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Alternating Thick and Thin Layers Observed in the Smectic Phase of Binary Mixtures of Rigid-Rod Helical Polysilanes with Different Molecular Lengths

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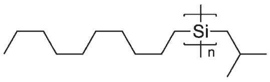
The entropy driven liquid crystalline (LC) phase formation of monodisperse hard-rod particle systems is both theoretically and computationally well understood. Since the initial approach of Onsager's theoretical work in the late 1940s,[1] it has been shown that the most common liquid crystal sequence of the nematic–smectic–columnar phases takes place in the systems of hard-rod particles based on the results of numerical experiments and computer simulations.[2] These theoretical predictions are in good agreement with the thermotropic LC phase behaviors of rigid-rod helical polysilanes with narrow molecular weight distributions,[3] which are the only available systematic experimental studies for the LC phase behavior of hard-rod particle systems.

Lately, these theoretical and computational approaches have been extended to binary systems of hard-rod molecules with equal diameters but different lengths, which are both capable of showing the LC phase in its pure form.[4] These studies might have been performed out of motives to see the much richer phase behaviors than the monodisperse rod systems and to clarify the role of excluded volume interactions in the stabilities of these mesophases. For binary mixtures of hard rods with the different length L_1 and L_2 ($L_1 > L_2$) with the aspect ratio (length-to-diameter ratio) in the range typical for reported polysilanes (7–30), Varga et al.[4f] predicted the following four different smectic structures: (i) the conventional smectic phase, in which both hard rods are packed into the same layer regardless of the mixing ratio (called smectic A1 phase), when the length ratio (L_1/L_2) is around 1.5; (ii) a smectic phase with two layers of short rods accommodated in a layer of long rods (smectic A2 phase), when the length ratio is around 2.0 and the long rods are in abundance; (iii) a smectic phase in which the long rods are arranged with their center of mass preferentially located in the interstitials between the two layers formed by the short rods (smectic A3 phase), when the length ratio is around 2.0 and the short rods are in abundance; and (iv) the microsegregated smectic phase with alternating smectic layers rich in short rods and long rods (smectic A4 phase), when the length ratio is around 3.3. See Figure 1 for the schematic representation of the different smectic structures found in the prediction.

On the experimental side, we recently reported the predicted smectic phase structures of the smectic A1, A2, and A3 in the thermotropic liquid crystal (LC) systems of the binary mixtures of long and short polysilanes, poly[*n*-decyl-(*S*)-2-methylbutylsilane] (PDMB), with narrow molecular weight distributions.[5] With the lower length ratio of 1.0 –1.7, the two polymers were randomly mixed within a layer and formed the conventional smectic A1 phase, while the binary mixture of two kinds of polymers with the higher length ratio of 1.7 –2.8 showed the smectic A2 phase when rich in the long polymer, and then almost quantitatively converted into the smectic A3 phase upon increasing the short polymer fraction, thus reproducing the theoretical prediction. Although there have been some experimental attempts to study the LC phase behaviors of the binary mixtures of rodlike particles, such as viruses[6] and mineral particles,[7] the polysilane can be considered as an ideal experimental system to verify the theoretical study of the hard rodlike particle systems with an excluded volume interaction mainly because of its extreme stiffness and nonpolar nature.

In this Communication, we present an experimental finding of the remaining smectic A4 phase, as schematically depicted in Figure 1D, in the binary mixture of long and short achiral polysilanes, poly[*n*-decyl-2-methypropylsilane] (PD2MPS), with the following formula:[8]



PD2MPS

The PD2MPS has excellent properties to test the theory. The rigid-rod nature of the PD2MPS comes from the 7-residue 3-turn (7_3) helical structure of the polymer backbone[9a] even though achiral polymers apparently have a number of helical reversals between the interconverting right- and left-handed helical segments because the repeating molecular unit is achiral, which may destabilize the rigidity of the polymer backbone. Thus, the cholesteric phase observed in the chiral PDMB should be converted into the nematic phase in PD2MPS, leading to a more precise verification of the theoretical predictions. The PD2MPS shows a well-defined LC polymorphism with the sequence of columnar–smectic A–nematic–isotropic liquid. The detailed structure of the smectic A phase was analyzed by small-angle X-ray scattering and AFM observations, which have been found to be an excellent way to collect information on the smectic layer order and spacing.[9]

The PD2MPS was synthesized and fractionated into samples with narrow molecular weight distributions according to the previously reported method.[3a,10] Two samples were then chosen to provide binary mixtures with a high molecular weight ratio (length ratio) above 3.0. The samples with the lower molecular weight ($M_w = 57.6 \times 10^3$, $M_w/M_n = 1.16$) and the higher molecular weight ($M_w = 181.0 \times 10^3$, $M_w/M_n = 1.44$) were labeled poly-**1** and poly-**1**$_{3.14}$, respectively, in which the subscript represents the molecular weight ratio of poly-**1**$_{3.14}$ to poly-**1** (poly-**1**$_{3.14}$/poly-**1**).[11]

The characteristic layer structure of the smectic A4 phase was confirmed by the AFM observations. Figure 2 shows the AFM images and corresponding Fourier transforms of the films of poly-**1**$_{3.14}$ (A, B), poly-**1** (I, J), and their binary mixtures at the mixing ratios (weight of poly-**1**$_{3.14}$/weight of the binary mixture) of 0.83 (C, D), 0.75 (E, F), and 0.50 (G, H). Fairly regular banded textures were observed in the pure form of poly-**1**$_{3.14}$ and poly-**1**, arising from the mass–thickness variations due to the smectic layers. The repeat distances of the observed bandings in parts A and I of Figure 2 are 104 and 40 nm, respectively, which are almost equal to the molecular lengths of 108.8 and 43.0 nm calculated using the M_n value of the corresponding polymers and 1.96 Å as the translational length per residue. In the binary

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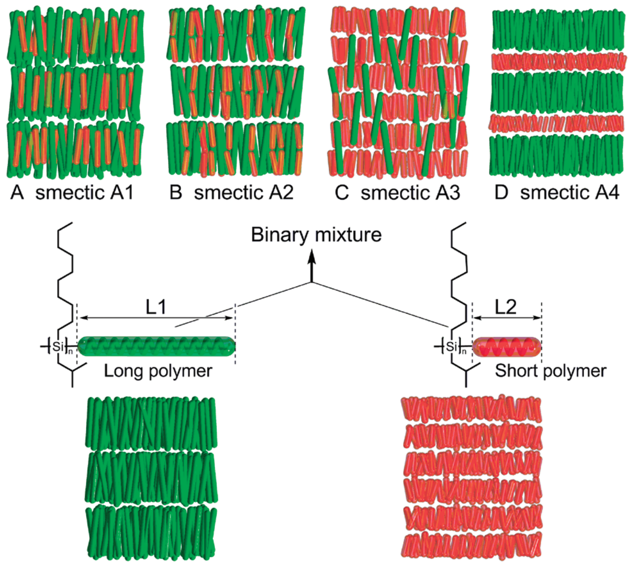

Figure 1. Schematic illustration of smectic phases occurring in binary mixtures of the helical polysilanes (PD2MPS) with different molecular weights. (A−C) Smectic A1, A2, and A3 phases as theoretically predicted and experimentally found in the mixture of the long polymer (green rods) and short polymer (red rods). (D) Smectic A4 phase found in the binary mixture of poly-$\mathbf{1}_{3.14}$ (green rods) and poly-**1** (red rods) with significantly different molecular weights.

mixture with the mixing ratio of 0.83 (Figure 2C,D), the narrow bandings for poly-**1** were partially intercalated between the wider banding for poly-$\mathbf{1}_{3.14}$. Of interest is that only one (not multiple) smectic layer of poly-**1** was selectively inserted in between a pair of smectic layers of poly-$\mathbf{1}_{3.14}$, leading to the alternating thick and thin smectic layers. With the mixing ratio of 0.75 (Figure 2E,F), the alternating thick and thin layers are in the correct proportion and cover the entire field of view, clearly reproducing the schematic illustration of the smectic A4 phase in Figure 1D. The banding repeat indicated in the Fourier transform is 144 nm, which is just the sum of those for poly-$\mathbf{1}_{3.14}$ and poly-**1** in their pure form. Upon further decrease of the mixing ratio to 0.5 (Figure 2G,H), poly-**1** in excess was squeezed out from the alternating thick and thin layers and formed a smectic phase in its pure form seemingly in equilibrium with the smectic A4 phase. These binary mixtures showed distinct smectic features in their polarized optical microscopic textures (see Figure S2 in Supporting Information); however, specific features for the smectic A4 phase could not be observed.

In the theoretical studies, the smectic phase is destabilized with respect to the nematic phase for the composition rich in short rods when the length ratio is high. In other words, the demixing of the smectic A1 phase and smectic A4 phase has not been predicted, but it was expected that the smectic A4 would be transformed into the nematic phase upon decreasing the mixing ratio. Furthermore, by careful observation of the AFM images, we noticed that a pair of thin layers is nested in a thick layer of the smectic A4 phase (see Figure 2G); i.e., a pair of smectic layers of poly-**1** are nested in a smectic layer of poly-$\mathbf{1}_{3.14}$ as in the smectic A2 phase, which is alternately stacked with a single smectic layer of poly-**1**, even though the length ratio is greater than 3. The experimental observation again differed from the theoretical predictions in that no smectic A2 ordering takes place for the length ratio when the smectic A4 phase is stabilized according to the theoretical studies.

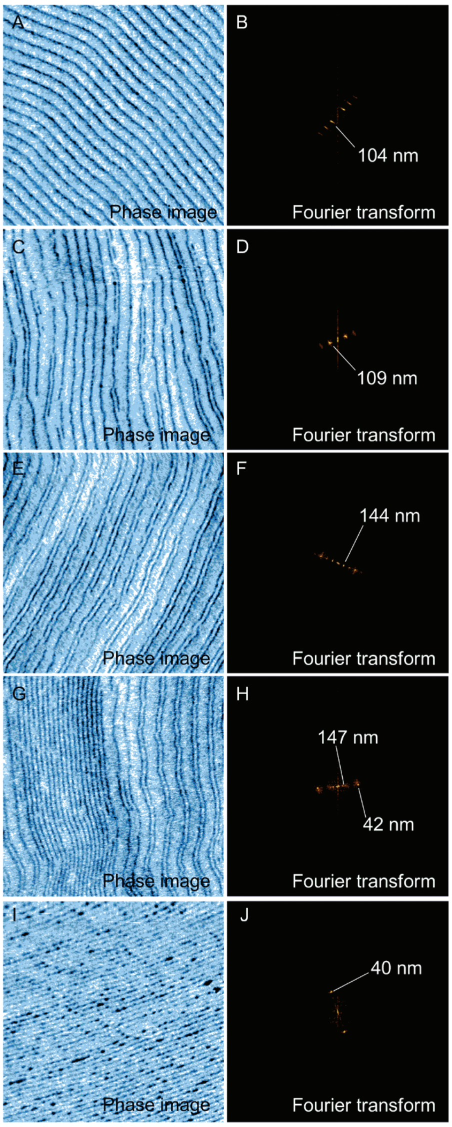

Figure 2. AFM images observed on the film surface of poly-**1**s and corresponding Fourier transforms: (A, B) poly-$\mathbf{1}_{3.14}$ (M_w = 181.0 × 10^3, M_w/M_n = 1.44), (I, J) poly-**1** (M_w = 57.6 × 10^3, M_w/M_n = 1.16), and (C−H) the binary mixture of poly-$\mathbf{1}_{3.14}$ and poly-**1** at the mixing ratio of 0.83 (C, D), 0.75 (E, F), and 0.50 (G, H). The film samples with thicknesses of 20−50 μm were cast on glass plates from the corresponding chloroform solutions, followed by very slow evaporation of the solvent, and then annealed at 140 °C for 5 h before the observations. See details in the Supporting Information. Scale = 2000 × 2000 nm.

On the basis of these results, one can easily envision that smectic ordering is likely to be more preferred in the thermotropic LC system of polysilane than in the theoretical predictions. The dispersion potential, which works for smectic ordering, is not negligible in a dense system like the thermotropic LC phase although Onsager's second-virial theory can reduce the cost of the numerical calculations in the less dense system in which the packing efficiency plays a dominant role. In this sense, the present system might not be capable enough to precisely reproduce the theoretical predictions, unless making use of lyotropic LCs of the polysilanes using nonvolatile solvents, such as alkanes, to dilute the system because of the difficulty in keeping volatile solvents within a vessel. This is worth implementing for the purpose of better understanding the formation of the smectic phase and will be the objectives of future investigations. Despite these facts, thermotropic LC polysilanes are rather better experimental systems to study the LC phase behavior of rodlike particle systems because Coulombic and hydrophobic interactions are intense in the other dispersion systems.

In summary, we observed the theoretically predicted smectic A4 phase in a binary mixture of long and short achiral PD2MPS with the high molecular weight ratio of 3.14. Upon the addition of the short polymer to the abundant long polymer, a smectic layer of the short polymers started to be inserted in between a pair of smectic layers of long polymers and then produced the characteristic and proportioned layer structure of the smectic A4 phase. Upon the further addition of the short polymer, the smectic A1 phase of the short polymer in excess was segregated from the smectic A4 phase, which was confirmed by the AFM observations. In the smectic A4 phase, a pair of smectic layers of short polymers is nested in a smectic layer of the long polymers like the smectic A2 structure. This smectic ordering preference has not been predicted by the theoretical studies but predicted to be transformed into the nematic phase when rich in the short polymer.

Although there still remains inconsistencies between the theory and experiments, a series of complex smectic structures predicted in the binary mixtures of the rodlike particles due to commensuration effects of the particle lengths, including the remaining smectic A4 phase, were successfully reproduced in the thermotropic LC polysilane in the present study. This might indicate that the second-virial theories are valid to some extent because the packing entropy still plays a major role in the present system. We hope our experimental studies on the LC phase behavior of the rodlike polymers provide a better understanding of how to manipulate the processing of the nanoscaled materials used in areas, such as optical devices and sensors, guided by the theoretical studies.

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Supporting Information Available: Detailed experimental procedures and figures showing additional experimental results (wide-area AFM images). This material is available free of charge via the Internet at http://pubs.acs.org.

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