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Compositionally modulated phase in crystalline *n*-alkane mixtures

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We report an x-ray scattering study of the compositionally modulated microphase separated state (μPSS) of binary *n*-alkane ($C_{23}H_{48}$:$C_{28}H_{58}$) mixtures. By employing a quenching technique, we obtained many orders of sharp lamellar and superlattice reflections. The μPSS is a regular superstructure consisting of pure C_{23} layers, and layers rich in C_{28} but containing up to ~14% C_{23} plus voids. A monolayer of the minority component regularly alternates with one or more layers of the majority. The mechanism for thermodynamic stability of the μPSS may be related to the entropy associated with longitudinal displacements of the molecules.

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We report x-ray scattering results that address the nature of the thermodynamic stability of an unusual compositional modulation that occurs in the orthorhombic phase of *n*-alkane (C_nH_{2n+2} abbrv. C_n) binary mixtures. We have found that the superlattice formed by layers of different compositions is well ordered and stable. By observing deviations from linearity in the modulation period and layer spacing versus composition, we show that the layers rich in the shorter chains are pure, while those rich in the longer chains contain some fraction of shorter chains and voids. The thermodynamic stability of the phase is suggested to result from entropy associated with the longitudinal motion of the shorter chains in the thicker layers.

Just below their melting temperature (T), *n*-alkanes exhibit plastic crystalline rotator phases (R), which can accommodate binary mixtures of chains with a substantial carbon-number difference (Δn) [1]. In the lower temperature nonrotator, herringbone orthorhombic crystal phase (X), only pairs with very small Δn are capable of forming stable *homogeneous solid solutions* (HSS). Macroscopic phase separation occurs for large Δn. For intermediate Δn, a HSS initially forms, but the system evolves with time to a *microphase separated structure* (μPSS). This novel modulated structure has recently been the subject of intense interest and investigated using a variety of techniques [2–6]. The μPSS is a compositional modulation along the layer normal, whose period is related to the stochiometry of the mixture; a (nearly) equimolar mixture produces a bilayer structure. For μPSS-forming mixtures, larger Δn results in a faster development of the modulation. The μPSS develops faster for shorter average $n(\overline{n})$, due to the faster diffusion of smaller molecules. The kinetics as a function of temperature exhibit a maximum rate caused by the competition between the increased driving force and the slowing diffusion on cooling [4]. On heating, the μPSS undergoes a disordering phase transition to the HSS [5]. The previous work has explained the mechanism of how molecular diffusion kinetically leads to the μPSS and explains its various compositional and T dependences in terms of conformational disorder and void reduction. Some work suggested that the μPSS occurs because of the ease by which it can form from the HSS [2]. However, the nature of the thermodynamic stability of the μPSS and the physics surrounding it have remained elusive. An important question is, therefore, whether the modulation is favored by the free energy. In other words, is this periodicity a well defined free-energy minimum or is it only a kinetically intermediate state on the path to full macroscopic phase separation? And if it is, then what interactions are responsible for it being so?

The packing of a pure *n*-alkane in the orthorhombic crystal phase provides an example of the lowest free-energy state. The molecules are mostly in their trans conformational states with the $-CH_2-$ groups close-packed in a herringbone arrangement. The molecules are in well defined layers with the optimal packing of the terminal CH_3- groups resulting in an ABAB . . . bilayer stacking. The free energy of a binary mixture is lowered by the entropy of mixing, however this is at the cost of incorporating disparate length chains in the same lattice. Doing this requires the presence of energetically unfavorable voids from the shorter chain and/or gauche defects at the end of the longer chains. For large Δn, the entropy of mixing can no longer compensate for the cost of the disorder in a mixed crystalline state, and the system favors phase separation where each component can pack in its ideal state.

Since the entropy of mixing is lost when individual components segregate into layers, how then might a modulated structure be favored? If the in-plane packing of both pure components are identical and the energetics of packing the terminal CH_3-'s are independent of *n*, one would obtain a phase with compositionally pure layers that are randomly stacked. This, however, would not result in an ordered modulation with sharp superlattice reflections, but rather only short-range order. A second possibility is that the μPSS is not an equilibrium modulation, but a kinetically intermediate structure [2], much like the short-range modulations of composition which occur during spinodal decomposition. A third possibility which is argued here, is that there is another mechanism thermodynamically stabilizing the μPSS.

Using a different quenching technique, we have obtained sharp lamellar and superlattice reflections and made accurate measurements of the layer and superlattice periods. By using shorter chain lengths than in previous studies, we were able

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*Email address Eric.B.Sirota@ExxonMobil.com to substantially speed up the μPSS development kinetics. We find that the modulation peaks are not broad, as expected from a simple kinetic argument, but rather as sharp as the nearly resolution limited principal lamellar peaks. The modulation period is a well defined function of composition and does not change with time, as would be expected for a coarsening phase-separating state. In fact, the modulated μPSS that formed from the HSS in minutes after quenching, was stable, with the same period, even after five months. However, the layers are not compositionally pure and we will suggest that the longitudinal positional entropy afforded by the voids, favors the regular structure as a stable phase, or at the very least a metastable phase with a deep local free-energy minimum.

Experiments were carried out using Cu $K\alpha$ radiation on a Rigaku 18-kW rotating anode x-ray generator with a Huber goniometer. The beam was defined with a bent graphite monochromator and slits, giving a effective resolution of $\Delta q \approx 0.012$ Å^{-1}. High resolution measurements were carried out at beamline X10A at the NSLS. The *n*-alkanes from Aldrich were used as obtained.

When a binary phase diagram allows for continuous mixtures of two components with differing melting temperatures, the equilibrium state is compositionally homogeneous. However, a higher than average composition of the higher melting material often crystallizes first. This leads to spatial variation in the composition of crystallites and is known as ''coring.'' Coring manifests itself in *n*-alkane mixtures causing the lamellar 001 reflections to have widths greater than resolution, and which increase with increasing harmonic number. This shows that the average chain length is not uniform over various correlated scattering volumes. The widths of the lamellar reflections in the R phase are typically comparable to a broad, low resolution; whereas, high-resolution synchrotron measurements clearly reveal the broadening. However, when the mixture is quenched from the melt down into the X phase, the resulting peaks are broad, even at low resolution. Such broadening makes study of the lamellar, order and superlattice structure very difficult and ambiguous. By quenching the mixtures in the melt, first into R and then into X, we obtained homogeneously mixed HSS that exhibited sharp lamellar reflections. A comparison of the scattering from the 002 lamellar reflection from both quench scenarios is shown in Fig. 1(a). Our procedure gives rise to much better defined lamellar reflections with peak widths of ~0.017 Å^{-1}, only slightly above resolution.

We chose C_{23}:C_{28} mixtures for most detailed study. Characteristic scattering patterns on samples annealed at 22 °C, for different mole fractions of C_{23} (ϕ), are shown in Fig. 1(b). These show the variation of the lamellar and superlattice reflections with composition. In Fig. 1(c) we show a typical scan on a (scaled) linear plot, showing the many orders of sharp peaks. The lamellar reflections appear at Nq_0, for integer *N*, where the average layer spacing is $d = 2\pi/q_0$. A modulation that develops along the layer normal with period $\lambda = 2\pi/q_m$ gives rise to reflections at $q = Nq_0 \pm q_m$. However, only one such set of them, at either $q_0 + q_m$ or $q_0 - q_m$ is visible. One might expect the intensity amplitude to be symmetric with respect to $\pm q_m$ in the small amplitude approximation. However, the full equation for the intensity of satellite peaks about principal peaks at $Q = 2\pi N/d$, associated with displacements u_m from average positions $R_m = md$, $I(Q, \pm q_m) = |\Sigma_m \exp\{i[\pm q_m md + Qu_m]\}| / |\Sigma_m \exp\{iQu_m\}|$, [7] shows that there can be extremely asymmetric intensities if the modulation is an asymmetric sawtooth shape and Qu is not small, as shown schematically in Fig. 2. The sign of this intensity asymmetry is consistent with the data and the model for the structure of the layers presented here. Specifically when the shorter (longer) molecule is the majority component, there will be a much stronger intensity associated with the $q_0 + q_m$ ($q_0 - q_m$) peak.

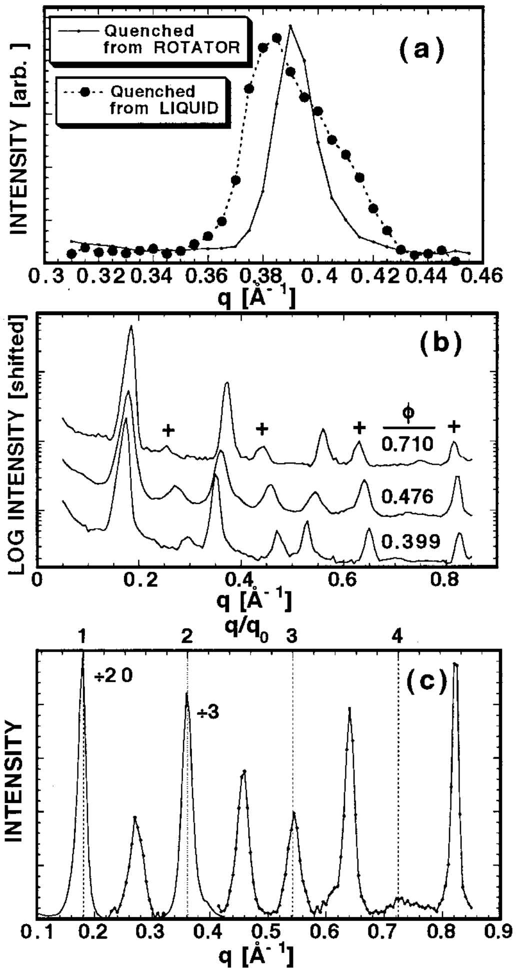

FIG. 1. (a) The 002 lamellar reflection obtained by quenching an equimolar C_{21}:C_{26} mixture (solid) from the melt to the X phase 0 °C; (dashed) from the melt to the R 38 °C and then to the X phase. (b) X-ray scattering showing the first four orders of the lamellar and superlattice reflections (labeled +) for three different ϕ of a C_{23}:C_{28} mixture. The data is shown on a base-10 semilog scale, and is offset. (c) X-ray scattering shows the sharp lamellar (integer q/q_0) and superlattice reflections (noninteger q/q_0) for an annealed $\phi = 0.476$ sample at 22 °C. The 001 and 002 peak heights are scaled as indicated.

In Figs. 3(a) and 3(b) we plot *d* and q_m/q_0 versus ϕ. At low $\phi < \phi_1$ ($\phi_1 = 0.14$), there is no modulation and *d* remains constant with increasing ϕ. This means that the C_{23}

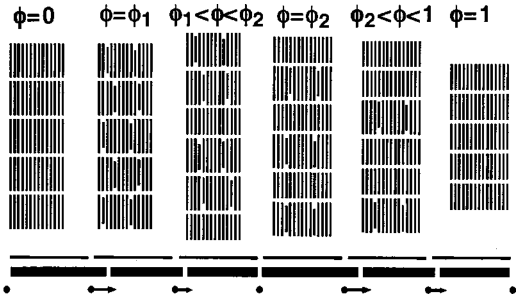

FIG. 2. (top) The observed structures in different ranges of ϕ, going from pure C_{28} $(\phi=0)$ to pure C_{23} $(\phi=1)$. (bottom) Schematic for a three layer period consisting of one C_{28} and two C_{23} layers showing the average layer (thin lines) the actual layer thickness (thick lines) and the displacements, u, of the interlayer region from their average positions (arrows). This gives an asymmetric sawtooth shape for u_m.

molecules enter the C_{28} layers, but do not change the average spacing. This implies that the C_{28} molecules remain straight. The presence of C_{23} in positions which could otherwise fit C_{28} leads to vacancies and positional entropy for the C_{23} molecules. This is illustrated schematically in Fig. 2. We point out that a 180° rotation coupled to a 1.27 Å translation will allow the molecules to maintain their packing within the orthorhombic lattice. For $\phi_1 < \phi \leq 1$, d decreases approximately linearly. As can be seen, there is no comparable flat region at high ϕ; in other words, the average layer spacing begins increasing linearly on adding the first C_{28} to pure C_{23}. For $\phi > \phi_1$, a modulation appears, with q_m/q_0 increasing linearly and smoothly until $q_m/q_0 = 0.5$ at $\phi = \phi_2 = 0.58$. This corresponds to a bilayer repeat. We note that this does not occur at $\phi = 0.5$, since the C_{28}-rich layer incorporates $\sim 14\%$ C_{23} molecules, while the C_{23} layers are essentially pure. For $\phi > \phi_2, q_m/q_0$ decreases again until the modulation disappears at $\phi = 1$. For $\phi_1 < \phi < \phi_2$ the structure is consistent with an alternation of a monolayer of C_{23} with $(1-\phi+\phi_1)/(\phi-\phi_1)C_{28}$-rich layers. This gives a period of $1/(\phi-\phi_1)$ layers and an average layer spacing of $d=(1-\phi+\phi_1)d_{C_{28}}+(\phi-\phi_1)d_{C_{23}}$. For $\phi_2 < \phi < 1$, the structure is an alternation of a C_{23}-saturated C_{28}-rich monolayer with multiple C_{23} layers. The observed incommensurate periods are then likely accommodated by having variability in the number of majority component layers, such that the average period is maintained.

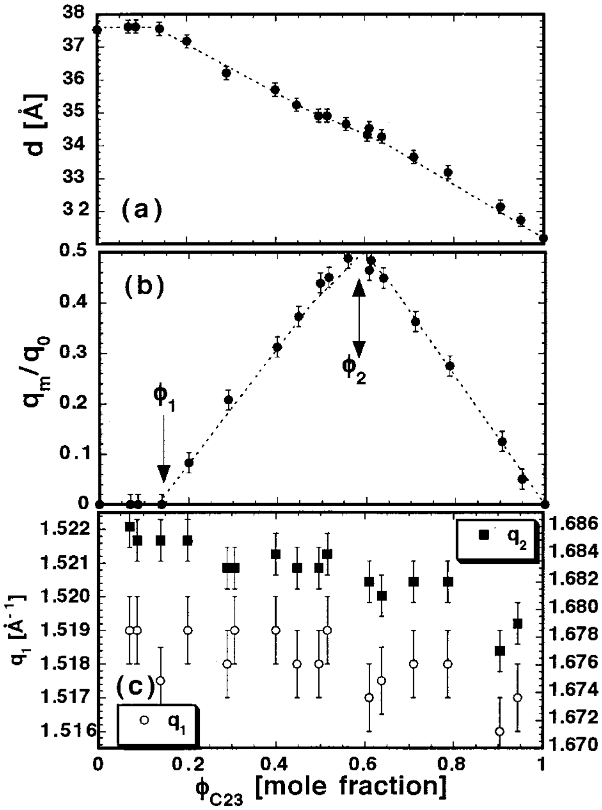

FIG. 3. (a) d spacing vs ϕ, showing clear deviation from Vegard's law. (b) q_m/q_0 vs ϕ. A constant C_{23} saturation of the C_{28}-rich layers would predict straight lines. The dashed curves are generated assuming a varying C_{23} saturation as described in the text. (c) Positions of wide-angle (in-plane) principal peaks at 22 °C as a function of ϕ, on annealed samples.

If the C_{23} concentration in C_{28}-rich layers were a constant (i.e., ϕ_1), then Figs. 3(a) and 3(b) would be made of straight lines. An increase in this saturation as the composition becomes more C_{23}-rich can cause the observed deviations. The dashed curves in Figs. 3(a) and 3(b) are calculated assuming that the C_{23} saturation increases linearly from 0.13 to 0.21 as ϕ varies for 0.47 to 0.66, and is not meant to be unique, but rather show that this small deviation from linearity can be accounted for simply.

The high-angle scattering peaks correspond to the in-plane orthorhombic packing with bilayer stacking. The variation of the peak positions with ϕ in the μPSS is shown in Fig. 3(c). A previously proposed model suggested that the longer chains are more disordered, resulting in a reduced packing density [6]. However, these results show only a weak lattice expansion with increasing ϕ.

While we measured only C_{23}:C_{28} in great detail, we believe the observed behavior is representative of μPSS forming n-alkane mixtures, in general. We have observed consistent results in C_{21}:C_{26}, C_{22}:C_{28}, C_{19}:C_{24}, C_{21}:C_{25}, and C_{25}:C_{30} systems. The lower-$\overline{n}$ mixtures tend to exhibit the R phase at room temperature and thus long-term annealing in the μPSS was not possible. The general trends observed were in agreement with previous work: this included faster superlattice ordering with shorter $\overline{n}$ and larger Δn, as well as a T maximum in the ordering rate. The melting of the superlattice at elevated T, while remaining in the X phase, could only be observed in the C_{25}:C_{30} system. In the others, the transition to the R phase occurred below the superlattice disordering temperature.

The sharp multiple order superlattice reflections that remain so, over a period of time four orders of magnitude longer that the time required to form them, attests to their relative stability. If a bilayer structure formed quickly, but was not specifically stabilized with respect to further phase separation, then coarsening to a four-layer (or longer) period that only requires diffusion over a single layer, would have been observed. Instead, we see structures which contain a single monolayer of the minority microphase spaced *regularly* and separated by the stochiometrically determined average number of majority microphase layers. Thus, the interactions between minority monolayers are apparently not attractive. If the minority monolayers were randomly located (with neither attractive nor repulsive interaction), the superlattice would be random. What is necessary to stabilize the observed state is an effectively repulsive interaction between the minority phase monolayers. This can be considered analogous to the hydration or undulation forces that stabilize swollen lipid bilayer membranes [8]. If each of the layers were compositionally pure and identical except for their length difference, such an interaction would be hard to imagine. However, our results have shown that the thicker (C_{28}-rich) monolayer includes C_{23} molecules and voids, which allow entropy associated with longitudinal motion. The presence of pure C_{23} layers adjacent to the layers with these voids also will allow longitudinal motion on their part. This freedom can propagate even to further layers. Thus, we suggest that a likely cause of the stability of the μPSS is entropic in nature caused by the longitudinal freedom allowed by the incorporation of shorter molecules and thus voids, in the layers rich in the longer molecules. This longitudinal freedom is already known to play a major role in the properties of *n*-alkanes, contributing to the stability of rotator phases and lowering the interfacial energies at liquid and vapor interfaces [9]. We encourage theoretical work to quantitatively determine the effect of internal voids on the interactions between layers and the stability of the μPSS.

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