

Mechanisms of Segmental Orientation in Deformed Polymer Melts

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Segments of probe polymer 2 sparsely dispersed in a stretched network of polymer 1 were shown to be oriented by two different mechanisms. One is related to the entanglement interaction, and accordingly probe chains longer than a critical length are relevant to this mechanism. The other mechanism is related to the interaction at a segmental level, and hence it is relevant to both long and short probe molecules. The magnitude and chain-length dependence of the segmental orientation induced by the latter mechanism well agree with the theoretical prediction of a lattice model, indicating that at least an important part of that orientation is driven entropically.

Keywords: Induced orientation/ Entanglement interaction/ Segmental interaction/ Equilibrium orientation/ Lattice model/ Excluded volume interaction

Almost all molecules, including chain polymers, are more or less anisotropic in shape at a molecular or segmental level. Shape anisotropy brings about anisotropy in intermolecular interactions, and this will cause various cooperative phenomena that cannot be observed in systems of symmetrical molecules. The most drastic of these phenomena is the spontaneous or liquid crystalline ordering exhibited by stiff or semiflexible polymers as well as low-mass mesogenic molecules [1]. The effects of anisotropic or orientation-dependent interactions are not usually explicit in flexible polymers and non-mesogenic compounds. However, once the system is made anisotropic by an external force field, for example, the effects are expected to appear explicitly, affecting whatever properties in which orientation matters. In fact, there has been a large body of experimental evidence indicating the existence of

orientational correlations in various polymer systems [2].

Theoretically, this problem was first considered by Tanaka and Allen [3] using a lattice model, hence from an entropic point of view, and by Jarry and Monnerie from an enthalpic point of view [4]. We recently extended the Di Marzio lattice model to a multi-component polymer system, and combined it with the modified freely jointed chain (F-chain) to obtain volume-induced orientations in a miscible blends of two polymers of arbitrary chain length and flexibility [5]. This F-chain is equivalent to the wormlike chain with respect to mean dimensions of the chain but somewhat different from that with respect to orientational entropy. 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

$$\eta_2/\eta_1 = (1/5)x_2(1-n_2^{-1})/(1+x_2n_2^{-1}) \quad (1)$$

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Scope of research

Basic studies have been conducted for better understandings of the structure/property or structure/function relations of polymeric materials and for development of novel functional polymers. Among those have been the studies on (1) the synthesis and properties of cellulose- and oligosaccharide-based functional polymers, e.g., bio-degradable polymers, liquid crystals and polymers of well-defined structure having pendant oligosaccharides, (2) the structure and mechanism of polymer gels and gelation, and (3) various phenomena originating in orientation-dependent interactions in polymer systems.



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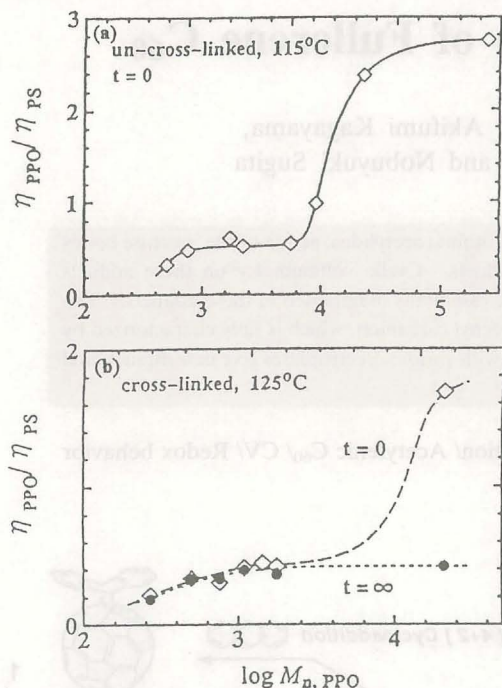


Figure 1. Plot of order parameter ratio η_2/η_1 vs. PPO molecular weight M_n in (a) un-cross-linked PS ($M_n=2.4 \times 10^5$) and (b) cross-linked PS matrices.

where $\eta = (3/2) \langle \cos^2 \theta \rangle - (1/2)$ is the order parameter, $\eta_2 = L/D$ and $x_2 = q/D$ with L , D , and q being the contour length, diameter, and persistence length of polymer 2.

Experimentally, we have studied cross-linked and un-cross-linked polystyrene (PS) containing a small amount (3 wt-%) of well fractionated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of various chain lengths [2]. By infrared dichroism (IRD), independent determination of η_1 (PS) and η_2 (PPO) of these miscible polymers is possible, enabling us to make a direct test of Eq. 1. Cross-linked samples were prepared by radical polymerization of styrene by use of divinyl benzene as a cross-linker. The blend film, about 50 μm thick, was uniaxially stretched in a temperature-controlled stretching device to a desired extension ratio λ , and studied by IRD as a function of time t .

At $t=0$, i.e., immediately after the stretching was completed, both PS and PPO segments showed finite orientations η_1 and η_2 , and the ratio η_2/η_1 vs. M_2 curves for the un-cross-linked and cross-linked systems were very similar to each other (Fig. 1): as M_2 increased, η_2/η_1 increased at first, approaching a plateau for $10^3 \leq M_2 \leq 10^4$, where $\eta_2/\eta_1 \approx 0.5$, and then steeply increased, approaching another plateau, where $\eta_2/\eta_1 \gg 1$. This enormous increase in η_2/η_1 is ascribed to the *entanglement interaction* of PPO chains with the PS matrix.

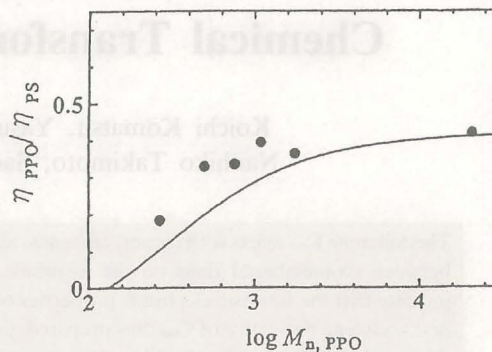


Figure 2. Comparison of the theory (full curve) and the experiment at $t=\infty$. The theoretical curve was obtained from Eq. 1 with the x_2 value of 2.1 estimated from literature data.

Examination of the cross-linked systems, where the PS orientation did not relax owing to the cross-links, has revealed that PPO segments exhibit a finite, unrelaxing orientation even after a long time, giving a constant η_2/η_1 ratio of about 0.4 for $M_2 \geq 10^3$ (Fig. 1b). This unrelaxing orientation observed after a long time ($t=\infty$) is ascribed to the *segmental orientation* between PPO and PS, and can be well interpreted by Eq. 1 with respect to both the magnitude of η_2/η_1 and its chain length dependence (Fig. 2). This indicates that at least an important part of the equilibrium (unrelaxing) orientation of PPO in the oriented PS matrix is driven entropically.

Similar results have been obtained also for cross-linked and un-cross-linked PS containing poly(vinyl methyl ether) (PVME) as a minor component [6]. This system is particularly interesting, because it is a partially miscible one exhibiting an LCST behavior. A preliminary result indicates that the miscibility of PVME in a PS network becomes lowered as the matrix segments are oriented, in line with the theoretical prediction of the same model on which Eq. 1 is based.

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