a homogeneous system in melts,[2] PPO likely exists in aggregated form in the case of PPO–PS blend solutions. Experimental results shown in Figures 2 and 6 confirm this view.

## References and Notes

(1) Cizek, E. P. U.S. Patent 3383435 (May 14, 1968).

(2) Prest, W. M., Jr.; Porter, R. S. *J. Polym. Sci., Part A-2* **1972**, *10*, 1639.

(3) Barrales-Rienda, J. M.; Pepper, D. C. *Eur. Polym. J.* **1967**, *3*, 535.

(4) Chitrangad, B.; Osmers, H. R.; Middleman, S. *Polym. Eng. Sci.* **1977**, *17*, 806.

(5) Pezzin, G.; Gligo, N. *J. Appl. Polym. Sci.* **1966**, *10*, 1.

---

# Rheological Properties of Anionic Polystyrenes. 7. Viscoelastic Properties of Six-Branched Star Polystyrenes and Their Concentrated Solutions

**Toshiro Masuda,* Yasuhiko Ohta, Mitsunobu Kitamura, Yoichiro Saito, Kyoko Kato, and Shigeharu Onogi**

*Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.*

*Received September 18, 1980*

ABSTRACT: The viscoelastic properties of six-branched star polystyrenes and their 50 wt % (0.641 g/mL) solutions were measured and compared with those of linear polystyrene. The dependence of zero-shear viscosity $\eta_0$ and steady-state compliance $J_e°$ upon molecular weight was obtained. $\eta_0$ for six-branched polystyrene is lower than that for linear polystyrene of the same molecular weight. The values of $J_e°$ for undiluted six-branched polystyrenes and their 50 wt % solutions depend on molecular weight even in the entanglement region. The $J_e°$ values also follow the Rouse–Ham relation in the wide ranges of molecular weights; $J_e°$ for star polymers exceeds that for linear ones at higher molecular weights. The entanglement compliance $J_{eN}°$ of branched polystyrenes is the same as that of linear ones, suggesting no effect of branching on the entanglement spacing.

In the past several years, the rheological properties of melts and concentrated solutions of branched polymers which are well characterized have been investigated, and numerous data on the effect of branching on rheology have been accumulated. The rheological properties of various types of branched polymers, such as star-shaped,[1-11] comb-shaped,[12-14] and randomly branched polymers[15] have been measured. The zero-shear viscosity, $\eta_0$, of branched polymers and their solutions is lower than that of linear polymers having the same molecular weights, at low molecular weights and/or concentrations.[5-8,12,13,15] On the other hand, the viscosity of branched polymer liquids becomes higher than that of linear ones as the molecular weight of branches increases at high concentrations. This enhancement behavior of viscosity has been observed clearly for concentrated solutions and melts of various star-shaped polymers.[1,3,6,8] This behavior implies that branched polymers with long branches have longer relaxation times in the terminal zone.[6]

The steady-state compliance, $J_e°$, which represents the elastic characteristics at long times, has also been investigated, but the behavior is still ambiguous. $J_e°$ for undiluted four-branched polystyrenes[4] and comb-shaped polystyrenes[12,13] was reported to be independent of molecular weight and higher than that for corresponding linear polymers by approximately one decade at high molecular weights. Extensive investigation recently reported[8,10] shows that $J_e°$ for undiluted four-branched[8,10]