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In situ optical observation of long-range diffusion in an n-alkane crystal

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The interdiffusion of n-alkane molecules in the crystal state is investigated in the binary system of $C_{21}H_{44}$ and $C_{23}H_{48}$. A mechanical junction between a single crystal of C_{23} and polycrystalline C_{21} is held at a temperature just above the transition to the rotator phase in C_{21}, and optical changes along the junction surface are studied *in situ*. Direct observation of the interdiffusion process is enabled by virtue of the fact that the interfacial region at the junction makes a mixing-induced transition to the rotator phase, which shows marked differences in optical properties from the surrounding low-temperature phase. Two ways of forming the mechanical junction are tested: the crystal of C_{21} is placed either on the side surface of the C_{23} single crystal (lateral junction) or on the upper surface of the C_{23} single crystal (upper junction). Both transverse chain diffusion within the lamella and longitudinal diffusion along the chain axis are studied separately. The mixed region and the low-temperature phase matrix are found to have a rather sharp boundary (diffusion front), and the interdiffusion rate is estimated quantitatively from the advance of the diffusion front. The transverse diffusion front at the lateral junction is found to advance by a distance that is proportional to the square root of time, which is clearly diffusion-controlled behaviour. The estimated diffusion constant shows fairly good correspondence with the self-diffusion coefficient determined by a tracer method. In the case of the upper junction, the molecules show longitudinal diffusion into deep layers followed by transverse diffusion therefrom. The transverse diffusion front is nearly circular; diffusion is considered to be nearly isotropic within the **a**–**b** plane. The transverse diffusion in this case is severely restricted by the matrix.

(Keywords: n-alkane crystals; interdiffusion; optical microscopy)

INTRODUCTION

The diffusion of atoms or molecules in a crystal is a very important process in modern solid-state technology: the diffusion of doped impurities in semiconductors, the interdiffusion of atoms in metallic alloys, etc. Various functions of biological membranes also depend largely on the diffusion of the constituent lipid molecules in its phase separation and mixing.

Polymer molecules do not usually mix in the crystalline state; molecular mixing is only observed in amorphous phases. On the other hand, relatively short hydrocarbons (n-alkanes, n-alcohols, etc.) of similar chain lengths make solid solutions when crystallized from the melt or from solution. Various investigations have been accumulated on the structures and the phase behaviours of these solid solutions[1–7]. However, the diffusion and interdiffusion of chain molecules in crystals have been neglected or have attracted scarce attention despite their great importance in polymer science.

More than 10 years ago, pioneering investigations were done on the long-range interdiffusion of n-alkane molecules in crystals[8,9]. The significance of these works was not fully recognized, and no further work followed except for a very recent i.r. study by Snyder *et al.* from a slightly different point of view[10].

Recently we investigated, by use of X-ray powder diffraction, solid-state interdiffusion and mixing in the binary system of heneicosane ($C_{21}H_{44}$) and tricosane ($C_{23}H_{38}$) (*Figure 1*). By a combination of low-angle reflections from the lamella structure and high-angle reflections from the subcell structure, we have shown that (1) interdiffusion is quite active in the temperature range where the shorter alkane C_{21} is in the rotator phase, (2) the molecules of the longer alkane C_{23} easily diffuse into the rotator phase crystal of C_{21}, while the shorter alkane molecules also migrate into the C_{23} crystal, which is still in the ordered phase, and (3) the lamella structure of shorter alkane C_{21} is greatly disturbed by the migration of the longer one C_{23}, while the lamella structure of C_{23} remains nearly intact[11]. Similar observations were also made on the binary system of n-alcohols, $C_{17}H_{35}OH$ and $C_{19}H_{39}OH$[12].

The details of the interdiffusion process (for example, the rate of diffusion, its dependence on the crystallographic direction, the molecular mechanism of interdiffusion, etc.) are still quite obscure. Here we present our direct *in situ* observation of the diffusion of C_{21} molecules into a crystal of C_{23} by optical microscopy. By choosing a proper diffusion couple and by use of a single crystal, we found that the *in situ* optical observation of the interdiffusion process is possible. The molecular diffusion 'front'—the boundary between the molecularly mixed region and the matrix crystal of C_{23}—is found to

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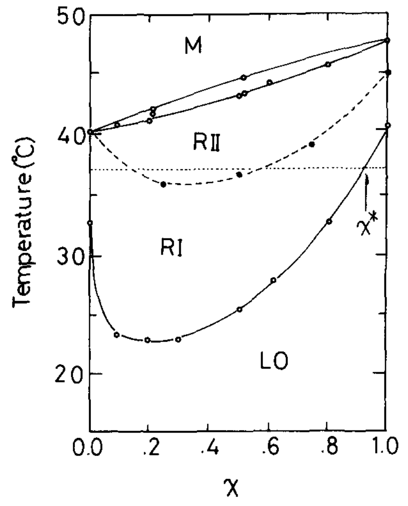

Figure 1 Phase diagram of the melt-crystallized binary mixture of C_{21}–C_{23} as a function of relative concentration χ of C_{23}. Thermal data for the transitions from the low-temperature orthorhombic (LO) phase to the rotator-I (RI) phase and from the rotator-II (RII) phase to the melt (M) are combined with our d.s.c. measurement of the transition from the RI phase to the RII phase (ref. 5). χ^* represents an upper critical concentration of C_{23} in the RI phase at 37°C

be clearly observed. It will be shown that molecules of C_{21} can diffuse macroscopically into a single crystal of C_{23}, in both the lateral direction and the chain-axis direction, within a rather short timescale.

EXPERIMENTAL

A single crystal of C_{23}, though very thin (of 0.02–0.03 mm thickness), was obtained by slow evaporation of *p*-xylene at room temperature; it was a sufficiently good single crystal showing uniform extinction in cross-polarized light, but the crystal has round side surfaces and showed no specific lateral habit. A single crystal of C_{21} was on the other hand, very difficult to prepare, and so we used a polycrystalline sample. A mechanical junction between the single-crystalline C_{23} and the polycrystalline C_{21} was prepared either by placing both crystals side by side (hereafter called 'lateral junction') or by placing the C_{21} on the upper surface of the C_{23} crystal ('upper junction'). Molecular diffusion near the contact surfaces was studied by optical microscopy.

The *in situ* optical observation of the molecular mixing process in a crystal would be possible if the binary system had the following characteristics: (1) the structures of both components are similar and the molecules are sufficiently mobile to ensure easy mixing in the crystal, (2) molecular mixing results in a crystalline transformation to a new phase that has different optical properties, and (3) a single crystal is available to enable optimum alignment for the detection of the crystalline phase transformation.

The binary system of n-alkanes C_{21}–C_{23} fulfils all these requirements. Our previous investigation showed that the molecules undergo macroscopic interdiffusion within several hours when C_{21} is in the rotator phase. Molecular mixing results in the rotator phase transformation in C_{23}, which phase has high optical isotropy around the chain axis; the crystals of C_{21} and C_{23} have the chain axis perpendicular to the basal plane and are suited to optical observation along the chain axis[11,13,14]. The rotator phase transition in C_{23}, induced by molecular mixing with C_{21}, will result in high optical isotropization around the chain axis, giving rise to dark regions in cross-polarized light (*Figure 2*).

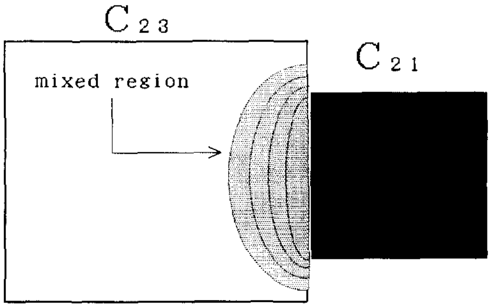

Figure 2 Schematic picture of the diffusion couple: single-crystalline C_{23} and polycrystalline C_{21}. We can easily detect the molecular diffusion of C_{21} into the single-crystalline region of C_{23} through the darkening due to the mixing-induced transition to the rotator phase

The crystals of C_{21} and C_{23} in contact were placed on a hot stage, the temperature of which was raised by an electric resistance furnace under a PID control; the temperature fluctuation was less than 0.1°C. The optical image was stored in a video tape through a CCD camera (Tokyo Electronic Industry Co. Ltd).

RESULTS

The low-temperature phase (LO) of C_{23} has the orthorhombic form. A slight difference in the refractive indices in the crystallographic **a** and **b** axis directions results in weak birefringence. Though our single crystal of C_{23} is very thin, it is sufficiently bright against the dark background in cross-polarized light. When the orthorhombic crystal transforms to the hexagonal or the pseudohexagonal rotator phase, the optical anisotropy around the chain axis is greatly diminished and shows marked darkening. The transformation induced by molecular mixing is therefore expected to be easily detected.

Here we consider two modes of interdiffusion separately. One is transverse diffusion, where chains neighbouring side by side exchange their positions. The other is longitudinal diffusion, in which chains in different layers interchange (*Figure 3*). Two ways of forming a mechanical junction, the lateral junction and

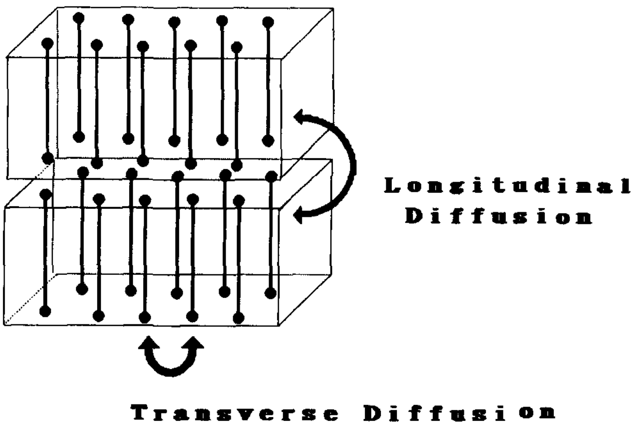

Figure 3 Two modes of interdiffusion, transverse and longitudinal, in an n-alkane crystal

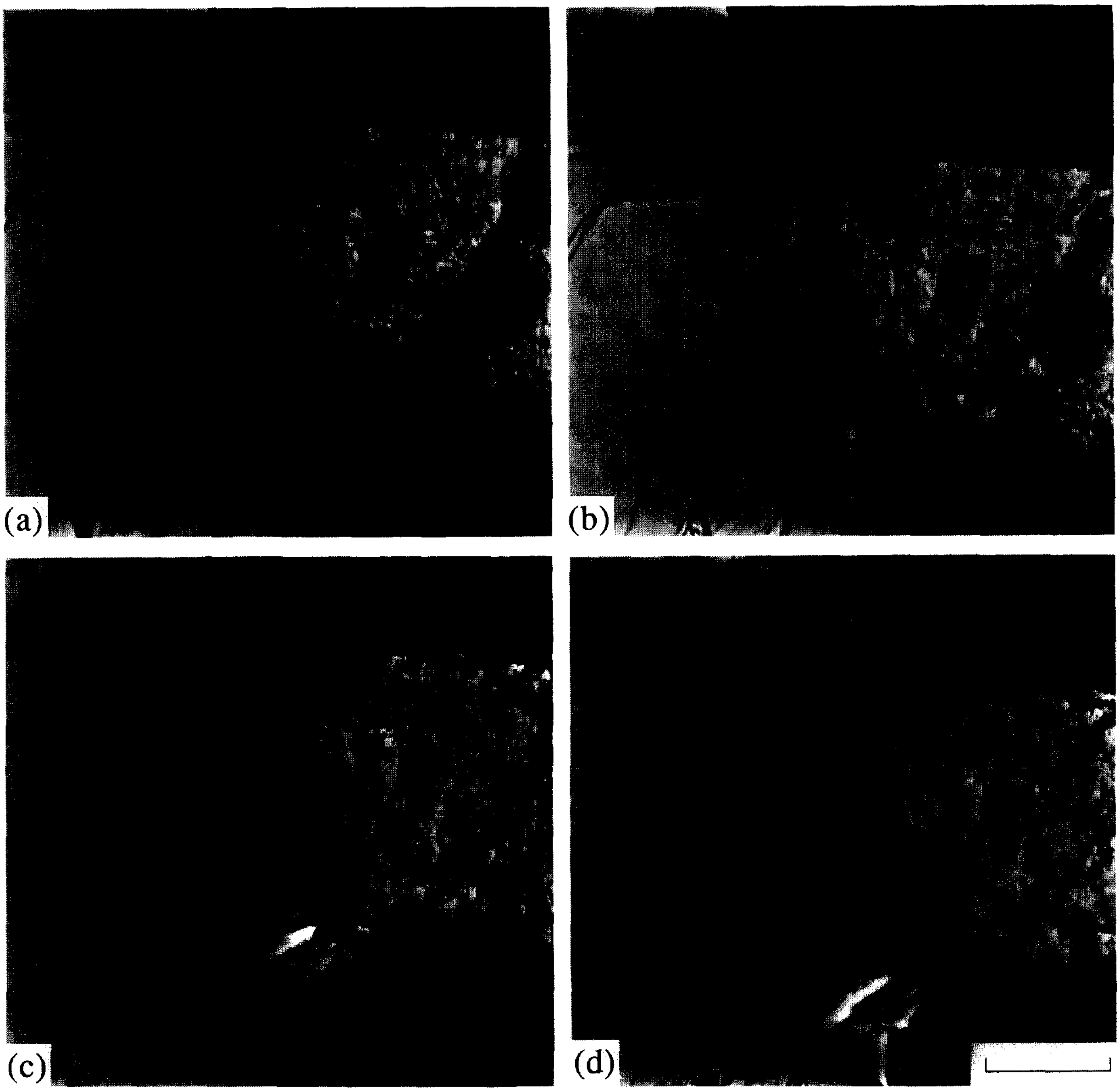

Figure 4 A series of optical images, at 37°C, during the molecular diffusion of C_{21} from the side surface of the C_{23} single crystal: (a) at 0 h, (b) at 5.5 h, (c) at 22 h and (d) at 42 h. The dark area around the junction is the mixed region. The scale bar at the lower right is 0.2 mm

upper junction, were accordingly tested. Below 33°C, where C_{21} is still in the low-temperature orthorhombic phase (LO) (*Figure 1*), we could not detect any change at the boundary. This is in agreement with our previous X-ray work[11]. Above the rotator transition temperature in C_{21}, the boundary between the two crystals demonstrated clear onset of molecular diffusion.

Transverse diffusion

The polycrystalline C_{21} was attached to the side surface of the C_{23} single crystal. The temperature was held at 37°C in the RI phase region of C_{21}. *Figure 4* shows the changes in the optical image. Within an hour a dark area appears in the single crystal along the surface of the junction; the surface region of C_{23} is considered to have transformed to the rotator phase by molecular mixing with C_{21}. The dark rotator phase region continuously grows with time; in 10 h the width of the mixed region grows several tens of micrometres, which is in qualitative agreement with our previous experiment[11].

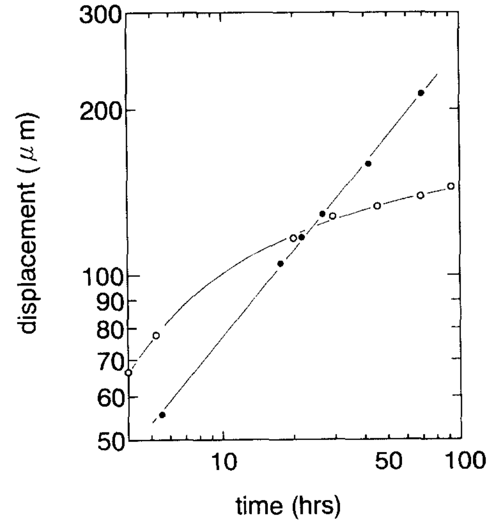

Figure 5 The advance of the transverse diffusion front versus time. In the case of the lateral junction (●) the log–log plot shows a straight line with a slope approximately 0.5, while in the case of the upper junction (○) the plot has an initial slope of 0.5 but it soon slows down above around 10 h

The chain axis in the mixed region remains perpendicular to the basal plane; this is the necessary condition for the mixing process to be optically observable, since the optical isotropy around the surface normal would be destroyed if the perpendicular chain axis were not preserved. The molecules of C_{21} can diffuse into the C_{23} crystal without seriously destroying the perfection of the single crystal.

The diffusion 'front' observed is considered to be a boundary where the concentration of C_{21} is just the critical concentration ρ^*, $\rho^* = 1 - \chi^*$, at 37°C (*Figure 1*). It should be noted that the front is rather sharp and is insensitive to small temperature changes. This indicates that there is a large concentration gap across the front, as will be discussed later (see *Figure 8*).

We examined quantitatively the advance of the diffusion front, the boundary surface between the low-temperature phase and the diffusion-induced rotator phase. The displacement of the front is plotted *versus* time in *Figure 5* (full circles). The log–log plot shows a straight line with a slope of approximately 0.5. This shows that the displacement Δl is proportional to the square root of time, and that the advance of the front is diffusion-controlled. Formal estimation of the diffusion coefficient D, with $(\Delta l)^2 = 4Dt$, gives $D = 2.8 \times 10^{-14}\,\mathrm{m^2\,s^{-1}}$. The value of D thus estimated shows unexpectedly good correspondence with the self-diffusion coefficient determined by the tracer method[15]: $D = 1.95 \times 10^{-14}\,\mathrm{m^2\,s^{-1}}$ at 36°C. The meaning of such good correspondence is now uncertain, but it may offer important information about the mechanism of interdiffusion.

When the temperature is lowered, the darkness in the mixed region gradually decreases owing to a phase transformation back to the low-temperature phase; local dark areas having the twin relation to the matrix often remain. The diffusion front, however, remains stationary, which shows that the mixing process is evidently irreversible.

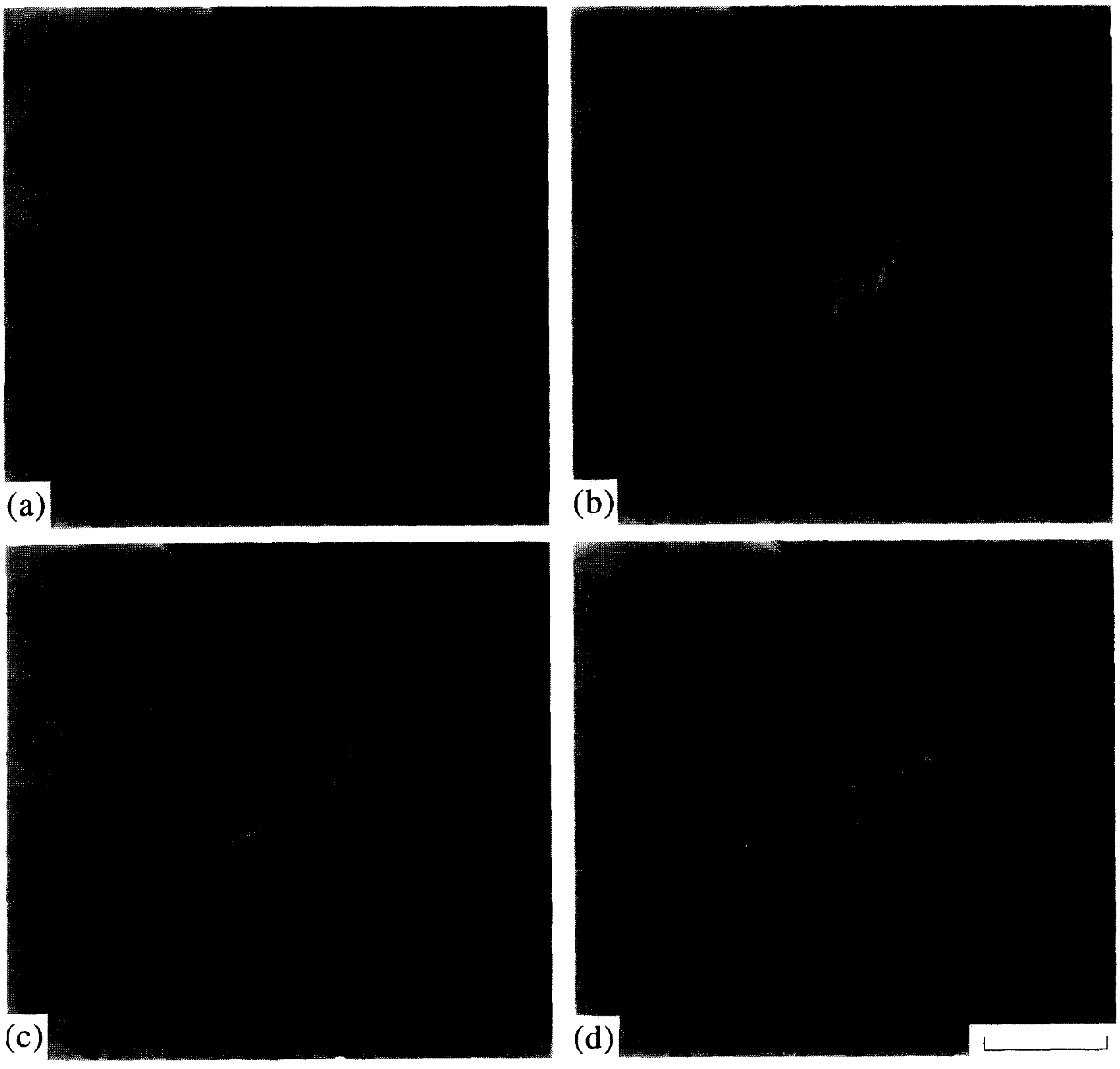

Figure 6 A series of optical images, at 37°C, during the molecular diffusion of C_{21} from the upper surface of the C_{23} single crystal: (a) at 0 h, (b) at 4 h, (c) at 20 h and (d) at 45.5 h. The scale bar at the lower right is 0.2 mm

Longitudinal diffusion

The polycrystalline C_{21} was placed on the upper surface of the C_{23} single crystal; the molecules of C_{21} will migrate into deep layers of the single crystal and will form a solid solution of both alkanes. The molecules of C_{21} that diffuse into deep layers will also diffuse further in transverse directions. Though the optical changes under the C_{21} crystal cannot be observed directly, we can study the subsequent transverse diffusion in layers of various depths.

Figure 6 shows a series of images of the diffusion process observed for the upper junction. The diffusion front is again rather sharp. The dark mixed region is nearly circular in shape; the rate of chain diffusion in the transverse direction is found to be nearly isotropic in the **a**–**b** plane, with no specific directions of easy diffusion.

The front of the transverse diffusion is most advanced in the uppermost layer, and it is plotted versus time in *Figure 5* (open circles). The initial slope is again nearly 0.5; the early stage of mixing is simple diffusion. But this time, the advance of the front soon slows down in about 10 h. The mixed region is in the rotator phase, and has a higher specific volume. The region is now fully surrounded by the low-temperature phase crystal with smaller specific volume. The mixed region will therefore be under a severe volumetric constraint. Such a constraint will restrict the further phase transition and will effectively hinder chain diffusion, leading to a marked slowdown in the mixing rate.

Another characteristic observed in the upper junction is the clear terraced structure of the front (*Figure 7*); the uppermost terrace is the most advanced one. The different front positions for layers at different depths from the upper surface are quite reasonable when we consider the delay in the onset of transverse diffusion at deeper layers. The reason why a terrace is formed, instead of a broad front, is however very difficult to understand at present.

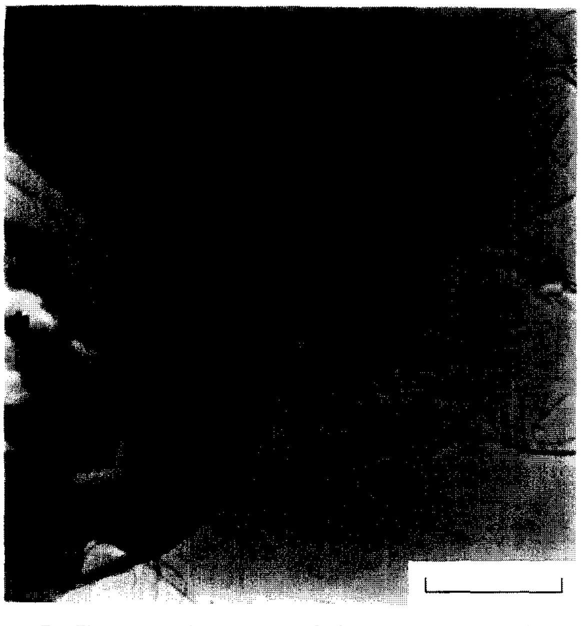

Figure 7 The terraced structure of the transverse diffusion front observed in the case of the upper junction. The scale bar at the lower right is 0.1 mm

Though the longitudinal diffusion rate cannot be estimated quantitatively, the presence of longitudinal diffusion is now evident. The longitudinal diffusion rate is probably comparable to or less than the transverse diffusion rate, since the width of the terraced front is of the same order of magnitude as the thickness of the single crystal.

DISCUSSION

The transverse diffusion from the side surface seems to follow a simple diffusion equation. However, the diffusion front we observed is the front of the phase transition induced by molecular mixing. As shown in *Figure 1*, the transition to the rotator phase occurs when the concentration of C_{21} reaches a critical value ρ^* at that temperature. If the concentration of the C_{21} molecules in the matrix is a gradually decreasing function of the distance from the junction, the temperature change will result in a sensitive shift of the boundary owing to the change in ρ^* (*Figure 1*). In reality, the boundary position is rather insensitive to the temperature change, and therefore the density profile around the boundary must be fairly sharp as given in *Figure 8*. Within the mixed region, there will be some concentration gradient that drives the C_{21} molecules to the front. However, the diffusion of the C_{21} molecules in the rotator phase would be much faster than the diffusion into the LO phase of C_{23}. Therefore, the gradient in the mixed region will be smaller (*Figure 8*).

When the C_{21} molecules diffuse into the ordered low-temperature phase, the mixed regions make a transition to the rotator phase with large specific volume. Therefore, there would be considerable lattice strain around the mixed region, which will serve to suppress further diffusion of the molecules. Such a constraint effect is most conspicuous when the mixed region is fully surrounded by the low-temperature phase (*Figure 6*). It is reasonable to consider that the constraint would also be effective in transverse diffusion from the side surface (*Figure 4*).

The transverse diffusion front in *Figure 6* is circular, which shows that diffusion in the **a**–**b** plane is nearly

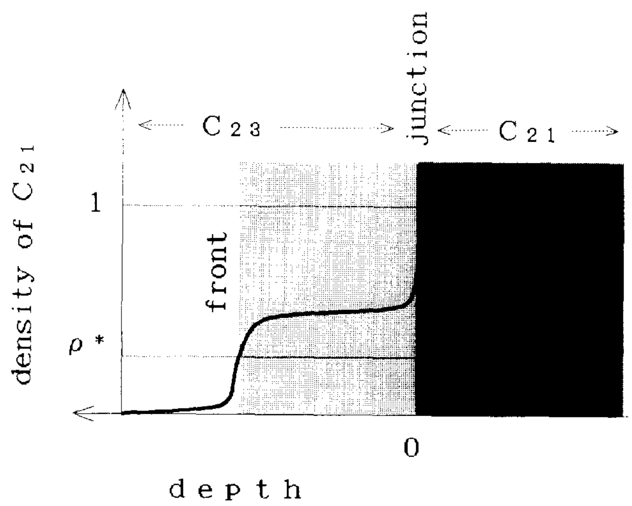

Figure 8 A schematic profile of the relative concentration of C_{21} in the C_{23} crystal. The profile is depicted versus depth inwards from the junction

isotropic. Dark terraces were observed around the diffusion front in *Figure 7*, and therefore transverse diffusion and longitudinal diffusion are considered to be quite different in nature. The details of the molecular interdiffusion mechanism, the temperature dependence of the diffusion rate, the effect of lattice strain, etc., are the subjects of future investigations.

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REFERENCES

1 Bonsor, D. H. and Bloor, D. *J. Mater. Sci.* 1977, **12,** 1559
2 Asbach, G. I., Kilian, H. G. and Stracke, Fr. *Colloid Polym. Sci.* 1982, **260,** 151
3 Denicolo, I., Craievich, A. F. and Doucet, J. *J. Chem. Phys.* 1984, **80,** 6200
4 Ungar, G. and Masic, N. *J. Phys. Chem.* 1985, **89,** 1036
5 Yamamoto, T., Nozaki, K. and Hara, T. *J. Chem. Phys.* 1990, **92,** 631
6 Dorset, D. *Macromolecules* 1990, **23,** 623
7 Nakafuku, C. and Sugiuchi, T. 1993, **34,** 4945
8 Ungar, G. and Keller, A. *Colloid Polym. Sci.* 1979, **257,** 90
9 Zerbi, G., Piazza R. and Holland-Moritz, K. *Polymer* 1982, **23,** 1921
10 Snyder, R. G., Conti, G., Strauss, H. L. and Dorset, D. L. *J. Phys. Chem.* 1993, **97,** 7342
11 Yamamoto, T. and Nozaki, K. *Polymer* 1994, **35,** 3340
12 Yamamoto, T. unpublished
13 Doucet, J., Denicolo, I., Craievich, A. and Collet, A. *J. Chem. Phys.* 1981, **75,** 5125
14 Ungar, G. *J. Phys. Chem.* 1983, **87,** 689
15 Narang, R. S. and Sherwood, J. N. *Mol. Cryst. Liq. Cryst.* 1980, **59,** 167