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研究課題名（和文）Unified View of Entanglements in Polymer Liquids

研究課題名（英文）Unified View of Entanglements in Polymer Liquids

研究代表者
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研究成果の概要（和文）：高分子はお互いに絡みあう。 高密度液体では、絡み合いは物性に大いに影響するが、その特性がすべて理解されているとは言えない。 過去の研究から単体では剛直鎖は柔軟鎖より絡みやすいことが分かっているが、それらをブレンドするとどうなるか分かっていない。 実験では、2つの高分子間の固さのみを変えることはほとんど不可能である。そこでシミュレーションを使用した。異なる固さの2つの鎖のブレンドにおいて、剛直鎖はブレンドすると絡み合いが減り、逆に柔軟鎖はブレンドすると、絡み合いが増えることが分かり、高分子管直径理論の拡張に繋がった。このことで、高分子の物性を分子の構造と力学に基づいて説明することが可能となった。

研究成果の概要（英文）：Long polymer chains can entangle with each other. In the dense liquid state, entanglements strongly affect the physical properties. However, only some of the characteristics of entanglements have thus far been elucidated. From past research, we know that stiff polymers can entangle more easily than flexible polymers. We wanted to address a more difficult question: what happens when we blend a stiff polymer with a flexible polymer?
Experimentally, it is difficult to definitively answer this question because it is almost impossible to vary only the stiffness between two polymers. So, we used simulations and found that, in a blend, stiff polymers become more entangled and flexible polymers become less entangled. More interestingly, they had essentially the same tube diameter! Building on these results, we were able to further extend the tube theory of polymers and take another step in linking the macroscopic physical properties to the structure and dynamics of the polymer molecules.

研究分野：　Soft Matter Physics

キーワード：　Entanglements　Polymer Blends　Polymer Melts　Polymer Dynamics　Polymer Rheology

1.研究開始当初の背景

The physical properties of dense polymer systems are strongly affected by entanglements. However, several aspects of entanglements remain poorly understood to this day. Past research focused on understanding the nature of entanglements in polymer melts has led to some success. For instance, it is known that in the melt state, stiff chains are more entangled than flexible ones.

Going further, the nature of entanglements in miscible blends is of great fundamental interest. In spite of extensive experimental efforts, several questions remain unanswered. For instance, can blends be described by a single tube diameter? How does the stiffness of a chain affect its tube diameter in a blend? What is the mixing rule for the tube diameter in blends?

Recently, 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 foundations are rather unclear.

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. For instance, a comprehensive physical understanding the results of Watanabe and coworkers can be thought of as one major motivation for this work. We know that Polyisoprene is a flexible polymer, while Poly(p-tert butyl styrene) is comparatively stiffer. Therefore, in this project we first seek to understand entanglements in blends of stiff and flexible polymers that are otherwise identical. As a first step, we focus on the mixing rule for the tube diameter in these blends.

3.研究の方法

Our research strategy comprises two parts: (1) Using simulations to directly observe entanglements in the blends and (2) Theoretically analyze the results based on the current understanding of entanglements in polymer melts.

The simulations consisted of two parts: (1) prepare well equilibrated chain configurations of stiff chain and flexible chain polymer melts, and their blends at different compositions and, (2) analyze the topological state of the equilibrated configurations to directly probe the topological state of the chains.

Theoretical analysis consisted of two parts: (1) extend the various ansatz proposed for polymer melts to describe polymer blends and, (2) compare the resulting mixing rules to the results of simulations.

4.研究成果

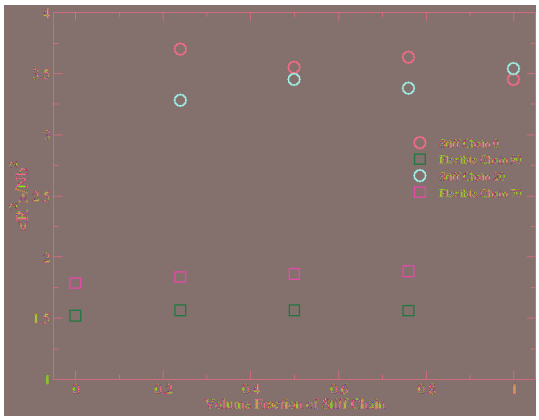

Figure 1: Mean-square end-to-end distance of the stiff and flexible chains at varying blend compositions.

First, we investigated the statistical properties of the chains in the blends. As indicated in Fig. 1, we found that blending had little effect on the chain statistics. This result could be interpreted as suggesting that the local environment of the stiff and flexible chains in the blend were not significantly different from their

environment in their corresponding melts.

Figure 2: Entanglement length of the stiff and flexible chains at varying blend compositions.

From the topological analysis of the chain configurations, the entanglement lengths of the stiff and the flexible chains were determined. In Fig. 2, data for two different blends are shown for varying blend compositions. Consistent with past results, we found that the entanglement length of the flexible chain to be significantly larger than that of the stiff chain – stiff chains entangle more easily than flexible chains. With increasing fraction of the second component, the entanglement length of the flexible chains decrease and the entanglement length of the stiff chains decrease.

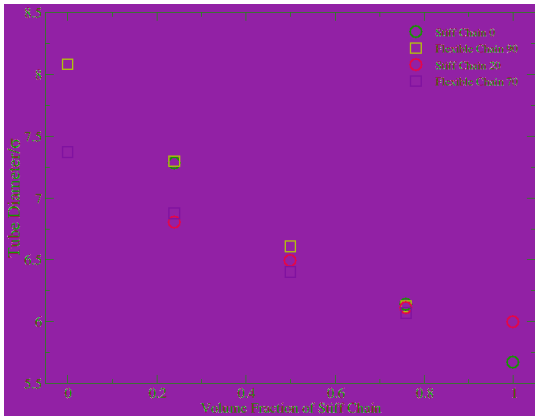

Figure 3: Tube diameter of the stiff and flexible chains at varying blend compositions.

Using the statistics of the chains, the entanglement lengths shown in Fig. 2 can be converted to the tube diameter of the flexible and the stiff chains. Such data is shown in Fig. 3. Interestingly, we find that the tube diameter of the flexible chains and the stiff chains, measured independently, are essentially identical! Based on experimental results, this had been hypothesized in the literature. However, to the best of our knowledge, this is the first direct demonstration of the result. Finally, we compared the tube diameters presented in Fig. 3 to two different mixing rules: (1) the extension of the Lin-Kavassalis/Noolandi (L-K/N) ansatz for polymer melts (2) the proposal of Chen and Watanabe (CW). From Fig. 4, it is clear that for both the blends, the L-K/N ansatz agrees well with the data but the CW ansatz works poorly.Therefore, for the flexible-stiff blends studied here using simple molecular models in simulations, the ansatz for polymer melts can extended to adequately describe the mixing rule for the tube diameter in the blend. Investigations into the reason for the success of the L-K/W mixing rule and, especially the failure of the CW mixing rule are currently in progress.

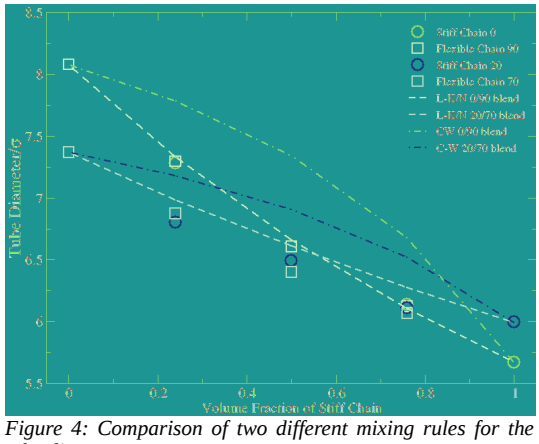

Figure 4: Comparison of two different mixing rules for the tube diameter.

5.主な発表論文等

〔雑誌論文〕(計　3 件)

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2) 2016 Correlation between Chains and Coarsegraining in Entangled Polymer Liquids, Sathish K. Sukumaran, Institute for Chemical Research International Symposium 2016 (ICRIS'16), March 7-8, Kyoto University, Uji, Japan.

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5) 2015 Bridging scales: using molecular simulations to understand the dynamics of entangled polymers, S. K. Sukumaran, J. Takimoto, 3rd International Workshops on Advances in Computational Mechanics (IWACOM-III) October 12-14, KFC Hall & Rooms, Tokyo, Japan. (Keynote)

〔図書〕（計　0 件）

〔産業財産権〕

○ 出願状況（計　0 件）

○ 取得状況（計　0 件）

〔その他〕

ホームページ等

6.研究組織

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