Crystal-Amorphous Polymer Interface Studied by Neutron and X-Ray Scattering on Labeled Binary Ultralong Alkanes

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(Received 18 October 2002; published 18 April 2003)

The recently discovered stable semicrystalline phase in binary ultralong alkanes is studied by small-angle neutron and x-ray scattering. Either the shorter or the longer alkane has $(CD_2)_{11}CD_3$ ends. It is confirmed that chains are tilted in the crystal layer and found that ca. seven end carbons of the shorter alkane are amorphous. It is also established that the longer chains protrude from the crystal at both ends and that their end groups are preferentially located in the middle of the amorphous layer, suggesting gradual dissipation of orientational order of the chains exiting the crystal.

DOI: 10.1103/PhysRevLett.90.155508 PACS numbers: 61.41.+e, 61.10.Eq, 61.66.Hq, 68.65.Cd

Semicrystalline polymers such as polyethylene, polypropylene, and nylon form thin (100–500 Å) crystalline lamellae separated by an amorphous layer containing chain folds, ends, and intercrystalline ties [1]. The long-standing controversy over the nature of the amorphous layer and, particularly, of the crystal-amorphous interface is partly due to a lack of experimental techniques for probing the interface directly [2]. Here we show how specially synthesized selectively deuterated model compounds studied by a combination of small-angle neutron (SANS) and x-ray scattering can provide the relevant experimental information with considerable detail.

Small-angle x-ray scattering (SAXS) has been used in the past to obtain the density correlation function across lamellar stacks in semicrystalline polymers [3–5], but the resulting structural information is of limited precision, due partly to poor positional order. This problem has been overcome by the use of very long model n-alkanes of perfectly uniform molecular weight [6]. The alkanes, several hundred carbons long, can crystallize as extended or multiply folded chains with high layer correlation [7]. A short-lived semicrystalline form ("noninteger form," NIF) has been found in pure long alkanes during melt crystallization [8] and a model was proposed [Fig. 1(a)], based on the electron density profile (EDP) Fourier reconstructed from a series of Bragg reflections [9]. In binary solid solutions of alkanes of lengths differing by up to 100 °C atoms, a related form ("semicrystalline form," SCF) was found to be the stable phase at elevated temperatures [10,11]. At lower temperatures this transforms to a highly crystalline superlattice [10,12]. According to the model of SCF [Fig. 1(b)], the shorter alkane molecules are fully extended and confined to the crystal layer, thus determining its thickness. Meanwhile, the longer molecules traverse the crystalline layer and leave their uncrystallized tails (*cilia*) outside to form the amorphous layer. In NIF, which occurs in pure alkanes, the role of shorter molecules is taken by chains folded in two [9]. The fact that SCF is an equilibrium structure [10,11] makes it ideally suited for experimental investigations of the crystal-amorphous interface. Dissipation of order of chains exiting the crystal and the resulting steric overcrowding have been studied extensively, theoretically [13], and by simulation [14]. Combining the above model of SCF and the fact that longer chain components phase separate for molar fractions above 0.44, it was concluded that a hydrocarbon chain increases its cross section by a factor of 2.8 on crossing the crystal-amorphous boundary [11].

In this work one component of the binary mixture is replaced by specially synthesized n-alkanes with deuterated chain ends. The SCF structure is studied by SANS in combination with SAXS, the former providing explicit information on the location of chain ends. The purpose is twofold: (a) to test the existing model of SCF and NIF, particularly the assumed chain tilt, and (b) to obtain detailed new information on the interface and the amorphous layer. Mixtures of short paraffin have been studied by combined SANS and SAXS using perdeuterated alkanes C_nD_{2n+2} as one of the components [15–17].

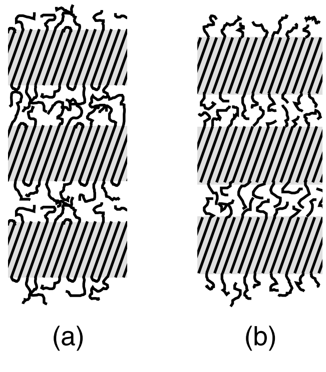
(a) (b)

FIG. 1. Schematic representation of molecular arrangement of (a) NIF in pure long alkanes and (b) the high temperature SCF in binary long alkanes.

However, their structures and phase behaviors are quite different from those of ultralong alkane mixtures and thus will not be discussed here.

Two recently synthesized [18] end-deuterated long alkanes, $C_{12}D_{25}C_{144}H_{288}C_{12}HD_{24}$ ("C168D") and $C_{12}D_{25}C_{192}H_{384}C_{12}HD_{24}$ ("C216D"), are used in this study, as are two previously synthesized [19] nondeuterated alkanes, $C_{162}H_{326}$ ("C162") and $C_{242}H_{486}$ ("C242"). Two 50:50 w/w binary mixtures were prepared: C162-C216D and C168D-C242. The molar fraction of the longer components for both samples (0.43 for C162-C216D and 0.41 for C168D-C242) is lower than 0.44, the stability limit of SCF [11]. The SANS experiment was performed on the LOQ station at ISIS, and the SAXS work was carried out on Station 8.2 of the Daresbury Synchrotron [9].

The first objective of studying C168D-C242 was to remove the uncertainty regarding chain tilt. This cannot be determined from lamellar spacing alone for phases such as SCF and NIF that contain an amorphous layer. For SCF, it was found by SAXS that the thickness of the high-density ("crystalline") layer l_c is only 75% of the length of the shorter alkane chain. A similar deficit relative to the folded chain length was observed in NIF [9]. This has been attributed to a 35° chain tilt in the crystals with respect to the layer normal, a common but not the only tilt angle in linear hydrocarbons [20]. Simulation studies on semicrystalline polyethylene provided a thermodynamic justification for the 35° chain tilt [21]. However, even the correction by $\cos 35° = 0.82$ left l_c too short by 7%. The SANS and SAXS spectra of the high temperature phase of C168D-C242 recorded at 120 °C are displayed in Fig. 2. They show the same fundamental periodicity of 216 Å, but distinctly different intensity distributions among diffraction orders. Integrated intensities are used in the reconstruction of the scattering length profile (SLP) from SANS and the electron density profile (EDP) from SAXS. The profiles normal to the lamellae can be reconstructed by one-dimensional Fourier analysis [9] since the in-plane dimensions of the lamellar crystals are much larger than their thickness [3].

The reconstructions of SLP and EDP ("experimental profiles") for the C168D-C242 mixture are shown in Figs. 3(a) and 3(b). The best-fit trapezoidal models [9] are also shown, along with their Fourier approximations using the same number of terms (diffraction orders) as in the reconstruction of "experimental" profiles. The simulated reconstructions coincide almost exactly with the experimental ones, showing that the ripples are artifacts of series truncation. The EDP from SAXS [Fig. 3(b)] is in line with those previously obtained for other mixtures and shows a high-density plateau of thickness $l_c' = 142$ Å ("crystalline plateau"), a low-density plateau of thickness $l_a' = 38$ Å ("amorphous plateau"), and a transition layer of thickness $l_t = 18$ Å with a linear density gradient. The SLP, on the other hand, contains two closely spaced maxima in each period (note the inverted ordinate scale), with a flat region between the doublets. The molecular model consistent with the best-fit EDP and SLP is shown in Fig. 3(c).

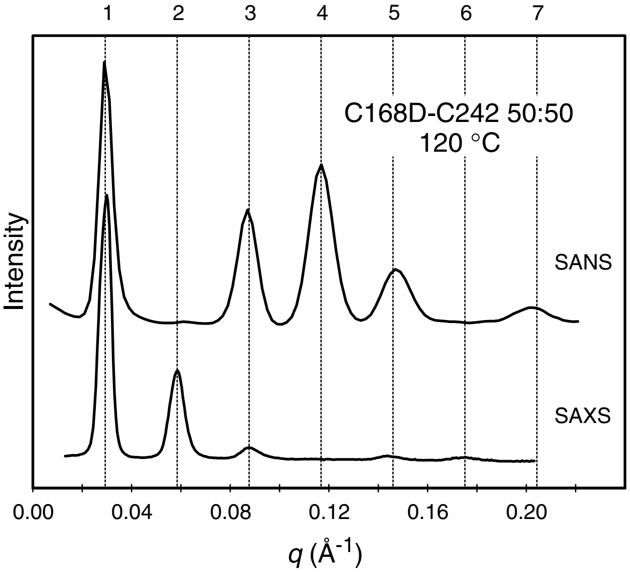

FIG. 2. SANS and SAXS curves of the $C_{12}D_{25}C_{144}H_{288}C_{12}HD_{24} + C_{242}H_{486}$, 50:50 w/w mixture (C168D-C242), recorded at 120 °C. Intensities are background and Lorentz corrected.

The two maxima in SLP of C168D-C242 locate precisely the chain ends within the structure. The distance between the maxima across the crystalline layer is 163 Å, matching exactly the calculated projected distance between the centers of the $C_{12}D_{25}$ chain caps (164 Å) taking the tilt angle of the crystalline chains as 35°. Thus, the SANS result upholds the previous assumption regarding chain tilt and, by implication, the conclusions stemming from the assumed structure of SCF and NIF. Furthermore, by comparing the SLP with EDP, it emerges that the density of the crystalline layer starts to decrease already 16 carbons away from the plane defined by the average position of C168D chain ends. The density drops to midway between crystalline and amorphous values 8 Å, or seven carbons, away from the end plane. Thus, in a simplified two-phase model, the terminal $(CD_2)_6CD_3$ groups fall in the amorphous region. Although a transition layer located between the crystalline and amorphous phases has been implied before [3], the results presented here give by far the most accurate detail of the "rough" crystalline-amorphous interface [Fig. 3(c)]. Incidentally, by measuring the widths of SAXS diffraction lines deconvoluted from the central beam profile [11,22], the correlation length is calculated as being equivalent to about 15 stacked lamellae.

The C162-C216D mixture is studied in order to gain information on the longer of the two chain components. The models in Figs. 1(a), 1(b), and 3(c) imply that the

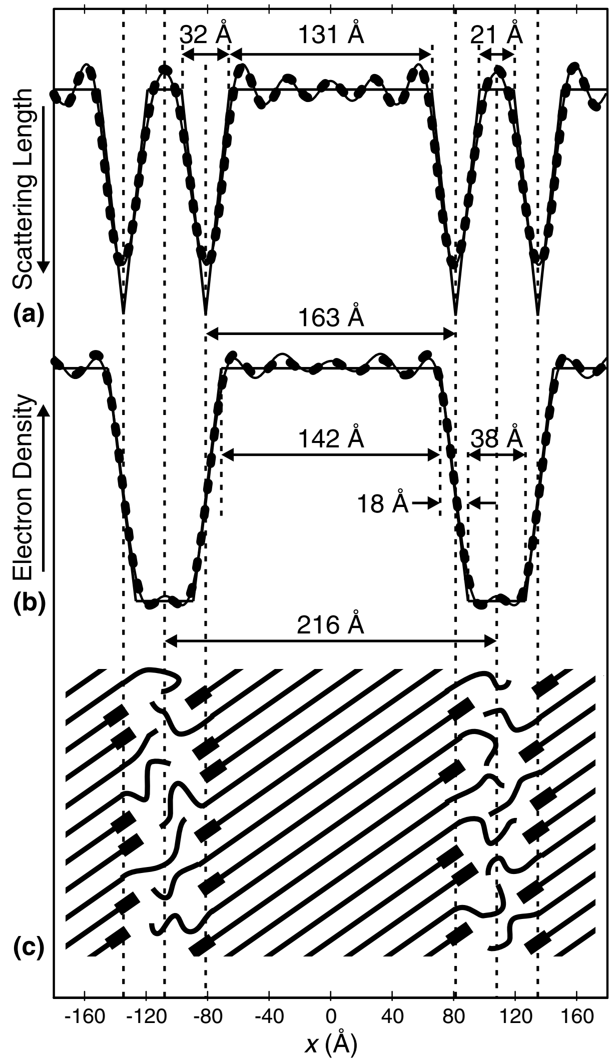

FIG. 3. Reconstructions (wavy lines), best fit models (straight lines), and approximations (dots) of (a) SLP from SANS and (b) EDP from SAXS. SLP: scattering length profile; EDP: electron density profile. For SANS the structure factor signs used are $+--+-+$ (diffraction orders 1,2,3,4,5,7) and for SAXS $+-+-+$ (diffraction orders 1,2,3,5,6). (c) Schematic drawing of the high temperature semicrystalline form showing the rough crystalline-amorphous interface and tilt angle.

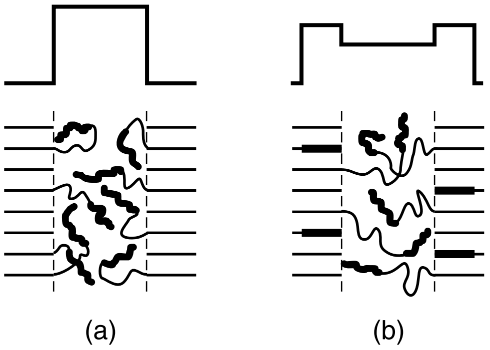

FIG. 4. Idealized models of molecular arrangement in the semicrystalline form where (a) both ends of longer molecules protrude from the crystal as cilia; (b) one end of the longer molecules is flush with the crystal surface. Deuterated chain ends are highlighted and the corresponding SLPs are drawn on top.

longer chains in SCF (or nonfolded chains in NIF) have a *cilium* at each end. This would be entropically favored, due to the longitudinal translational entropy $R\ln(n_l - n_s)$, where n_l and n_s are the numbers of carbons in the longer and the shorter alkane. However, the overcrowding at the interface would be reduced significantly if one of the ends of the longer chain was flush with the interface. The two alternatives are schematically shown in Figs. 4(a) and 4(b), together with their respected idealized scattering length profiles.

The scattering functions of mixture C162-C216D recorded at 115 °C are shown together in Fig. 5(a). The series of diffraction orders in both spectra correspond to the same lamellar spacing of $2\pi/q_1 = 204$ Å. The peak intensity decreases sharply with increasing q, becoming approximately zero at q_4 in SAXS and at q_5 in SANS. The best-fit trapezoidal EDP and SLP models are shown in Figs. 5(b) and 5(c). While the regions of high and low electron density in EDP correspond, respectively, to the crystal and amorphous layers, the maxima in SLP show the location of deuterated chain ends. Notably, the scattering length peak is more pointed than the corresponding electron density dip. The base of the trapezoid is 66 Å in both EDP and SLP. However, the flat plateau is 30 Å wide in EDP but only 8 Å in SLP. This means that the model in Fig. 4(b) is incorrect, i.e., the number of C216D chain ends flush with the interface is negligible. Moreover, the comparison between the EDP and SLP shows that chain ends are not uniformly distributed throughout the amorphous layer, but are instead concentrated in the middle. The situation is illustrated schematically in Figs. 5(d) and 5(e). The concentration of chain ends in the middle of the amorphous layer is consistent with a gradual dissipation of orientational order of the *cilia* emanating from the crystal layers, confirming recent simulation results [14]. The rebuttal of the model in Fig. 4(b) is in line with the comparatively large translational entropy $R\ln(n_l - n_s)$, which is believed to be primarily responsible for the stability of the SCF [11].

In conclusion, the previously assumed chain tilt in the semicrystalline form of binary long alkanes is confirmed. This validates the structure of the unusual semicrystalline phase in binary alkanes and, by implication, that of the related metastable noninteger form in pure alkanes. The derived parameters, such as the 2.8-fold chain expansion on leaving the crystal [11], are thereby also reaffirmed. The crystal-amorphous interface is centered seven carbons from the average end position of shorter molecules. The longer chains protrude from the crystal at both ends and their end groups are preferentially located

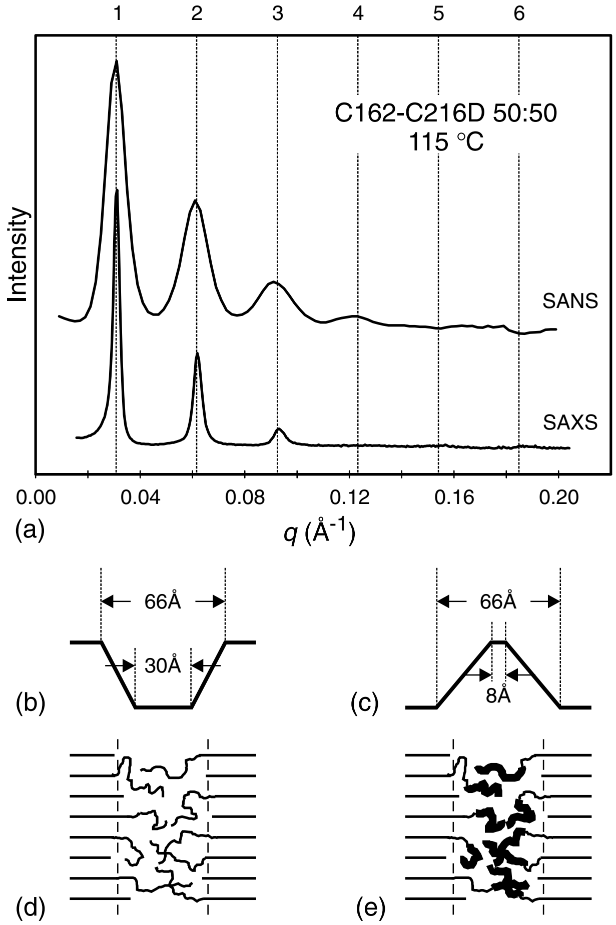

FIG. 5. (a) SANS and SAXS curves of mixture C162-C216D recorded at 115 °C; (b),(c) corresponding best fit trapezoidal model profiles (EDP and SLP); (d),(e) schematic drawings of molecular arrangement in the semicrystalline form consistent with the profiles in (b) and (c). Deuterated segments are highlighted in (e). Chain tilt is ignored in (d) and (e) for clarity.

in the middle of the amorphous layer, consistent with a gradual loss of orientational order of the *cilia.* The information on interface roughness and the gradual dissipation of orientational order of chains emanating from the crystal layer should be applicable to semicrystalline polymers as well. The difference between the present model system and long polydisperse polymers is that, in the latter case, the overcrowding problem is solved by sharp chain folding, while in mixed alkanes it is solved by phase separation of the excess longer chain component when its molar fraction exceeds a critical value [11].

We thank Dr. S. King of ISIS and Dr. N. Terrill of Daresbury Laboratory for help in setting up the SANS and SAXS experiments, respectively. The work was funded by EPSRC.

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