Novel Phase Behavior in Normal Alkanes

E. B. Sirota, H. E. King, Jr., G. J. Hughes, and W. K. Wan

Corporate Research Science Laboratories, Exxon Research and Engineering Co., Route 22 East, Annandale, New Jersey 08801
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X-ray scattering studies on aligned films of binary mixtures of the normal alkanes $C_{23}H_{48}$ and $C_{28}H_{58}$ reveal, for the first time in such materials, the existence of a new equilibrium phase having the symmetry of a smectic liquid crystal, possibly a hexatic. This phase occurs between the hexagonally packed R_{II} and the lower-temperature orthorhombic R_I, plastic crystalline, layered, rotator phases. We argue that this loss of order is due to local distortion fluctuations in the hexagonal phase. Furthermore, we have identified an ABC-to-$ABAB$ restacking transition within the ordered R_{II} phase.

Normal alkanes $[CH_3-(CH_2)_n-CH_3]$, consisting of linear chains of saturated hydrocarbons, are among the most fundamental of molecular series. These simple molecular chains are important constituents of many molecules in organic, biological, and polymeric systems, for example, liquid crystals, surfactants, and lipids. In addition, the normal alkanes themselves are important components of petroleum, and thus play an important role in many products such as fuels and lubricants. Those alkanes having carbon numbers from about 18 to 100, often known as waxes, have a surprisingly complex phase behavior between the isotropic liquid and the low-temperature crystal. It is obvious that any molecule containing alkane moieties will be strongly influenced by such behavior. Thus, a detailed understanding of alkane phase behavior is likely to aid in understanding many other systems. In particular, it can help sort out the influence of the various interactions typically present in these complex materials; for example, in surfactants much of the phase behavior can be explained as a competition between the head group interactions and those between the alkanelike tails.

Being such a fundamental and important system, the alkanes have been studied in great depth over many years [1-5] and a plethora of phases occurring between the isotropic liquid and fully crystalline states have been identified. We will be concerned here with those found for alkanes of carbon number 22 through 26. The phase sequence in the range of interest is the following. [The numbers quoted are those measured for $C_{23}H_{48}$ (C23) in the present study.] At high temperatures, the chains are disordered in a liquid state. Below $T = 46.9\,°C$ the R_{II} rotator phase forms. In this layered phase the molecular chains are packed in a hexagonal array within the layer, freely rotating about their long axes with no significant correlation in this rotation [3]. The axes are oriented normal to the layer. The molecules possess long-range positional order, thus, making R_{II} a crystalline phase; however, the large degree of both rotational and positional disorder, evidenced by strong diffuse x-ray scattering about the Bragg peaks, leads to the term "plastic" crystal in some of the literature [3]. The stacking of the layers in this phase has been determined to be an ABC trilayer structure [4]. This phase is very similar to the crystalline-B phases which exist in many liquid crystals [6].

As the temperature is reduced below $44.3\,°C$, the system undergoes a first-order transition to the R_I rotator phase in which the hexagonal packing within the layer distorts and the stacking goes from trilayer to bilayer [4]. The resulting phase has an orthorhombic face-centered structure with an asymmetry parameter $\delta = 1.011$, where δ is defined as the ratio between the in-plane next-nearest-neighbor and nearest-neighbor distances. There is no significant change in layer spacing across the transition signifying that the molecules remain perpendicular to the layers. While there continues to be molecular rotation in this phase, steric models, differential scanning calorimetry (DSC), and spectroscopic measurements [3] suggest that there are short-range correlated rotational motions. The resulting local herringbone packing is believed to be responsible for the orthorhombic distortion. Below $39\,°C$ the system orders into a fully crystalline state (C) where molecular rotation is frozen out resulting in long-range herringbone order.

Studies of binary mixtures of alkanes [1] have shown that in the liquid state all chain lengths are fully miscible; but in the solid phases the miscibility is strongly influenced by the carbon number difference and odd/even carbon number effects. An additional general feature of binary mixtures is that they often assume untilted structures even when the pure components are tilted. In general, it is also known that the R_I-to-C transition temperature is depressed in mixtures. Few detailed studies of aligned samples in the rotator phases of binary mixtures have been made; therefore, we undertook an x-ray scattering study of the C23-C28 binary system, in which we discovered an unexpected new type of melting phenomena in a region of the phase diagram believed to be understood.

Our material was obtained from Sigma Chemical: stated purity 99%. Initial measurements were done on a Rigaku 12-kW rotating anode x-ray generator on powder samples held in 2-4-mm-thick cells with Kapton windows. The samples were temperature controlled to $\pm 0.02\,°C$. The spectrometer was configured with a bent graphite monochromator and slits giving an in-plane resolution corresponding to a 2θ arm-zero width of $0.135°$ FWHM.

The equilibrium phase diagram we obtained is shown in Fig. 1. The high-temperature phase is an isotropic

liquid, with a broad peak at $q = 1.35$ Å^{-1}. As the temperature is reduced, a region of phase coexistence appears, below which is the R_{II} phase. The scattering from this phase is typified by two types of peaks: interlayer and intralayer. The interlayer peaks are a set of 00l Bragg reflections at $2\pi l/d$, where l is an integer and d is the layer spacing. Throughout the rotator phases the layer spacing remains essentially unchanged with temperature, varies linearly with composition, and is in close agreement with the weighted average length of the molecules, implying that the two species are well mixed. It should also be noted that we have not observed any reflections at half-integer values of l, which would result if the two species segregated to alternating layers within the same phase as was reported for longer chain alkanes in the crystalline phases [5].

With the low-resolution x-ray setup, the high-angle intralayer peak, which corresponds to the chain-chain packing, exhibits a single maximum at $q \sim 1.525$ Å^{-1} along with strong tails. For the compositions studied between $\phi = 0.1$ and 0.7 (where ϕ is the C28 weight percent), as the temperature is reduced in the R_{II} phase, the peaks *appear* to broaden *reversibly*, to a width of $\Delta q = 0.09$ Å^{-1} FWHM (for $\phi = 0.46$) at the lowest temperature. This width was smaller for mixtures where the R_{II} temperature range was smaller. Furthermore, as the temperature is reduced, the position of the peak moved from $q = 1.524$ to 1.531 Å^{-1}, corresponding to a contraction of the in-plane hexagonal structure. As the peak broadened, we did not observe the appearance of any new peaks. The broadening of the peaks with reducing temperature is clearly an anomalous feature requiring more detailed study. We will return to this shortly.

On further decreasing temperature, a discontinuous

transition (with a coexistence of < 0.5 °C) occurred to the R_I phase which is characterized by two sharp peaks at $q = 1.504$ and 1.601 Å^{-1} for $\phi = 0.5$ (see Fig. 2). As the temperature was reduced through the R_I phase, the splitting of the two peaks increased and the area/molecule decreased: a typical behavior [2].

To better understand the unusual peak broadening in the R_{II} phase, we studied the same system at high resolution at the National Synchrotron Light Source (NSLS), Exxon beam line X10B, where our 2θ resolution, FWHM, was 0.008°. This measurement showed that instead of a single peak which broadens, there are a pair of Bragg peaks separated by $\Delta q = 0.002$ Å^{-1} sitting on a strong broad peak with a FWHM of 0.08 Å^{-1}. At $T = 49.6$ °C for $\phi = 0.5$, $\sim 10\%$ of the integrated intensity was in these Bragg peaks. As the temperature was reduced, in addition to a shift to larger q, the intensity of the Bragg peaks diminished, until the Bragg component was unobservable (see Fig. 2).

To further elucidate the nature of the structure and correlations in the R_{II} phase, we prepared aligned samples by evaporating a concentrated solution in hexane of the C23-C28 mixture onto a 76-μm-thick silicon wafer [7]. Subsequent annealing left the sample aligned with the layers parallel to the surface, often to better than 0.1°, determined by rocking the substrate while sitting at one of the 00l layer reflections. The aligned samples were less than 0.1 mm thick; however, all the peak positions, transition temperatures, and other effects were consistent with those observed in the bulk powder samples, and we, therefore, can rule out that these thin aligned samples are showing surface or finite-size effects [6]. Scattering measurements were performed on the aligned samples in transmission geometry through the silicon wafer, which with Cu $K\alpha$ radiation gave a transmission of 40%. The
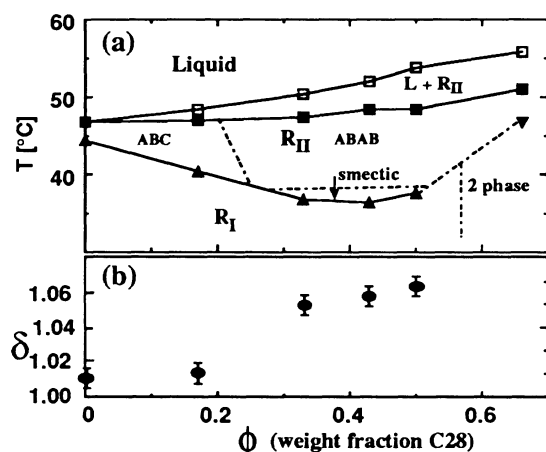

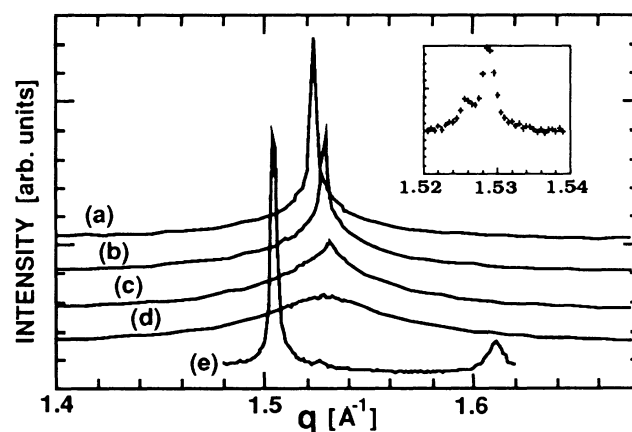FIG. 1. (a) Equilibrium phase diagram for C23-C28 mixtures; ϕ is the weight fraction of C28. (b) The ratio of the in-plane next-nearest-neighbor to nearest-neighbor distances (δ) at the R_I-to-R_{II} transition in the R_I phase, as a function of ϕ. The transition is more strongly first order when the transition temperature is depressed.

FIG. 2. High-resolution scans on a powder sample of $\phi = 0.5$ C23-C28 phase at (curve a) $T = 48.5$ °C, (curve b) 43.7 °C, (curve c) 40.0 °C, and (curve d) 37.5 °C in the R_{II} and at (curve e) $T = 36.1$ °C in the R_I phase. Inset: A scan with a finer step size shows the double peak in the $ABAB$-R_{II} phase at 43.7 °C.

spot size on the sample was approximately 1 mm×2 mm and the sample appeared to be a 2D powder of rotation about the layer normal. Figure 3 shows a series of q_z scans through the peak in q_r, where q_z is the momentum transfer normal to the layers and q_r is in the plane of the layers. At high temperature, the main feature [Fig. 3(b)] is a series of three peaks, two strong ones at $q_z = \pm 0.09$ Å^{-1}, corresponding to half the q_z value of the first reflection from the layers, and a weak peak (approximately $\frac{1}{3}$ the intensity of the strong ones) at $q_z = 0$: all three occurring at the same q_r value at any given temperature. The width of these peaks is limited in the q_z direction by mosaic spread, and in the q_r direction by resolution. These aligned samples were also studied at a synchrotron, and these peaks were confirmed to be resolution limited at high resolution implying that there is true 3D crystalline order. The other important feature of the scattering is the strong diffuse ridge under the Bragg peaks. This ridge is centered at essentially the same q_r value as the Bragg peaks, and has a width $\Delta q_r = 0.02$ Å^{-1} FWHM. The width of the ridge along q_z corresponds to the molecular form factor. The positions of the peaks along q_z are consistent with an ABAB bilayer stacking and not the ABC trilayer stacking which was reported in pure C23 [Fig. 3(a)] [4]. Upon reducing tem-

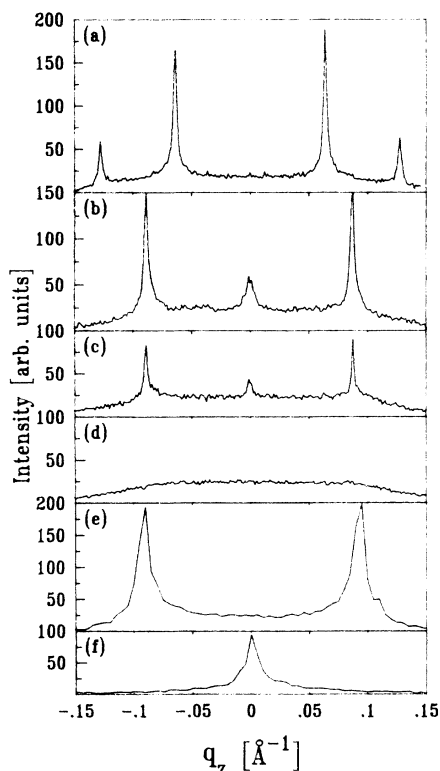perature, the Bragg peaks diminish in intensity continuously and reversibly, without broadening and the diffuse ridge appears to broaden along q_r from FWHM =0.02 to 0.045 Å^{-1} just above the R_{II}-to-R_I transition. The intensity of the Bragg peak component in the R_{II} phase is plotted versus temperature in Fig. 4, strongly suggesting the existence of an order-disorder transition within the R_{II} phase. By the lowest temperature in the R_{II} phase [Fig. 3(d)], the Bragg component of the peaks is unobservable, even at high resolution in aligned samples. Thus, from the x-ray scattering we conclude that, while there is long-range order of the density normal to the layers made evident by resolution-limited 00l reflections, there is only short-range positional order in the plane of the layers. This phase has the symmetry of a smectic liquid crystal, not previously observed in normal alkanes. Since this structure is not tilted [6], and we do not have a single 2D domain, we cannot presently determine whether this structure has long-range bond-orientational order which would make it a hexatic [8]. However, the in-plane correlation length of 45 Å, determined from the longitudinal width of the in-plane peak, is typical of those found in hexatic liquid crystals [6,9].

Upon reducing temperature further, we enter the R_I phase which is characterized by q_z scans shown in Figs. 3(e) and 3(f). For $\phi = 0.5$ and $T = 35$°C, the peaks at $q_z = \pm 0.09$ Å^{-1} are at $q_r = 1.495$ Å^{-1} and are more intense than those at $q_z = 0$, $q_r = 1.602$ Å^{-1}. This is the expected scattering from an orthorhombic-F structure. We point out that at this transition sharp in-plane Bragg peaks reappear, signifying reentrance of long-range order in the plane of the layers.

To resolve the discrepancy between the stacking reported for pure C23 [4] and our measurement in the mixture, we studied aligned samples at several C23/C28 ratios. Figure 3(a) shows a q_z scan for $\phi = 0.18$. The peaks at $q_z = \pm 0.065$ and ± 0.13 Å^{-1} are at q values corresponding to $\frac{1}{3}$ and $\frac{2}{3}$ of the first-layer reflection. This, in addition to the absence of first-order peaks at $q_z = 0$, shows that the structure here is indeed a trilayer ABC stacking. Measurements of the other members of the series at the highest-temperature point in the R_{II} phase revealed the

FIG. 3. q_z scans through the in-plane peaks in aligned samples. (a) $q_r = 1.525$ Å^{-1}, R_{II} ABC structure, $\phi = 0.18$, $T = 42.2$°C; (b)–(d) R_{II} ABAB, $\phi = 0.5$, at $T = 48.4$, 42.0, and 38.1°C, respectively; (e),(f) R_I phase at $T = 35.0$°C, $q_r = 1.495$ and 1.602 Å^{-1}.
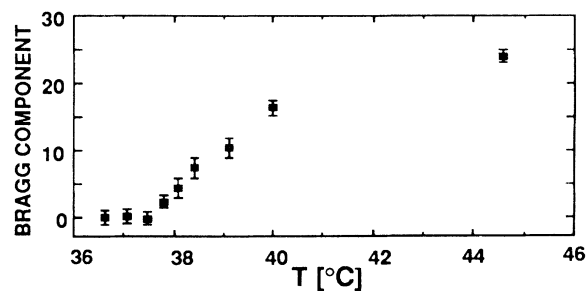

FIG. 4. Bragg peak intensity vs temperature for $\phi = 0.5$ C23-C28 mixture in the R_{II} phase showing the disappearance of long-range order.

ABC stacking at $\phi = 0$ and 0.18 and the *ABAB* stacking at $\phi = 0.25$, 0.33 0.46, 0.5, and 0.66 [Fig. 1(a)]; thus, there is a restacking transition within the region denoted R_{II}.

To determine the generality of the diminishing Bragg peak intensity as well as the restacking transition, we investigated several other mixtures of chain lengths (C21-C25, C23-C25, C23-C26, C23-C27, C23-C29) and found these same effects in mixtures of different average lengths and different chain length differences regardless of odd/even carbon numbers [7].

The reentrance of crystalline order observed in this system is very different from that commonly observed in liquid crystals. The most common such reentrance [6] is the untilted crystal-*B* phase undergoing an abrupt change to the tilted-hexatic-smectic-*F* phase (where positional order is replaced by tilt order) and then nearly continuously ordering to the tilted-crystal-*G* phase, as temperature is reduced. In the system studied here, the disordered phase evolves continuously from the higher-temperature phase and the sixfold symmetry is broken at the lower-temperature transition.

We can understand the R_{II}-to-R_I transition as a distortion of a hexagonal lattice along one of three equivalent directions, with the distortion $(\delta - 1)$ being the primary order parameter. While molecular rotation is being inhibited as the temperature is lowered through these two phases, they are both rotator phases, and the long-range herringbone order of the rotational degree of freedom is not established and thus it is not the order parameter for this transition. (The orthorhombic phase breaks a threefold symmetry while the long-range herringbone order requires an additional twofold symmetry breaking [10].) As molecular rotation becomes inhibited, *local* herringbone packing gives rise to *local* orthorhombic distortions and greater average packing density. For reasons probably related to the interlayer stacking and ordering, which are coupled to the intralayer distortion, the presence of mixed chain lengths suppresses the formation of the orthorhombic-*F* R_I phase. A simple explanation for this is that in the R_{II} *ABAB* and *ABC* phases, the molecules are aligned with interstitial sites of the hexagonal lattice in adjacent layers, allowing slight interpenetration of the longer chains into the adjoining layers as must occur when chain lengths were randomly mixed. However, in the R_I phase the stacking places adjacent layers over nearest-neighbor bonds, making interpenetration less favorable [11]. Typically a depressed transition temperature can be associated with *local fluctuations of the lower-temperature order parameter in the higher-temperature phase.* As the temperature is decreased through the expanded range of the R_{II} phase, the local orthorhombic distortions grow. But, since the distortion fluctuations are oriented in all three equivalent directions with equal probability, the lattice maintains its *macroscopic* hexagonal symmetry, as probed by x-ray scattering. The effect of the fluctuations, in addition to a slight

contraction of the average lattice, would be a reduction or destruction of the long-range positional order. One might suspect that such contractions may not destroy bond-orientational order, leading to a possibility that a hexatic phase may be produced [8]. The transition to R_I occurs when the fluctuations spontaneously break symmetry and orient along one of the three directions. From Fig. 1 it is apparent that the wider the R_{II} range, the larger the jump in lattice distortion at the onset of the R_I phase. The fluctuations may be driving this transition first order in a way similar to the ordering of N_2 on graphite [10]. We would not expect this effect to be observed in bulk solid-state systems because the strong interactions would prohibit randomly oriented distortion fluctuations, which could exist in "soft" condensed matter.

In summary, we have found a novel set of phenomena in the R_{II} rotator phase of binary mixtures of normal alkanes, including a smectic, possibly hexatic, phase occurring reversibly on cooling out of the hexagonal crystalline phase, likely due to the frustration of positional order by local fluctuations of the lower-temperature distorted phase. The nature of the transition between the ordered and disordered R_{II} phases is not yet established. In addition to the positional disordering, we have identified the existence of restacking transitions within the R_{II} rotator phase. Further studies involving DSC, neutron scattering, NMR, and optical microscopy are in progress to help better understand these phenomena.

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