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Triple-Layer Superlattice in Deuterium-Labeled Binary Ultralong Alkanes: A Study by Small-Angle Neutron and X-ray Scattering

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Introduction. Binary mixtures of long-chain *n*-alkanes C_nH_{2n+2} ($150 < n < 400$) have been found to cocrystallize,[1] even if the components differ in length by as many as 100 C atoms as, for example, in $C_{194}H_{390}$ + $C_{294}H_{590}$.[2] Previous X-ray and Raman studies on these mixtures have suggested two main types of lamellar structures: the semicrystalline form (SCF) at high temperatures[3] and the triple-layer superlattice at low temperatures.[4] Because of their high degree of order and resulting high-definition diffraction, these structures are valuable models for semicrystalline polymers. Direct diffraction studies of polydisperse polymers are limited by poor lamellar stacking order.[5]

Selective deuteration is commonly used for neutron scattering because deuterium is a strong scatterer of neutrons.[6] This is useful in retrieving structural details that are unavailable by other methods. For this reason we are presently using binary mixtures in which one of the component alkanes has deuterated end portions of the chain. This allows chain ends to be located by neutron scattering. By using this technique, we have recently been able to confirm the structure of the SCF phase and obtain new information on the distribution of chain ends within the amorphous layer.[7] In this communication we present preliminary results on chain end distribution in the low-temperature phase. By combining SAXS and SANS data from the same sample, we confirm the general structure and obtain a more detailed picture of this phase.

Experimental Section. Two specially synthesized alkanes with deuterated end portions were used: $C_{12}D_{25}$-$C_{144}H_{288}CHDC_{11}D_{23}$ and $C_{12}D_{25}C_{192}H_{384}CHDC_{11}D_{23}$ (for synthesis see ref 8). Hereafter, these will be referred to as C168D and C216D, respectively. Two 50:50 w/w mixtures were prepared: C168D + C242H and C162H + C216D, where C242H and C162H stand for alkanes $C_{242}H_{486}$ and $C_{162}H_{326}$.[9]

Small-angle neutron scattering experiments were carried out on the LOQ station at ISIS, Rutherford Appleton Laboratory. Prior to the experiment the mixtures (100−150 mg) were melt-crystallized and annealed below the transition from SCF to the low-temperature phase, i.e., at around 85 °C.[4] After SANS experiments, small pieces of the samples were packed into thin-wall glass capillaries and studied by SAXS at station 8.2 of the Daresbury Synchrotron Radiation Source. Overlapping scattering peaks were resolved using Peaksolve.

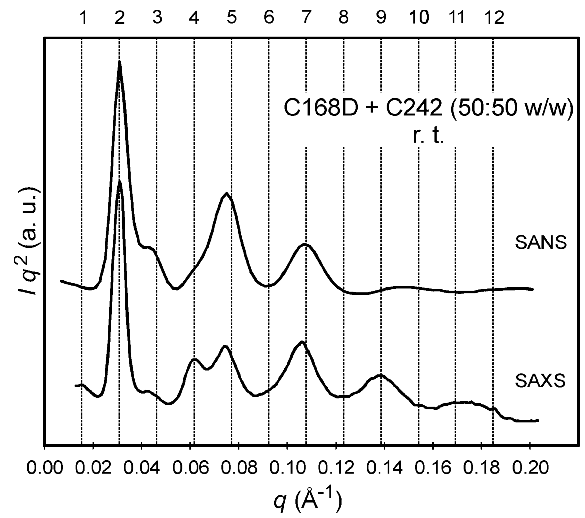

Figure 1. Small-angle neutron and X-ray scattering (SANS and SAXS) curves of the mixture C168D + C242H (50:50 w/w). Intensities are Lorentz corrected. All diffraction peaks are different orders of the same 412 Å *d* spacing, as indicated by the vertical lines.

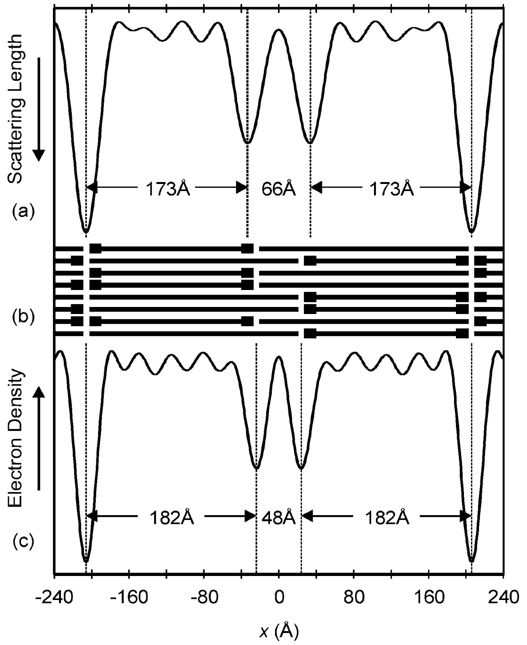

Figure 2. Reconstructed (a) scattering length profile from SANS, (c) electron density profile from SAXS, and (b) the triple-layer superlattice model for C168D + C242H (50:50 w/w). Chain tilt to the lamellar surface is neglected for clarity in (b).

Results and Discussion. The triple-layer superlattice model has been proposed previously for the low-temperature phase of binary long alkanes based on the evidence from SAXS and Raman spectroscopy.[1,2,4] According to this model, one period of the superlattice consists of three crystalline layers: two thicker outer ones and a thinner middle layer. It was implied that the shorter molecules are extended and fully crystallized within the outer layers. At the same time longer molecules, which cocrystallize with the shorter ones in the outer layers, have one end at an outer surface of the triple stack, traverse the outer layer, and form the third layer in the middle as they interdigitate with the long chains emerging from the opposite outer layer (see Figure 2b).

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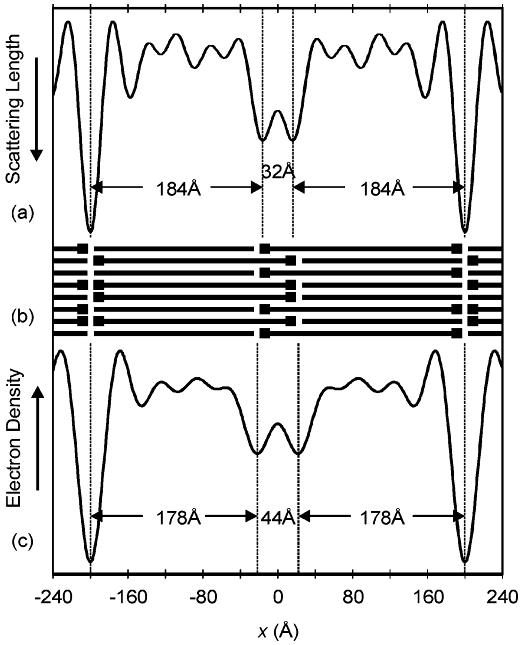

Figure 3. Reconstructed (a) scattering length profile from SANS, (c) electron density profile from SAXS, and (b) the triple-layer superlattice model (chain tilt neglected) for C162H + C216D (50:50 w/w).

To test this model, we start with the C168D + C242H mixture. SANS and SAXS scattering curves are plotted together in Figure 1. Both spectra show a series of orders corresponding to the same 412 Å *d*-spacing, although the intensity distributions among diffraction orders are different. The SAXS spectrum is almost identical to that of a similar but fully hydrogenous mixture ($C_{162}H_{326}$ + $C_{246}H_{494}$, 50:50 w/w) studied before.[1,4] This confirms that deuterium labeling did not affect the lamellar structure.

The resolved SANS and SAXS diffraction intensities were used to reconstruct respectively the scattering length profile (SLP, Figure 2a) and the electron density profile (EDP, Figure 2c) normal to the lamellar stacks. Details of the methods are described in ref 10. The match between the resulting profiles and the triple-layer superlattice model, which is drawn schematically in Figure 2b, can be clearly seen. In SLP, peaks at ±206 Å correspond to deuterated chain ends of C168D on both sides of the outer boundary of the layer triplet, while the weaker peaks at ±33 Å represent the deuterated portions at the other end of the C168D chains, next to the outer layer−middle layer interface. In EDP, dips at ±206 Å correspond to the outer surface of the triple layer, and the shallower dips at ±24 Å correspond to the inner interfaces.

SANS and SAXS curves for the second mixture, C162H + C216D (50:50 w/w), show a series of diffraction peaks, all of which are orders of a 400 Å spacing fundamental. Peak intensities were resolved and used to reconstruct the SLP and EDP (see Figure 3a,c). The triple-layer model drawn in Figure 3b shows good qualitative correspondence with the main features of both reconstructed profiles.

From the reconstructed profiles we measure the projected lengths of short and long molecules (l_S and l_L, respectively), the thickness of the middle layer ($l_m = l_L - l_S$), and the total lamellar thickness ($l = l_L + l_S$) of the triple-layer structure. Values for l_S and l_L obtained from SANS are the distances between the respective SLP peaks corrected for the half-length of the $C_{12}D_{25}$ cap. The overall match with calculated projected chain lengths[11] is satisfactory, as shown in Table 1. However, there are systematic deviations from the ideal model:

1. The projected length of the shorter component l_S measured experimentally is slightly higher (~4%) than that predicted by the ideal model, which assumes the usual 35° chain tilt angle with respect to the lamellar normal.[12] At the same time, l_L is less than the theoretical value (by ca. 10% for the C168D + C242H mixture).

2. As a result of the above discrepancies, the observed thickness of the middle layer ($l_m = l_L - l_S$) is significantly less than predicted. We note that a similar discrepancy has been observed for the triple-layer superlattice structure in other alkane mixtures studied.[2,4]

In considering these deviations, we must take into account that in both mixtures the molar fraction of the longer component is less than 0.5 as required by the ideal model. Consequently, there are too few tails of longer molecules to fill the space in the middle layer. This problem of material deficiency could be solved by extra tilting of the tails in the middle layer (see Figure 4), thus reducing l_m as well as the projected total length of the longer molecules l_L. Layer thickness calculation, assuming that the density of the middle crystalline layer is the same as that of the outer layers, indeed gives a better fit with the experimental data (Table 1). In the case of the C168D + C242H mixture, this would imply an increase of the tilt angle in the middle layer from 35° to 48°. Additional evidence that the chains in the middle layer are indeed straight and not folded comes from Raman LAM experiments on the triple-layer form in several nondeuterated mixtures.[4]

There are certain residual deviations from the model regarding the second mixture, C162H + C216D. The overall measured spacing l = 400 Å matches closely the

Figure 4. Schematic drawing of the triple-layer superlattice model with the tails in the middle layer adopting a higher tilt angle to counter the deficit of long chains: when the binary mixture contains more short alkane molecules (gray lines) than long ones (black lines).

Table 1. Experimental and Calculated Values (in Å) of Projected Lengths of the Shorter Alkane (l_S), the Longer Alkane (l_L), the Middle Layer Thickness ($l_m = l_L - l_S$), and the Total Lamellar Thickness (l) for C168D + C242H, 50:50 w/w, and for C162H + C216D, 50:50 w/w[a]

	l_S	l_L	l_m	l
C168D + C242H, 50:50 w/w				
SANS exp	179	233	54	412
SAXS exp	182	230	48	412
1:1 molar, ideal model	176	254	78	430
1:1 w/w, model with high tilt in the middle layer	176	240	64	416
C162H + C216D, 50:50 w/w				
SANS exp	178	222	44	400
SAXS exp	178	222	44	400
1:1 molar, ideal model	170	226	56	396
1:1 w/w, model with high tilt in the middle layer	170	218	48	388

[a] The two models are described in the text.

ideal model but is 12 Å longer than that expected from the model with extra tilt in the middle layer. A similar situation as in the present mixture is also observed in the undeuterated mixture $C_{162}H_{326} + C_{210}H_{422}$.[4] Otherwise, in all other binary long alkanes that display the superlattice,[2,4] the observed l value complies more closely with the model with extra tilt in the middle layer. Further experiments, e.g., a study of the possible effect of composition on chain tilt in the middle layer, are in progress.

Conclusion. The use of ultralong *n*-alkanes with deuterated chain ends has enabled a combined study of a novel lamellar structure. The previously proposed triple-layer superlattice model has been confirmed in general. The additional information on the precise position of chain ends allows us to proceed with a detailed investigation of deviations from the ideal model.

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