Evidence of active chain diffusion in the rotator phase of n-alkanes: solid-state mixing of $C_{21}H_{44}$ and $C_{23}H_{48}$

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Solid-state diffusion of n-alkane molecules, tricosane $C_{23}H_{48}$, into the crystal of heneicosane $C_{21}H_{44}$, is detected by X-ray diffraction. It is found that the diffusion is temperature dependent and is greatly accelerated in the rotator phase.

(Keywords: n-alkanes; interchain diffusion; rotator phase)

Introduction

Long-chain polymers generally do not mix in the crystalline state. However, low molecular weight analogues of very similar carbon numbers, e.g. n-alkanes and n-alcohols, are known to form solid solutions when crystallized from the melt or a solution of the corresponding mixtures[1–5]. Even in such low molecular weight substances, the coefficients of self-diffusion in the crystals are very small[6–8], and therefore the possibility of molecular mixing through solid-state diffusion seems to have been forgotten or ignored. High mobility expected in the rotator phases will, however, enable chain diffusion, which leads to the formation of the mixed crystals.

The word 'mixture' is used to describe two quite distinct states of matter. The mechanical mixture is simply a mixture of powders, for example, of the component materials. Each powder particle is a crystallite of pure component; the system is completely phase separated. The molecular mixture or the solid solution, on the other hand, represents the molecularly mixed state.

In this communication, we report evidence of active chain diffusion in the rotator phase and the resulting formation of molecularly mixed crystals in a binary system of n-alkanes heneicosane (C_{21}) and tricosane (C_{23}). The molecular mixing in the crystal could be efficiently detected through X-ray diffraction by virtue of the well known characteristic properties of this system: (1) the molecular mixture shows a series of low-angle reflections from lamellae whose average thickness changes continuously with relative concentration[9]; and (2) the temperature region of the rotator phase markedly broadens by molecular mixing[2].

Diffusion and self-diffusion in the crystals are known to be very important processes in materials science, for example in precipitation hardening, sintering, etc. In polymer science, on the contrary, chain diffusion in crystals has attracted little attention. An understanding of the detailed mechanism of solid-state diffusion and mixing will suggest new possibilities to design polymer and oligomer alloys by mixing control.

Experimental

For odd-numbered alkanes C_nH_{2n+2} ($17 \leqslant n \leqslant 27$), two kinds of rotator phases have been observed besides the usual low-temperature orthorhombic phase (LO phase). The first is the rotator I (RI) phase with pseudo-hexagonal face-centred orthorhombic lattice; the second is the rotator II (RII) phase which has true hexagonal symmetry[10,11]. Heneicosane (C_{21}) has only the RI phase, while tricosane (C_{23}) has both the RI and the RII phases. We here investigated a binary system of n-alkanes, C_{21} and C_{23}; both alkanes were purchased from Tokyo Kasei Kogyo Co., Ltd. The phase behaviour of this binary system has already been well studied; the system forms stable solid solution in any relative concentration, and the temperature region of the rotator phase widens remarkably by molecular mixing (*Figure 1*)[1–3]. We prepared an initial sample at room temperature by mechanically mixing equal amounts of powder of both alkanes; the sample was a mechanical mixture of C_{21} and C_{23}, with weight ratio 50:50, both in the LO phase. Structural changes induced by molecular mixing, with temperature and time, were investigated by conventional

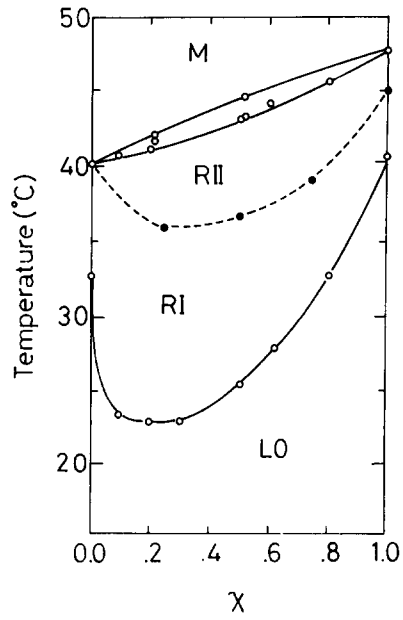

Figure 1 Phase map of the melt-crystallized binary mixtures of C_{21}–C_{23} as a function of relative concentration χ of C_{23}. Thermal data from refs 1–3 (○) for the transition from the LO phase to the RI phase and from the RII phase to the melt (M), are combined with our d.s.c. measurements (●) of the transition from the RI phase to the RII phase

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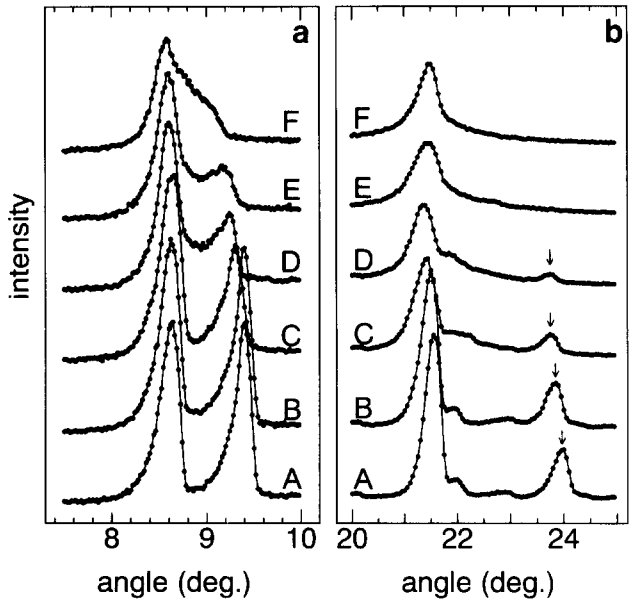

Figure 2 (a) The low-angle reflections 0 0 6 from the lamellar structure, and (b) the high-angle reflections 1 1 0 and 2 0 0 from subcell structures, where the usual polyethylene-type orthorhombic subcell is taken. Arrows in (b) indicate 2 0 0 reflection from the LO phase. The successive diffraction patterns are: A, at 16°C; B, after being held for 9 h at 29°C; C, at 37°C; D, after being held for 14 h at 37°C; E, at 39°C; F, after being held for 11 h at 39°C

X-ray powder diffractometry; small-angle reflections from the lamellar structure and wide-angle reflections from the subcell structure were studied. The sample was mounted on a heating device, the temperature of which was regulated within 0.05°C by a PID controller.

Results and discussion

The structural changes with temperature and time in the mechanically mixed powder of C_{21} and C_{23}, with weight ratio 50:50, were studied through the small-angle reflection 0 0 6 and the wide-angle subcell reflections 1 1 0 and 2 0 0 (*Figure 2*). The temperature of the sample was raised in a stepwise fashion (*Figure 2*): at 16°C (curve A) and 29°C (curve B) both pure alkanes are in the LO phase, although at 29°C the appropriate solid solution should have the RI form; at 37°C (curves C, D) the shorter alkane C_{21} is in the RI phase while the longer one C_{23} is still in the LO phase; 39°C (curves E, F) is at the higher end of the RI phase of C_{21}, while C_{23} is still in the LO phase but near the transition point to the RI phase.

The initial state (curve A) is a simple mechanical mixture of C_{21} and C_{23}, both in the LO phase; the separate peaks at small angles (*Figure 2a*) are 0 0 6 reflections from both pure alkanes, and each high-angle peak (*Figure 2b*) is a superposition of very close subcell reflections from both components. At 29°C, the diffraction patterns showed almost no change; this was true even after annealing for 9 h at that temperature (curve B); the sample remained phase separated, indicating a very slow rate of molecular diffusion.

The sample was then heated up to 37°C. The shorter alkane C_{21} transformed to the RI phase (curve C). The 0 0 6 reflection from C_{21} around $2\theta = 9.4°$ showed an appreciable intensity decrease and a slight shift to lower angle, as expected from rough lamellar surfaces and increased long spacing in the rotator phase[12] (*Figure 2a*). The broad subcell reflection $2\,0\,0_{RI}$ from the RI phase of C_{21} appeared around $2\theta = 22°$, and the intensity of the 2 0 0 reflection from the LO phase, $2\,0\,0_{LO}$, considerably decreased (*Figure 2b*). The $2\,0\,0_{LO}$ reflection around $2\theta = 24°$ is now an efficient indicator of the amount of the almost pure C_{23} component; remember that the mixed crystal as well as C_{21} at this temperature must be in the rotator phase. Annealing at this temperature for 14 h resulted in remarkable structural changes (curve D). The intensity of $2\,0\,0_{LO}$ reflection decreased appreciably. In addition, the small-angle reflection 0 0 6 from C_{21} greatly diminished and shifted to lower angle. These results evidently show that the molecules of C_{23} can easily diffuse into the rotator phase crystals of C_{21}, resulting in the formation of the mixed crystals. The long spacing, however, was not homogeneous; the lamellar structure is still considered very irregular.

By further heating up to 39°C, both reflections, $2\,0\,0_{LO}$ and $2\,0\,0_{RI}$, disappeared and a single peak from the RII phase, $1\,1\,0_{RII}$, remained (curve E). The intensity of the small-angle reflection from C_{21} decreased further. After 11 h of annealing at 39°C (curve F), the small-angle reflection from C_{21} was completely lost, and the two small-angle peaks were apparently fused into a broad, though very asymmetric peak. Molecular diffusion is very activate at this temperature.

That the molecular mixing really occurred in the heating and annealing process described above was further confirmed in the following way. The sample that went through the thermal process described above was cooled to room temperature and reheated, monitoring the transition to the rotator phases (*Figure 3*); the heating rate this time was much faster, with only 30 min at each temperature, thereby allowing no further chain diffusion during the experiment. The room-temperature structure was again the usual orthorhombic form (curve G). However, the sample showed the transition to the RI phase at a fairly low temperature of 27°C (curve H); the RI phase persists up to 37°C (curve J). The rotator transition at such a low temperature, and a marked widening of the temperature ranges of the rotator phase,

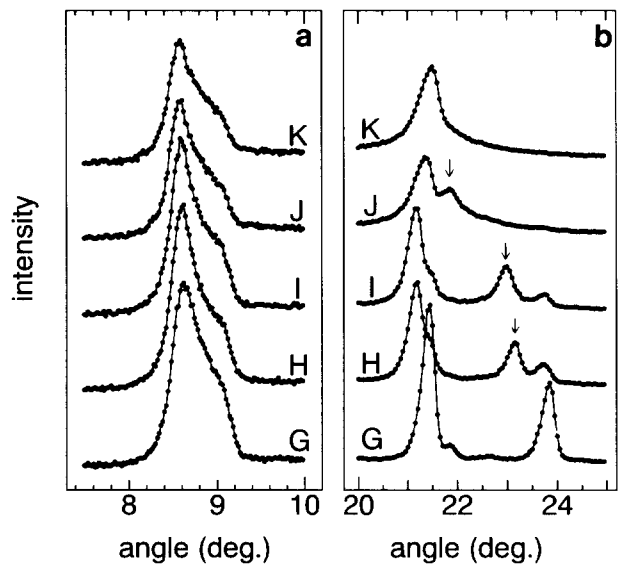

Figure 3 Changes in (a) the low-angle and (b) the high-angle diffraction patterns with increasing temperature for the mixture obtained after the heating and annealing procedures of *Figure 2*. Arrows in (b) show $2\,0\,0_{RI}$ reflection from the mixed crystals. The successive patterns are: G, at 15°C; H, at 27°C; I, at 29°C; J, at 37°C; K, at 39°C

are clear indications that molecular mixing of the two component alkanes really occurred in the previous heating and annealing process.

The 200_{RI} and 200_{LO} reflections co-existed for an appreciable temperature range, which shows that molecular mixing is not homogeneous throughout the system. It is readily seen that the 200_{RI} reflection shows remarkable shift to lower angles with increasing temperature (curves H–J). This corresponds to the known characteristic of the RI phase. The RI phase is known to show fairly large thermal expansion in the *a*-axis direction; this thermal expansion becomes more marked in the mixture owing to the wide temperature range of the RI phase[3]. During the heating process, the lamellar structure showed no significant changes (*Figure 3a*).

The molecular mixing of the chains in a timescale of 10 h was thus clearly evidenced in the rotator phases; the rotator phase crystallite of the mixture grows by taking longer chain alkanes into the lamella. The obtained lamellar structure was, however, very inhomogeneous, and its structure is not clear. The characterization of the lamellar structure, the dependence of the mixing rate on temperature, and the detailed process of mixing in single crystals, will be the subjects of future studies. Theoretical calculations by use of rigorous computer simulation methods, which have previously been applied to alkane systems[13,14], are also very promising.

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