3980 *Macromolecules* 1993, *26*, 3980–3985

Orientation-Dependent Interactions in Polymer Systems. 3. Segmental Orientation in Poly(2,6-dimethyl-1,4-phenylene oxide)/Polystyrene Miscible Blends

Kenji Kawabata,† Takeshi Fukuda,* Yoshinobu Tsujii, and Takeaki Miyamoto

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Received January 11, 1993; Revised Manuscript Received April 22, 1993

ABSTRACT: The segmental orientations in a uniaxially stretched, fully entangled polystyrene (PS) melt containing a small amount (3% by weight) of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were studied as a function of the molecular weight of PPO, $M_{n,2}$, by means of infrared dichroism spectroscopy. The PS matrices were either cross-linked (by use of divinylbenzene) or un-cross-linked. At time $t = 0$, i.e., immediately after a stretch was applied to the blend film, both PS and PPO segments showed finite orientations η_1 and η_2, respectively, where η denotes the order parameter $P_2(\cos\theta)$. The η_2/η_1 vs $M_{n,2}$ curves for the cross-linked and un-cross-linked systems at $t = 0$ were very similar to each other: for $M_{n,2} \lesssim 10^3$, the orientation ratio η_2/η_1 increased with increasing $M_{n,2}$, approaching a plateau for $10^3 \lesssim M_{n,2} \lesssim 10^4$, where $\eta_2/\eta_1 \cong 0.5$. With a further increase in $M_{n,2}$, η_2/η_1 steeply increased, approaching another plateau, where $\eta_2/\eta_1 \cong 2.7$ (un-cross-linked systems) or 1.7 (cross-linked systems). This enormous increase in η_2/η_1 is ascribed to the *entanglement* interaction of PPO chains with the PS matrix. Examination of the cross-linked systems, where the matrix orientation did not relax owing to the cross-links, has revealed that PPO segments exhibit a finite, unrelaxing orientation with a constant η_2/η_1 ratio of about 0.4 in both unentangled and entangled regions (excepting the oligomeric region, where η_2/η_1 depended on $M_{n,2}$. The η_2/η_1 vs $M_{n,2}$ curve in the unentangled region was substantially the same as the $t = 0$ curves for the cross-linked and un-cross-linked systems). This unrelaxing orientation of PPO is ascribed to the *segmental* interaction between PPO and PS. The packing entropy theory proposed previously (Fukuda, T., et al. *Macromolecules* 1992, *25*, 2196) gives a reasonable description of this equilibrium orientation of PPO.

Introduction

There has been a large body of experimental evidence indicating the existence of segment–segment or segment–solvent orientational correlations in various polymer systems under deformation.[1–16] For example, it was observed that small molecules[4,5,7] as well as segments of a free probe polymer[13,14] dispersed in an oriented polymer network exhibit a nonzero equilibrium orientation along the direction of the matrix orientation. This "induced" orientation is often comparable in magnitude to that of the matrix segments and appears to be more significant for molecules with higher shape anisotropy.[5] Since this effect is understood as being a cooperative phenomenon arising from local intermolecular interactions of either entropic or enthalpic origin (or both), the matrix polymer itself should not be free from this effect either. That is, the segments of an oriented pure polymer would, whether cross-linked or not, generally exhibit an "excess" orientation over what would be expected for a hypothetical gaslike system (without any intersegmental interactions). Experiments indicate that this actually occurs.[1–3,6,18]

Theoretically, this problem was first considered by Fukuda and Allen[18] using a lattice model, hence from an entropic point of view, and by Jarry and Monnerie[19] from an enthalpic point of view. Of the subsequent papers[13,14,20–24] which have discussed the same or related problems, the one by us[24] has the advantage of offering analytical equations that predict the amounts of the excess and induced orientations in a miscible blend as a function of the composition, chain lengths, and chain flexibilities of the two polymers. For example, the segments of polymer 2 sparsely dispersed in a weakly stretched network of polymer 1 are predicted to be oriented, at equilibrium, by an amount

$$\eta_2/\eta_1 = (1/5)x_2(1 - n_2^{-1})/(1 + x_2 n_2^{-1}) \qquad (1)$$

where $\eta_i = (3/2)\langle\cos^2\theta_i\rangle - (1/2)$ is the order parameter, x_i is the axial ratio of the segment, and n_i is the chain length index. This equation is based on the Di Marzio-type lattice model and the freely-jointed-chain model *with a statistical distribution of the segment length*:

$$x_i = b_i/D_i \qquad (i = 1 \text{ or } 2) \qquad (2)$$

$$n_i = L_i/D_i \qquad (i = 1 \text{ or } 2) \qquad (3)$$

where b_i is the average segment length, which may be identified with the persistence length, and L_i and D_i are the contour length and diameter of the chain, respectively. Note that η_1 is the sum of the gaslike contribution $\eta_1{}^*$ due to the external force field and the excess orientation due to the segmental interaction. The flexibility index of the matrix polymer, x_1, is not explicit in eq 1, but it appears in the expression for $\eta_1/\eta_1{}^*$. It is also noted that the energetic interaction terms[24] are neglected in eq 1. In this context, it gives a "minimum" estimate of induced orientation. Equation 1 and the related theoretical results appear to interpret many of the experimental observations, at least qualitatively.[24]

In this work, we have studied cross-linked and un-cross-linked polystyrenes (PSs) containing a small amount of fractionated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of varying chain length. By infrared dichroism (IRD), independent determination of η_1 and η_2 of this miscible pair of polymers is possible.[25,26] There are two main purposes in this work. One is to test eq 1 experimentally, particularly with respect to the chain length dependence of the orientation of the probe polymer. The other is to clarify the effect of chain entanglement on segmental

---

* To whom correspondence should be addressed.

† Permanent address: Hirakata Laboratory, Ube Industries, Ltd., Hirakata, Osaka 573, Japan.

0024-9297/93/2226-3980$04.00/0

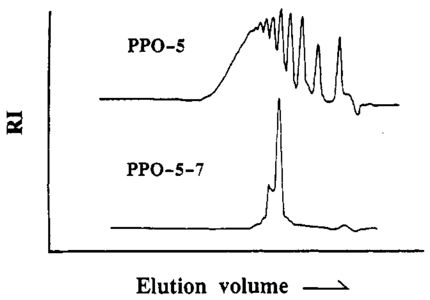

Figure 1. Gel permeation chromatograms of a crude PPO sample (PPO-5) and one of its fractions (PPO-5-7).

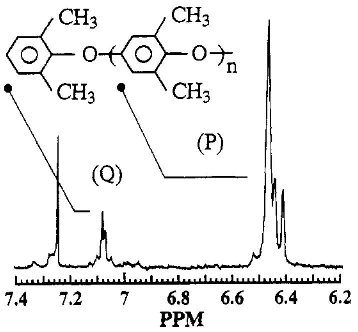

Figure 2. ^{1}H-NMR spectrum of PPO-5-6.

orientations. Interesting results on the latter topic have been reported for the same system by Zhao et al.[27] We hope to provide a further understanding of this nonequilibrium behavior by studying both cross-linked and un-cross-linked systems and both short and long probes polymers.

Experimental Section

Polymer Samples and Characterization. Five PPO samples (coded PPO-1 through PPO-5) were prepared by oxidative coupling of 2,6-dimethylphenol with copper(I) chloride as catalyst and pyridine as ligand and solvent.[28] To prevent the redistribution reaction,[29] they were acetylated at the hydroxyl end groups using an acetic anhydride/pyridine system. Sample PPO-5 was separated into 10 fractions (PPO-5-1 through PPO-5-10) by use of a semipreparative gel permeation chromatograph (GPC; Toso, Japan). Figure 1 shows the GPC chromatograms of a crude sample (PPO-5) and one of its fractions (PPO-5-7).

The number-average molecular weights, M_ns, of the samples with a relatively low degree of polymerization (DP) were established by proton magnetic resonance (^{1}H NMR): Figure 2 shows the ^{1}H NMR spectrum of PPO-5-6, in which the signals of the phenyl protons at the chain end (Q) are clearly separated from those at other positions (P). The number-average DP may be given by

$$\mathrm{DP_n} = (3[\mathrm{P}]/2[\mathrm{Q}]) + 1 \tag{4}$$

where [P] and [Q] denote the corresponding signal intensities. This method was accurate enough for samples with $\mathrm{DP_n}$ no greater than about 40. A polystyrene-calibrated GPC curve was corrected on the basis of these M_n data and employed to estimate the M_n of higher-mass samples and the polydispersity index, M_w/M_n, of all samples.

Two PS samples (PS-1 and PS-2) were used as a matrix polymer for the un-cross-linked systems. PS-1 ($M_n \cong 2.4 \times 10^5$) was commercially obtained from Aldrich, and PS-2 ($M_n \cong 3.3 \times 10^6$) was anionically prepared with cumylpotassium as initiator and tetrahydrofuran (−78 °C) as solvent.[30] These samples were characterized by GPC.

The molecular characteristics of the PPO and PS samples are summarized in Table I. It can be seen that all the PPO fractions have a fairly narrow distribution in molecular weight. The M_n value of 270 for sample PPO-5-10 closely agrees with the value of 283 expected for the acetyl-end-capped dimer. Similarly, samples PPO-5-8, 5-7, and 5-6 are nearly pure tetramer, pentamer, and hexamer, respectively.

Table I. Molecular Weight Characteristics of PS and PPO Samples

code	$10^{-2}M_n$	M_w/M_n
PS-1	2400	1.75
PS-2	33000	1.25
PPO-1	2500	3.16
PPO-2	210	1.80
PPO-3	92	1.08
PPO-4	57	1.06
PPO-5-1	23	1.15
PPO-5-2	18	1.16
PPO-5-4	11	1.01
PPO-5-6	7.6	1.01
PPO-5-7	6.4	1.01
PPO-5-8	5.0	1.01
PPO-5-10	2.7	1.04

Preparation of Blend Films. Un-cross-linked films of PPO/PS blend were prepared by casting a chloroform solution of a PPO/PS mixture (5% by weight), containing 3% by weight of PPO, onto a glass plate. They were dried under vacuum for 24 h at room temperature and for another 24 h at 80 °C. The film thickness was about 50 μm (after drying) in all cases. Cross-linked blend films with composition and thickness similar to those of the un-cross-linked films were prepared by radical polymerization of PPO-containing styrene with azobis(isobutyronitrile) (0.2 wt %) as initiator and divinylbenzene (1.2 wt %; technical grade) as cross-linking agent. Polymerization was carried out in a closed system between a Teflon vessel and a glass plate for about 24 h at 60 °C, followed by vacuum-drying at 80 °C for 5 h.

Each film, cut into a strip measuring 30 mm in length and 10 mm in width, was uniaxially stretched at 120 ± 0.5 °C by use of a Tensilon UTM-I-5000B equipped with a temperature-controlled chamber. Immediately after a predetermined draw ratio $\lambda = l/l_0$ was attained, where l_0 and l are the sample lengths before and after the stretch, the film was quenched to room temperature to freeze the orientation and subjected to the below-mentioned IRD analysis.

Infrared Dichroism (IRD). The order parameter of η of the PS and PPO segments in the stretched film was determined by an IRD analysis[25] on the basis of the relation

$$\begin{aligned}\eta &= (3/2)\langle\cos^2\theta\rangle - (1/2)\\ &= [(R_0+2)(R-1)]/[(R_0-1)(R+2)]\end{aligned} \tag{5}$$

where θ is the angle between the chain axis and the direction of stretch, $R = A_\parallel/A_\perp$ is the infrared dichroic ratio with $A_\parallel$ and $A_\perp$ being the absorbances of the electric vector parallel and perpendicular, respectively, to the direction of stretch, and $R_0 = 2\cot^2\alpha$ with α being the angle between the dipole moment vector of the vibration considered and the chain axis. For PPO, the intense absorption band at 1190 cm^{-1} due to the asymmetric ether stretching vibration ($\alpha = 20.6°$) was mainly used: this band was partially overlapped by the band of the acetyl group introduced to the chain end (see above), whose contribution, not being negligible for low-DP samples, was appropriately subtracted by referring to the less intense but unoverlapped band at 1305 cm^{-1} assigned to the $\nu_2(\mathrm{A_1})$ mode of the 1,2,4,6-tetrasubstituted benzene ring ($\alpha = 22.4°$). For PS, the 906-cm^{-1} out-of-plane band of the benzene ring ($\alpha = 35°$) was used, which was the only one not overlapping any of the PPO bands.[25]

IR spectra were recorded on a JASCO 8800 FT-IR spectrometer equipped with a JASCO PL-81 polarizer and a Mettler FP-82 hot stage. The stretched and quenched sample film was fixed in the hot stage, and the $A_\parallel$ and $A_\perp$ spectra were recorded at room temperature (time $t = 0$). Subsequently, the temperature was allowed to jump to a predetermined temperature (above T_g) to record the spectra at that temperature as a function of relaxation time t. Typical IR spectra are presented in Figure 3.

Results

Un-Cross-Linked, Unrelaxed Systems. Figure 4 shows the order parameters η_1 and η_2 of the PS and PPO

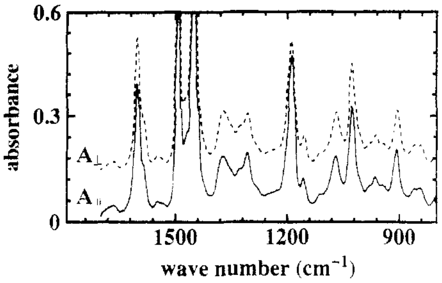

Figure 3. IR spectra of PPO-2 in PS-1 (t = 0, λ = 2.5). The $A_\perp$ spectrum was displaced upward by 0.12 in absorbance for easy recognition.

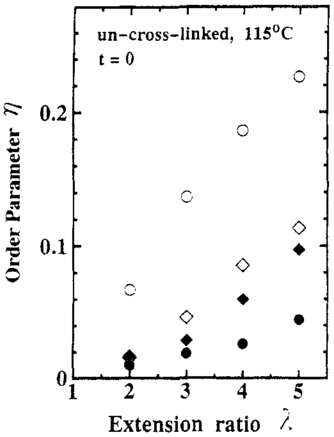

Figure 4. Order parameter η as a function of extension ratio λ: PPO-2 (○)/PS-1 (◇) and PPO-4 (●)/PS-1 (◆).

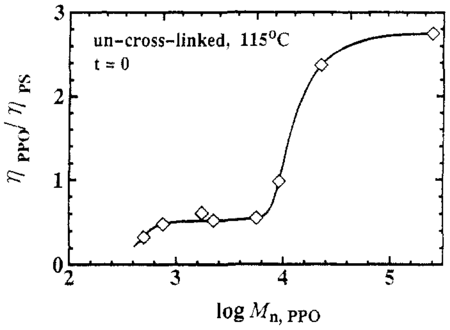

Figure 5. Plot of orientation ratio η_2/η_1 vs PPO molecular weight M_n; in the PS-1 matrix (t = 0 and $\lambda \cong 3$) at 115 °C.

segments, respectively, in the PPO-2/PS-1 and PPO-4/PS-1 blends, unrelaxed (t = 0), as a function of the extension ratio λ. In both cases, η_1 and η_2 increase nearly linearly with increasing λ for λ not greater than about 3.5. It is noted that PPO-2 is exceedingly more oriented than PPO-4, a shorter chain, despite the fact that the matrix PS orientations are roughly the same in the two systems.

Figure 5 demonstrates the orientation ratio η_2/η_1 as a function of the molecular weight M_n of the PPO in the PS-1 matrix (t = 0, $\lambda \cong 3$). Two features are noted in the figure: First, the ratio slightly increases with M_n for $M_n \lesssim 10^3$ and exhibits a plateau extending from about 10^3 to about 10^4, where $\eta_2/\eta_1 \cong 0.5$. Second, the ratio starts to increase drastically for M_n about 1×10^4, approaching a second plateau with a further increase in M_n, where the ratio is as large as about 2.7.

Un-Cross-Linked, Relaxed Systems. Four systems, PPO-5-2/PS-1, PPO-5-2/PS-2, PPO-2/PS-1, and PPO-2/PS-2, were examined with the relaxation behavior at 115 °C. Figure 6 shows the order parameter η_1 of the matrix polymers PS-1 and PS-2 as a function of the relaxation time t. Clearly, PS-1 relaxes more rapidly than PS-2, the longer chain.

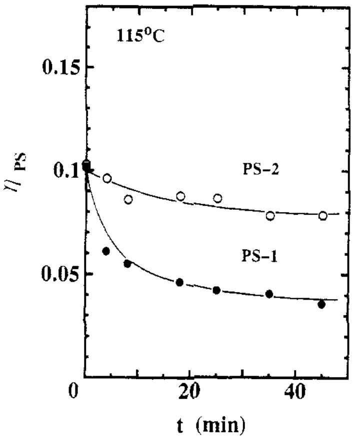

Figure 6. Plot of PS order parameter η_1 vs relaxation time t: PS-1 (●) and PS-2 (○); at 115 °C.

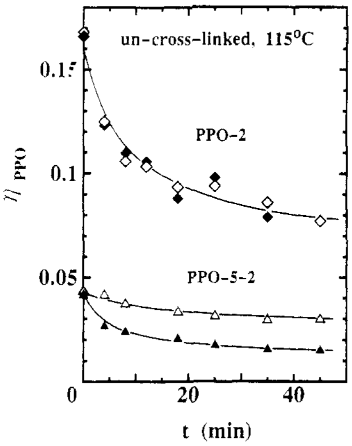

Figure 7. Plot of PPO order parameter η_2 vs relaxation time t: PPO-2 (◆) in PS-1, PPO-2 (◇) in PS-2, PPO-5-2 (▲) in PS-1, and PPO-5-2 (△) in PS-2; at 115 °C.

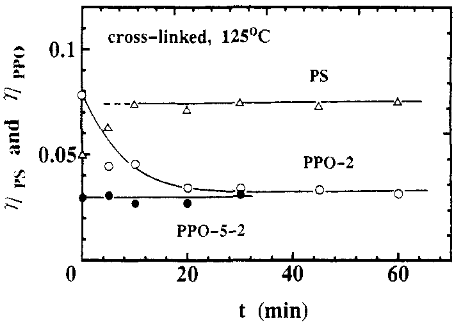

Figure 8. Plot of order parameter η vs relaxation time t for PPO-2 (○) and PPO-5-2 (●) in a cross-linked PS matrix (△); at 125 °C.

Figure 7 shows the relaxations of the PPO segments in these two matrices. For the shorter polymer (PPO-5-2), the relaxation is faster in the shorter matrix (PS-1) than in the longer matrix (PS-2), while for the longer polymer (PPO-2), the relaxation behavior is nearly independent of the matrix molecular weight.

Cross-Linked Systems. Figure 8 gives a typical example of the orientation behavior of a cross-linked PS matrix as a function of time (λ = 3, T = 125 °C). Owing to the cross-links introduced, the applied orientation does not relax even after a long time. Actually, some non-equilibrium behavior can be observed at short times ($t \lesssim$ 10 min). Perhaps it comes from the rather involved experimental procedure (see above), but it is not very important for our discussion.

Figure 8 also shows the orientations of PPO-5-2 and PPO-2 dispersed in a cross-linked matrix ($\lambda \cong 3$, 125 °C).

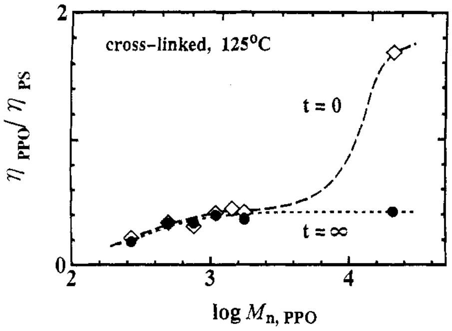

Figure 9. Plot of orientation ratio η_2/η_1 vs PPO molecular weight M_n at $t = 0$ (◇) and $t = \infty$ (●); in a cross-linked PS matrix at 125 °C.

Even though the two systems were prepared under the same conditions, the matrix components were not exactly identical, and for this reason, the matrix orientations for a given extension ratio were somewhat different from each other. The extension ratio of the PPO-5-2 system was so adjusted as to give nearly the same matrix orientation as in the PPO-2 system. Clearly in Figure 8, the orientation of PPO-2 is originally higher than that of PPO-5-2, but after about 30 min, it becomes nearly identical with the latter, which shows no time dependence. These apparently unrelaxing orientations may be regarded as equilibrium ones that would be observed at $t = \infty$.

The orientation ratios η_2/η_1 at $t = 0$ and $t = \infty$ are plotted as a function of PPO molecular weight in Figure 9. The $t = 0$ curve is qualitatively similar to that for the un-cross-linked systems (Figure 5). The $t = \infty$ curve, while nearly the same as the $t = 0$ curve in the low-M_n region, levels off in the high-M_n region, where the η_2/η_1 ratio is about 0.4.

Discussion

Un-Cross-Linked Systems. Zhao et al.,[27] who have made an IRD study on uniaxially stretched, un-cross-linked blend films of PPO ($M_n = 2.1 \times 10^4$) and PS ($M_n = 1.1 \times 10^5$ and 2.0×10^6) with 1 or 2 wt % of PPO, observed values of η_2/η_1 exceeding 2 when the orientations were unrelaxed, i.e., at $t = 0$. Close counterparts to their systems are the present PPO-2/PS-1 and PPO-2/PS-2 blends, for which we have also observed large η_2/η_1 at $t = 0$ (cf. Figure 5). These authors have interpreted the orientation of PPO being much higher than that of PS in terms of the entanglement interactions. We follow their interpretation.

According to Wu,[31] the molecular weight M_e between entanglements is about 18 000 for pure PS and about 3000 for pure PPO. For a PPO/PS system with a small fraction of PPO, PPO chains will be entangled predominantly with PS chains. The relevant molecular weight, M_e(PPO–PS), is estimated to be 7000,[31] or in terms of the number of Kuhn segments, $n_K \cong 18$. This value is smaller than the n_K value for PS (about 33), which allows us to expect that the PPO segments will be more oriented than the PS segments in a PPO/PS blend.[27] Moreover, since the critical molecular weight M_c above which entanglement effects manifest themselves is about twice M_e,[32,33] the M_c for the PPO in a PS matrix is estimated to be some 14 000. Thereabout in fact we have observed an enormous increase of η_2 (Figure 5).

The relaxational behavior of entangled (long) PPO is clearly different from that of unentangled (short) PPO. As Figure 7 shows, sample PPO-2, a "long" polymer, relaxes nearly independently of the matrix molecular weight,[34] while sample PPO-5-2, a "short" polymer, has a relaxation behavior which depends on matrix molecular weight.

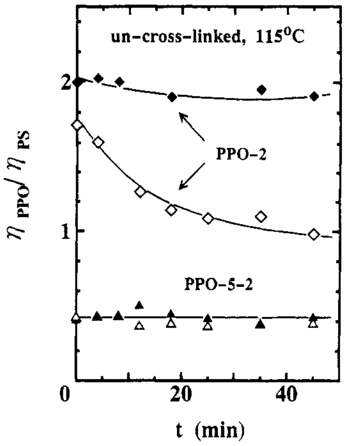

Figure 10. Plot of orientation ratio η_2/η_1 vs relaxation time t: PPO-2 (◆) in PS-1, PPO-2 (◇) in PS-2, PPO-5-2 (▲) in PS-1, and PPO-5-2 (△) in PS-2; at 115 °C (data from Figures 6 and 7).

Figure 10 shows the orientation ratio η_2/η_1 as a function of time (data from Figures 6 and 7). This ratio for PPO-2 decreases more rapidly in PS-1 than in PS-2, simply reflecting the difference of the matrix relations. On the other hand, the ratio for PPO-5-2 is the same in the two matrices and independent of time. This clearly indicates that the orientation of PPO segments is strongly coupled with that of PS segments in these short-PPO systems.

These results suggest that PPO segments in a PS matrix are oriented by two different mechanisms. One is through the entanglement between PPO and PS chains, and accordingly, only PPO chains longer than a critical length (about 10^4 in molecular weight) are subject to this mechanism. The other is related to the intermolecular interactions on a segmental scale. The amount of PPO orientation η_2 due to this latter mechanism is about 0.4 of the PS orientation η_1 (Figure 10).

Cross-Linked Systems. As already noted, the behavior of the cross-linked systems at $t = 0$ is substantially similar to that of the un-cross-linked systems. In comparison of Figures 5 and 9, however, we note that the η_2/η_1 ratio in the high-molecular-weight region is considerably smaller in the cross-linked systems than in the un-cross-linked systems. This is because cross-linking enhances the matrix orientation relative to the solute orientation: the aforementioned preparation recipe of the cross-linked samples suggests that the molecular weight between cross-links will be on the order of several thousands, which is much smaller than the entanglement molecular weight (about 18 000). Therefore, the matrix orientation for a given stretch will be higher in these systems than in the un-cross-linked systems, while the orientation of PPO brought about by the entanglement mechanism will be similar in the two types of systems. In the low-molecular-weight region, there is no essential difference in the η_2/η_1 ratio between the cross-linked and un-cross-linked systems.

An obvious merit of studying the cross-linked systems is that it permits the observation of the relaxational behavior of the PPO segments in the unrelaxing PS matrix. Figure 11 demonstrates the η_2/η_1 ratio in the PPO-2/cross-linked PS system recorded for a sufficiently long time, which confirms the existence of the two mechanisms of segment orientation suggested by the un-cross-linked systems: the large orientation of PPO segments due to the entanglement mechanism relaxes almost perfectly in about 1 h and thereafter remains a finite, unrelaxing orientation induced by the segmental interaction.

Comparison with Theory. Now we turn to the other main topic of this work. In Figure 12, the values of the

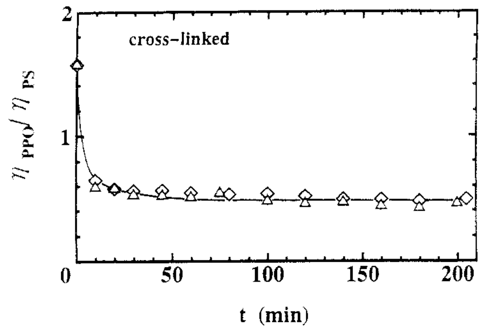

Figure 11. Plot of orientation ratio η_2/η_1 vs relaxation time t for PPO-2 in a cross-linked PS matrix; at 125 (◇) and 130 °C (△).

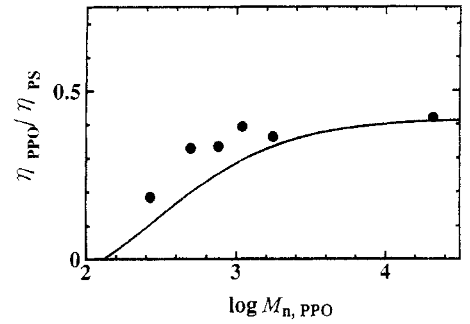

Figure 12. Comparison of the theory (full curve) and the experimental data (●) from Figure 9, $t = \infty$: the theoretical curve was obtained from eq 1 with $x_2 = 2.1$ (see text).

unrelaxing (equilibrium) orientation exhibited by the cross-linked systems are compared with the theoretical prediction, eq 1. The persistence length b_2 (half the Kuhn length) and the diameter D_2 of PPO were taken from the literature[35,36] to be 1.23 and 0.59 nm, respectively, which yielded $x_2 = b_2/D_2 = 2.1$. The number of submolecules n_2 may be given by n_2 $(l_2/D_2) \times$ DP with the contour length l_2 per repeat unit being 0.54 nm.[37] It can be seen that the theoretical curve describes the experimental data fairly well with respect to both the chain length dependence and the absolute values of η_2/η_1.

As already noted, eq 1 is based on the Di Marzio-type lattice model and the freely-jointed-chain (FJ) model. Since the accuracy of these models is not necessarily clear, the theoretical result should be regarded as semiquantitative at best. In addition, the FJ model, even though defined differently[24] from the conventional one, would not too accurately represent the chain length dependence of flexibility of very short polymers. A similar criticism may apply to the IRD analysis of the order parameter of short PPO chains, for which the angle α between the chain axis and the dipole moment vector of vibration would, in a strict sense, be different from that for sufficiently long chains. Nevertheless, the trend, indicated by both theory and experiment that η_2/η_1 decreases as the chain becomes shorter would be acceptable as a qualitative fact.

An important question is as to the nature of the segmental interaction that causes the orientation correlations observed in this and many other systems (see under Introduction). It has believed that these correlations are of an enthalpic origin because they exhibit a distinct temperature dependence.[4,5,7] However, Fuller and coworkers, who studied poly(ethylenepropylene)[17] and polybutadiene[38] melts, each containing a short probe polymer homologous to the matrix polymer, have observed no temperature dependence in the orientation correlations between the probe and matrix molecules. This suggests that those correlations are entropically driven, arising from excluded-volume effects. As for the present system, it turned out technically difficult to conduct measurements over a sufficiently wide temperature span. (Figure 11 indicates that the η_2/η_1 ratios observed at two temperatures, 125 and 130 °C, are not exactly identical at large as well as small t, but the differences in both temperature and the data are much too small to discuss this problem.) However, the fair agreement between the packing entropy theory (eq 1) and experiment demonstrated in Figure 12 does indicate, despite the semiquantitative nature of the theory, that at least an important portion of orientation correlations in PPO/PS blends is entropic in origin.

Conclusions

Segments of PPO molecules sparsely dispersed in a PS matrix are oriented by two different mechanisms. One is related to the entanglement interaction between PPO and PS, and accordingly PPO chains longer than a critical length (about 10^4 in molecular weight) are relevant to this mechanism. The orientation of PPO relative to that of PS according to this mechanism is very large at $t = 0$, and its relaxation process depends on the molecular weights of both PS and PPO. The other mechanism is related to the interaction of PPO and PS at a segmental level, and hence it is relevant to both long and short PPO chains.

The orientation ratio η_2/η_1 according to the latter mechanisms is about 0.4, independent of the chain length of PPO, excepting an oligomeric region ($M_{n,\text{PPO}} \lesssim 10^3$), where η_2/η_1 decreases with decreasing chain length. The packing entropy theory provides a reasonable description of the experimental observation with respect to both the magnitude of η_2/η_1 and its chain length dependence. This indicates that at least an important portion of the segmental orientation of PPO is entropically induced.

The orientations of short (unentangled) PPO chains observed at $t = 0$ in the un-cross-linked and cross-linked systems are very similar to each other and also to that observed in cross-linked systems after a long time ($t = \infty$). This means that the PPO orientation induced by the segmental interaction mechanism has attained an equilibrium state within the time scale of the present experimental procedure (order of a minute).

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research, the Ministry of Education, Science and Culture, Japan (Grant-in-Aid 02650647).

References and Notes

(1) Gent, A. N.; Vickroy, V. V., Jr. *J. Polym. Sci., Polym. Phys. Ed.* **1967**, *5*, 47.
(2) Ishikawa, T.; Nagai, K. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1123.
(3) Fukuda, M.; Wilkes, G. L.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 1417.
(4) Deloche, B.; Samulski, E. T. *Macromolecules* **1981**, *14*, 575.
(5) Thulstrap, E. W.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 5594.
(6) Erman, B.; Flory, P. J. *Macromolecules* **1983**, *16*, 1607.
(7) Schmidt, P.; Schneider, B. *Makromol. Chem.* **1983**, *184*, 2075.
(8) Gronski, W.; Stadler, R.; Jacobi, M. M. *Macromolecules* **1984**, *17*, 741.
(9) Jacobi, M. M.; Stadler, R.; Gronski, W. *Macromolecules* **1986**, *19*, 2884.
(10) Toriumi, H.; Deloche, B.; Herz, J.; Samulski, E. T. *Macromolecules* **1985**, *18*, 304.
(11) Erman, B.; Queslel, J.-P.; Monnerie, L. *Polymer* **1988**, *29*, 1823.
(12) Tassin, J. F.; Monnerie, L.; Fetters, L .J. *Macromolecules* **1988**, *21*, 2404.
(13) Sotta, P.; Deloche, B.; Herz, J.; Lapp, A.; Durand, D.; Rabadeux, J.-C. *Macromolecules* **1987**, *20*, 2769.
(14) Sotta, P.; Deloche, B. *Macromolecules* **1990**, *23*, 1999.

(15) Kornfield, J. A.; Fuller, G. G.; Pearson, D. S. *Macromolecules* **1989**, *22*, 1334.

(16) Ylitalo, C. M.; Kornfield, J. A.; Fuller, G. G.; Pearson, D. S. *Macromolecules* **1991**, *24*, 749.

(17) Ylitalo, C. M.; Fuller, G. G. *Macromolecules* **1991**, *24*, 5736.

(18) Tanaka (Fukuda), T.; Allen, G. *Macromolecules* **1977**, *10*, 426.

(19) Jarry, J. P.; Monnerie, L. *Macromolecules* **1979**, *12*, 316.

(20) Gao, J.; Weiner, J. H. *Macromolecules* **1988**, *21*, 773.

(21) Erman, B.; Bahar, I.; Kloczkowski, A.; Mark, J. E. *Macromolecules* **1990**, *23*, 5335.

(22) Bahar, I.; Erman, B.; Kloczkowski, A.; Mark, J. E. *Macromolecules* **1990**, *23*, 5341.

(23) Fukuda, T.; Takada, A.; Miyamoto, T. *Macromolecules* **1991**, *24*, 6210.

(24) Fukuda, T.; Kawabata, K.; Tsujii, Y.; Miyamoto, T. *Macromolecules* **1992**, *25*, 2196.

(25) Lefebvre, D.; Jasse, B.; Monnerie, L. *Polymer* **1981**, *22*, 1616.

(26) Bouton, C.; Arrondel, V.; Rey, V.; Sergot, Ph.; Manguin, J. L.; Jasse, B.; Monnerie, L. *Polymer* **1989**, *30*, 1414.

(27) Zhao, Y.; Prud'homme, R. E.; Bazin, C. G. *Macromolecules* **1991**, *24*, 1261.

(28) Endres, G. F.; Kwiatek, J. *J. Polym. Sci.* **1962**, *58*, 593.

(29) White, D. M. *Macromolecules* **1979**, *12*, 1008.

(30) Tanaka (Fukuda), T.; Kotaka, T.; Inagaki, H. *Macromolecules* **1974**, *7*, 311.

(31) Wu, S. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 2511.

(32) Porter, R. S.; Johnson, J. F. *Chem. Rev.* **1966**, *66*, 1.

(33) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.

(34) Zhao et al.[27] have observed some matrix-molecular weight dependence of the "entangled" PPO in their systems. Since the M_n of their PPO sample is virtually the same as that of PPO-2 here, the difference between their and our observations is ascribed to the difference in M_n between their shorter PS ($M_n = 1.1 \times 10^5$) and our shorter PS (PS-2, $M_n = 2.4 \times 10^5$). It is suggested that the matrix dependence will disappear (but not perfectly, because of the segmental interactions; see text) for sufficiently high matrix molecular weights compared to PPO molecular weight. In any case, the matrix dependence noted by Zhao et al. is rather minor (cf. Figure 5 in ref 27).

(35) Aharoni, S. M. *Macromolecules* **1986**, *19*, 426.

(36) Horikiri, S. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 1167.

(37) Akers, P. J.; Allen, G.; Bethell, M. J. *Polymer* **1968**, *9*, 575.

(38) Ylitalo, C. M.; Zawada, J. A.; Fuller, G. G.; Abetz, V.; Stadler, R., cited in ref 17.