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研究課題名(和文) Unified View of Entanglements in Polymeric Liquids: Binary Blends

研究課題名(英文) Unified View of Entanglements in Polymeric Liquids: Binary Blends

研究代表者

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研究成果の概要(和文)：モノマーのサイズが異なることでブレンドの管直径の異常な混合則を示すのに十分とこのことをモノマーサイズが2:1と3:1比率のブレンドを用いて確認出来た。ブレンドの局所的な液体構造は、動径分布関数(RDF)で検討し、混合がランダムでなく、小さなモノマーが大きなモノマーの隣にある可能性が高かった。異常混合則の起源は非ランダム混合と思われ、その影響の理解のため混合則の一般化に取り組んでいる。驚くべきことに、ブレンドでは単体より大きなモノマー鎖の緩和時間が増加し、小さなモノマー鎖の緩和時間は減少した。

研究成果の学術的意義や社会的意義

Traditionally, the precise local liquid-like structure (monomer packing) is ignored in understanding the properties of dense polymeric liquids. Polymer blends with monomer size disparity present a major challenge to this view and suggest that concepts from liquid state physics are also necessary.

研究成果の概要(英文)：The major outcomes of the project are as follows: (1) Disparity in the size of monomers is sufficient for polymer blends to exhibit anomalous mixing for quantities related to entanglements, for instance the plateau modulus or equivalently, the tube diameter. We have verified this for blends of polymers that were nearly identical except their monomer sizes were either in the ratio 2:1 or 3:1. The local liquid-like structure of the blend was investigated using the radial distribution function (RDF). The RDF indicated that the mixing was nonrandom with an increased probability for the small monomers to be the non-bonded neighbors of the large monomers. We suspect that the origin of the anomalous mixing rules is related to this nonrandom mixing and efforts are underway to generalize the available mixing rules to account for this effect. Surprisingly, we also found that the relaxation time of the large monomer chains increased and that of the small monomer chains decreased upon blending.

研究分野：Soft Matter Physics

キーワード：Miscible Polymer Blends Polymer Dynamics Local Structure Polymer Entanglements Polymer Melts

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1. 研究開始当初の背景

The dynamics and rheology of dense polymer liquids are dominated by entanglements. Past research has clarified several aspects of entanglements in polymer melts and solutions. For instance, strong evidence indicates that certain ad hoc ansatz can adequately describe entanglements in polymer melts. However, the failure of these ansatz for polymer solutions indicate that considerable gaps in our understanding remain. Therefore, we investigated miscible polymer blends as they combine features of both blends and solutions. In a past project, we investigated questions such as (1) can blends be described by a single tube diameter? (2) How does the stiffness of a chain affect its tube diameter in a blend? (3) What is the mixing rule for the tube diameter in blends? Regarding the last question, Watanabe and coworkers have proposed a mixing rule that can adequately describe the results of their meticulous experiments on Polyisoprene/Poly(p-tert butyl styrene) blend. This mixing rule is qualitatively different from the mixing rules proposed in the past and its physical basis remains to be elucidated.

2. 研究の目的

Building on the foundation of understanding achieved in the case of polymer melts, this project seeks to understand the nature of entanglements in polymer blends. A comprehensive understanding of the results of Watanabe and coworkers is one major motivation for the present work. In past work, we found that the mixing rules for blends of polymers which differed only by their stiffness disagreed with that proposed by Watanabe and coworkers but agreed with straightforward extensions of the ansatz proposed for melts. Therefore, in this work we focused on blends whose monomer sizes were different. In addition to the mixing rules, we also began investigating the dynamics of these blends.

3. 研究の方法

Our research approach consisted of two major steps: (1) use simulations to determine the entanglement network, and (2) analyse the results based on the current understanding of entanglements in polymer melts and solutions. The simulation step comprised two parts: (1) prepare well equilibrated chain configurations of polymer chains with differing monomer sizes and their blends at different compositions and, (2) determine the primitive path of the equilibrated chain configurations to directly capture the topological state of the chains. Analysis of the simulation results involved two steps: (1) extensions of the ansatz proposed for polymer melts and solutions so as to be applicable polymer blends and, (2) compare the resulting mixing rules to the results of simulations.

4. 研究成果

Blends with size disparity in their monomer sizes were immiscible. However, introducing stronger repulsion between only the monomers of the “large” chains, it was possible to obtain a miscible blend. In the miscible regime, the Flory-Huggins χ was obtained directly from the scattering function using de Gennes’ RPA approximation. In the immiscible regime, the interfacial width was used to obtain the χ parameter.

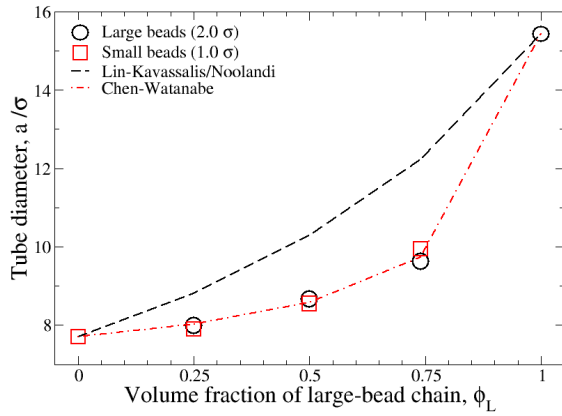


Fig. 1: Composition dependence of the tube diameter for a large-small blend. The two sets of symbols correspond to the individual tube diameters of the components. The predictions of the packing model and the Chen-Watanabe mixing rule are shown.

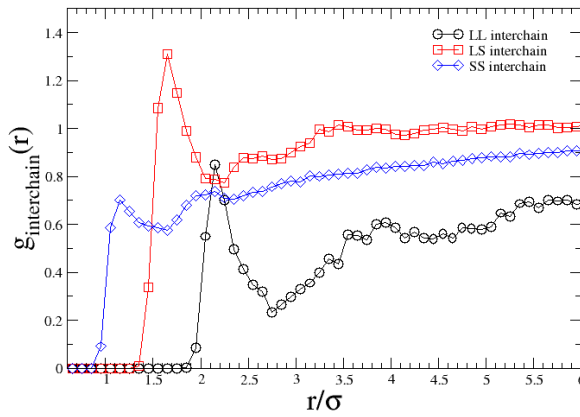


Fig. 2: Interchain radial distribution function for the large-large (L-L), large-small (L-S), small-small (S-S) monomers for a 50:50 blend.

Topological analysis of the equilibrated chain configurations yielded the the entanglement lengths for the two different kinds of chains that constitute the blend. In Fig. 1, tube diameters for a blend whose monomer diameter ratio was 2:1 is shown for several blend ratios. Two different mixing rules were compared: (1) the extension of the Lin- Kavassalis/Noolandi (L-K/N) ansatz for polymer melts (2) the proposal of Chen and Watanabe (CW). It is clear that the CW ansatz agrees well with the data but the L-K/N ansatz works poorly. This suggests that a monomer size disparity of 2:1 is sufficient for the mixing rule to become anomalous and agree with the CW ansatz.

An intriguing suggestion regarding the origin of the anomalous mixing rule can be found in the interchain radial distribution shown in Fig. 2. The figure clearly indicates that the mixing of the chains in the blend is nonuniform with the large monomers being preferentially surrounded by the small monomers. We are currently exploring how the effect of nonuniform mixing can be incorporated into existing ansatz to further elucidate the origin of the anomalous mixing rules in polymer blends. Even in blends of short (unentangled)

chains, the monomer size disparity has unexpected consequences for the chain relaxation. The relaxation time of the chains composed of large monomers, τ_L , and the terminal relaxation time of the chains composed of small monomers, τ_s , both decrease with increasing volume fraction, ϕ_L , of the large-monomer chains. In other words, upon blending, the relaxation of the fast component (chains composed of “small” monomers) further speeds up and the relaxation of the slow component (chains composed of “large” monomers) further slows down! Further, the relaxation time of the “small” monomer chains τ_s is independent of the length of the “large” monomer chains. A tentative explanation for these findings can be proposed by taking into account the greater prevalence of the “small” monomers next to the “large” monomers due to the nonuniform mixing of the components mentioned earlier. However, these ideas appear to be insufficient to explain the weak dependence on N_s observed for τ_L (refer Fig. 4). We are currently trying to understand these results and exploring its consequences for the time-dependent relaxation modulus. In addition, we are also currently investigating the consequences of the monomer size disparity for the entangled dynamics in blends with monomer size disparity.

Fig. 3: Terminal relaxation time of chains with large monomers, τ_L , and with small monomers, τ_s , against the volume fraction of the chains with large monomers, ϕ_L , for several N_L for $N_S = 10$.

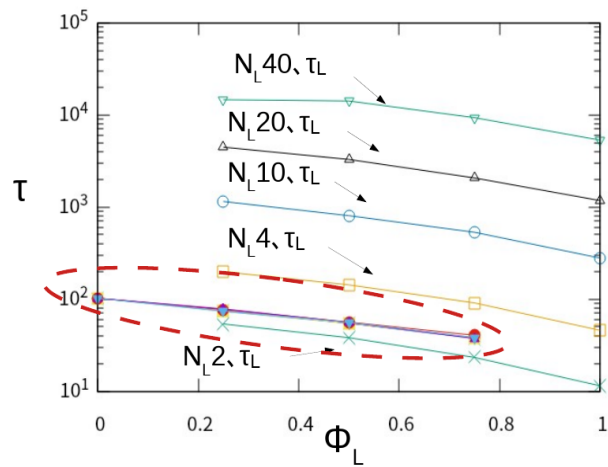
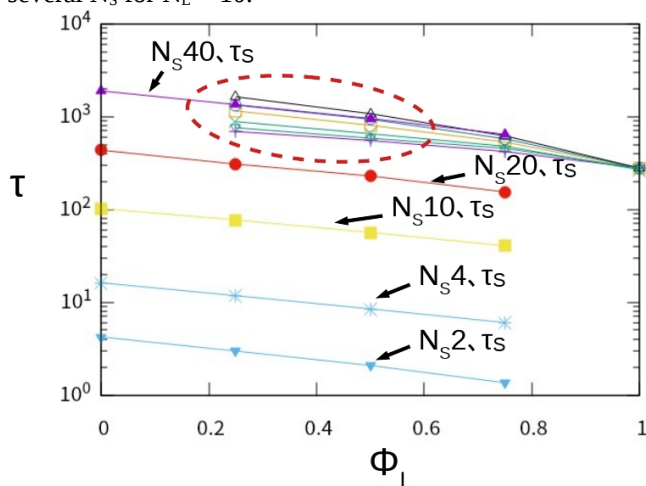


Fig. 4: Terminal relaxation time of chains with large monomers, τ_L , and with small monomers, τ_s , against the volume fraction of the chains with large monomers, ϕ_L , for several N_S for $N_L = 10$.



5. 主な発表論文等

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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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