

In situ optical observation of the chain diffusion in an *n*-alkane crystal: temperature dependence of the chain diffusivity

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The interdiffusion process of *n*-alkane molecules in the crystal and the temperature dependence of the diffusivity are investigated *in situ* by optical microscopy. The optical observation of the molecular interdiffusion is possible owing to the mixing-induced solid state transition to the rotator phase; the molecularly mixed region and the low-temperature phase matrix form a sharp interphase boundary which is visible under the polarized microscope. We make a diffusion couple by a mechanical junction of single-crystalline C₂₃H₄₈ and polycrystalline C₂₁H₄₄. The chain diffusivity at each temperature is determined from the advance of the interphase boundary. The diffusivity, measured at various temperatures from 31 to 39°C, shows a marked temperature dependence; the interdiffusion is rather active above 33°C but it becomes remarkably inactive below 33°C. An apparent activation energy for the interdiffusion above 33°C is estimated to be about 300 kJ mol⁻¹. The mechanism of the interphase-boundary motion is discussed on the basis of the formulation devised for the moving boundary problem (the Stefan problem). © 1997 Elsevier Science Ltd.

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INTRODUCTION

Diffusion is a long-range migration of atoms or molecules in space. It is of great significance in polymer science as well as in the science of low molecular mass materials. Polymer diffusion plays an important role in deformation, annealing, phase separation, crystallization, etc. Numerous investigations have been made using various experimental^{1,2}, theoretical³ and computational methods^{4,5}.

Investigations of polymer diffusion have hitherto been exclusively on polymer solutions, melts or other loosely aggregated states such as gels. Polymer diffusion in crystals is very slow and hard to study experimentally⁶. The inhomogeneous two-phase structure of crystalline polymers makes interpretation of experimental results even more difficult.

Relatively short *n*-alkanes, on the other hand, are known to show long-range diffusion in crystals^{7–11}, both along the chain axis and perpendicular to it. The molecular diffusion process of such anisotropic molecules is expected to have very interesting features, and it also gives insight into the molecular motion in polymer crystals^{12–14}. Furthermore, molecular diffusion in the crystalline state also has a close connection with molecular diffusion in thin membranes¹⁵. For detailed investigation of the chain diffusion in a crystal, we need a perfect single crystal since molecular diffusion is very sensitive to crystalline defects. Unfortunately, the preparation of a high-quality single crystal that can be used for macroscopic diffusion measurements such as the tracer experiment is very difficult; only very small and thin crystallites are available.

In our previous study, we examined the interface of the diffusion couple of the *n*-alkanes heneicosane (C₂₁) and tricosane (C₂₃) by optical microscopy. We found it possible to observe *in situ* the interdiffusion of C₂₁ molecules into a single crystal of C₂₃ taking advantage of the solid state transition to the rotator phase induced by the molecular mixing of C₂₁ and C₂₃¹⁶; we could observe the movement of the boundary between the mixing-induced rotator phase and the matrix low-temperature phase. We also found that the boundary moves a distance which is proportional to the square root of time; it was clearly indicated that the boundary movement is a diffusion-controlled process.

In this paper we study the interdiffusion at various temperatures by our *in situ* optical observation method. We also discuss the detailed mechanism underlying the method.

PRINCIPLE AND METHOD OF MEASUREMENTS

A binary system of *n*-alkanes of similar chain length has the pronounced feature that the mixed crystals exhibit transition to the rotator phase at remarkably low temperatures (Figure 1)^{17,18}. This feature, if a single crystal is available, enables high-resolution monitoring of the molecular mixing process *in situ* by the optical microscope. Figure 2 shows the basic principle of our method. We consider a mechanical junction of two alkanes C₂₁ and C₂₃. If the molecular interdiffusion occurs at a suitable temperature, the mixed region at the junction should transform to the rotator phase. The rotator phase has high optical isotropy around the

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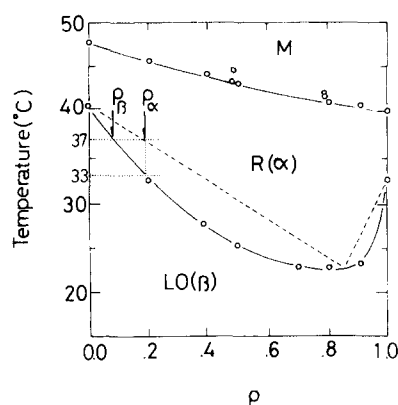


Figure 1 Phase diagram of the binary system C_{21} - C_{23} as a function of ρ , the relative concentration of C_{21} ^{17,18}. The system consists of the rotator phase R (also denoted the α phase), the low-temperature orthorhombic phase LO (also denoted the β phase), and the melt M. The α phase line of the coexisting α and β phases, which is depicted by a dashed line, is only a schematic line and not a measured one. The equilibrium concentration of C_{21} for the coexisting phases at 37°C are denoted by ρ_α and ρ_β .

molecular axis. The transition can therefore be easily detected, if a good single crystal is available, by the darkening under cross-polarized light (*Figure 2a*). The dark rotator phase region is considered to have a relative concentration of C_{21} higher than a critical ρ_α at that temperature (*Figure 1*).

The mechanical junction we have made here consists of polycrystalline C_{21} and single-crystalline C_{23} , both of approximately the same thickness 0.02 mm. We made a lateral junction by placing the C_{21} sample at the side surface of the C_{23} single crystal; we considered the transverse diffusion of the molecules perpendicular to the molecular axis¹⁶. To assure good contact, the diffusion couple was held at 37°C, the temperature at which C_{21} is in the rotator phase. After the intermixing at the junction

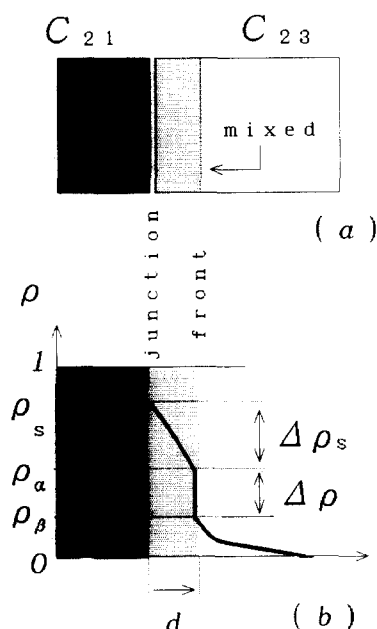


Figure 2 (a) Schematic illustration of the diffusion couple of single-crystalline C_{23} and polycrystalline C_{21} . The molecular intermixing at the junction is easily detected through the darkening due to the mixing-induced transition to the rotator phase. (b) The possible relative concentration of C_{21} around the junction. The concentration gap $\Delta\rho = \rho_\alpha - \rho_\beta$ is expected at the boundary

surface was confirmed, the diffusion couple was heated/cooled to each temperature at which the diffusion rate was to be measured. The movement of the diffusion front was monitored by a CCD camera and stored on a video tape. The temperature was controlled by a PID controller within 0.1°C.

RESULTS

Optical changes at the junction

Figure 3 shows typical changes observed at the junction. Within a few hours a dark interfacial region appears. The dark region grows continuously, which is clear evidence of the diffusion of C_{21} molecules into the single crystal of C_{23} . The boundary between the dark rotator phase region and the bright low-temperature phase region is rather sharp, which indicates that the transverse diffusion proceeds at an equal rate at any depth from the upper surface of the crystal; this is in contrast to the terraced diffusion observed in the upper surface junction¹⁶. As described in our previous paper¹⁶, the relative concentration of C_{21} , ρ , is considered to show a steep change at the boundary between the α phase and the β phase (*Figure 2b*); we will henceforth call the boundary the diffusion front. In addition to the molecular diffusion into the inner crystalline region, we can readily observe the diffusion along the outer side-surface of the single crystal; the dark region grows fairly rapidly, showing the presence of a fast diffusion path along the crystal surface. We can also notice a considerable outward shift of the junction surface (*Figure 3d*), which is reminiscent of the Kirkendall effect in metals¹⁹ and suggests that the diffusion of C_{21} is faster than that of C_{23} .

Motion of the diffusion front

The diffusion of molecules is a thermally activated process that should depend very sensitively upon temperature. In order to examine the temperature dependence of the chain diffusivity, the movement of the diffusion front was studied at various temperatures. The lateral junction formed at 37°C was cooled or heated to each temperature, and the optical changes followed were monitored. Since C_{21} is in the melt state above 39°C and the interdiffusion rate becomes extremely slow below 31°C, the measurement was possible only between 39 and 31°C. The temperature interval was thus very limited.

In our previous work¹⁶, the movement of the front was found to be a simple diffusion process, where the square displacement d^2 is proportional to time t . In the present experiment, the initial junction formation at 37°C and the subsequent temperature adjustment result in an inevitable uncertainty of the time $t = 0$. In *Figure 4*, where d^2 is plotted against t , the time $t = 0$ is chosen so that each curve passes the origin. It is clearly shown that, at each temperature, d^2 is proportional to t ; the movement of the front is evidently governed by the molecular diffusion process. The chain diffusivity, the rate of the movement of the front, shows a great change with temperature. The chain diffusion is much faster at higher temperatures than at lower temperatures; it becomes extremely slow at temperatures lower than 33°C.

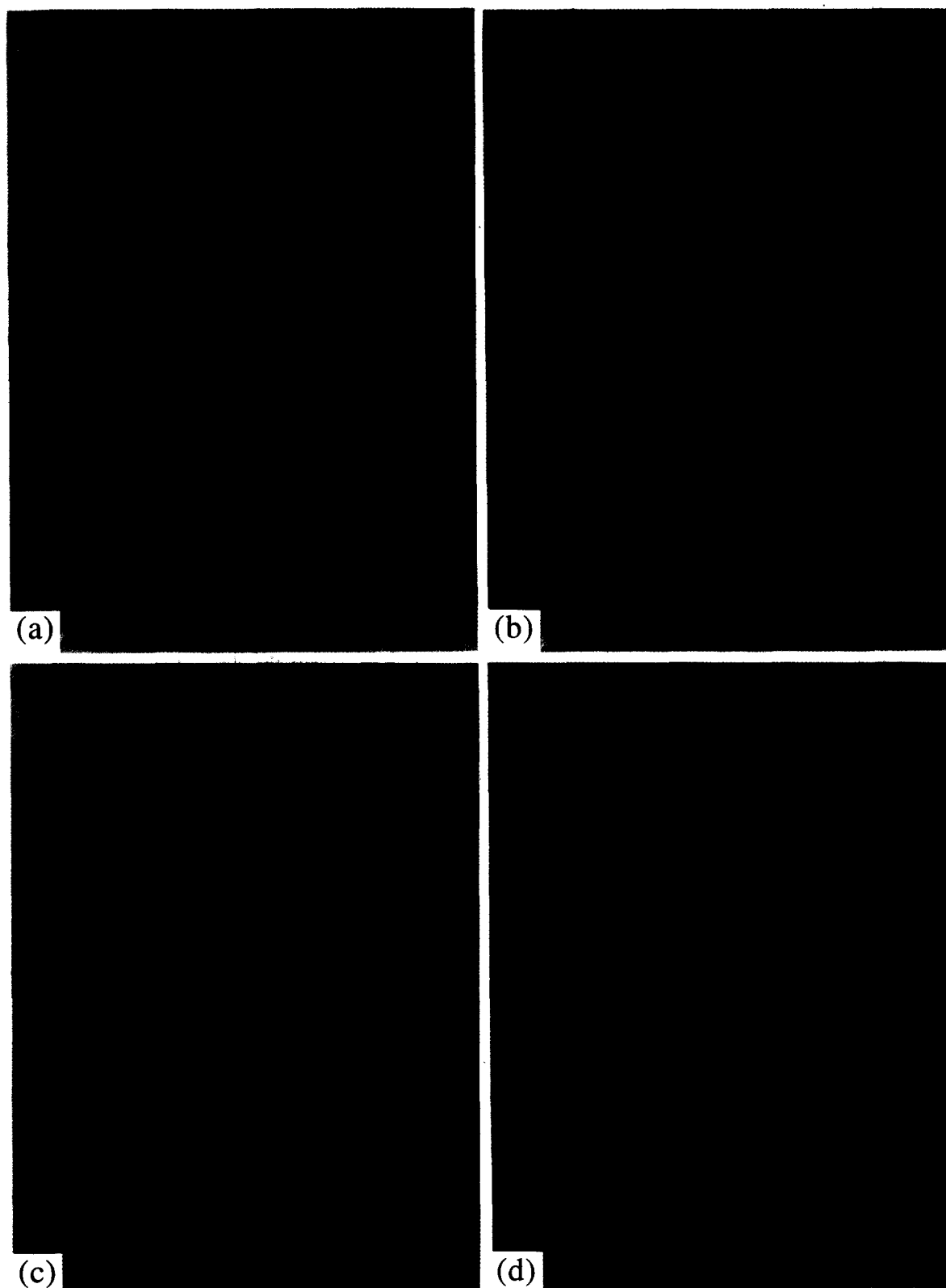


Figure 3 A series of optical images, under cross-polarized light, at 36°C during the molecular diffusion of C₂₁ (the upper rectangular-shaped sample) from the side surface of the C₂₃ single crystal (the lower half of the photograph): (a) at 0 h, (b) at 10.5 h, (c) at 24.5 h and (d) at 48 h. The dark area around the junction is the mixed region. The scale bar at the lower right represents 0.2 mm

Temperature dependence of the diffusivity

As shown in Figure 4, d^2 increases fairly linearly with time. From the slope of the curves, we can estimate the diffusivity by $D = d^2/4t$. The diffusivity D is expected to follow the Arrhenius-type temperature dependence, $D = D_0 \exp(-\Delta H/kT)$, where ΔH is the activation

enthalpy for the diffusion. Therefore, we plotted $\log(D)$ versus $1/T$ in Figure 5. At higher temperatures, $33^\circ\text{C} < T < 39^\circ\text{C}$, the change in $\log(D)$ with $1/T$ is nearly linear. Below 33°C , however, $\log(D)$ shows a remarkable drop. From the linear portion of the curve at higher temperatures, the activation enthalpy ΔH was

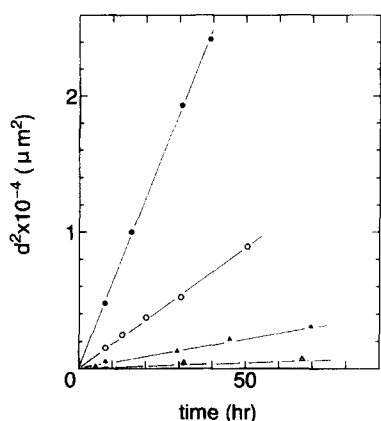


Figure 4 Squared advance d^2 of the transverse diffusion front versus time: ●, at 39°C; ○, at 35°C; ▲, at 33°C; △, at 32°C

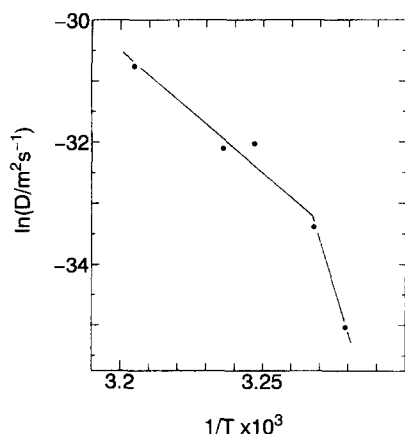


Figure 5 The diffusivity D , estimated from the slope of the curve in Figure 4 by $D = d^2/4t$, plotted against $1/T$

estimated to be about 300 kJ mol^{-1} . This is of the same order of magnitude as those previously reported for self-diffusion in the β phase; the tracer method yielded $\Delta H = 198 \text{ kJ mol}^{-1}$ ⁷, though the measurement was suspected of being seriously affected by many crystal defects, whereas the computational study estimated the value of $\Delta H = 200 \text{ kJ mol}^{-1}$ ¹³. The diffusion we consider here is not a self (tracer) diffusion but an interdiffusion of two molecules with different chain lengths under a steep density gradient. Furthermore, the present measurement is for the chain diffusion in a single crystal of C_{23} , which has fewer crystalline defects than that used in the previous tracer experiment.

DISCUSSION

The Stefan problem of chain diffusion

The molecular diffusion in the crystal was directly observed by optical microscopy taking advantage of the mixing-induced solid state transition to the rotator phase. The movement of the diffusion front showed the characteristic time dependence $d^2 \propto t$, which is clear evidence that the front movement is a diffusion-controlled process. The diffusion in a two-phase system with moving interphase boundary has been well investigated by theories of atomic diffusion and crystal growth. Figure 2b shows our model, consisting of the α phase (the rotator phase) and the β phase (LO phase) regions,

where the two phases have the interdiffusion coefficients D_α and D_β , respectively. The diffusion-controlled advance of the front implies that the molecular process at the interphase boundary is sufficiently fast and that the local equilibrium is attained at the boundary. The concentration at the boundary should therefore show a gap $\Delta\rho$ as depicted in Figures 1 and 2. In general, the diffusion coefficient, such as D_α and D_β , is considered to depend on the concentration ρ . However, we neglect here such unknown complicated factors. Then the problem can be deemed to be the well-known Stefan problem^{19,20}; the advance of the interphase boundary is governed by the difference between the flow into the boundary from the α phase (left side of the front in Figure 2b) and the flow out of the boundary to the β phase (right side of the front). If we assume $D_\alpha \gg D_\beta$, it can be shown that the advance of the boundary, i.e. the diffusivity D , is dominated by the molecular flow-in from the α phase,

$$D = \gamma^2 D_\alpha \quad (1)$$

The coefficient γ , which has a value of the order of 1, is determined by the solution of the flowing equation,

$$\exp(-\gamma^2)/[\gamma \operatorname{erf}(\gamma)] = \sqrt{\pi} \Delta\rho/\Delta\rho_s \quad (2)$$

where erf is the error function. Since the observed diffusivity D is rather small and is comparable to the self-diffusion coefficient in the β phase⁷, the interdiffusion coefficient in the α phase D_α is also considered to be rather small. From equations (1) and (2) the temperature dependence of D comes from both γ^2 and D_α , and both terms are considered to make comparable contributions when we assume $\Delta\rho$ and $\Delta\rho_s$ depend on temperature as depicted in Figure 1. The obtained activation enthalpy ΔH therefore comes from both contributions.

The diffusivity D showed a remarkable drop below 33°C (Figure 5). The origin of such anomaly is not clear. One possible explanation is that the intermixed α phase region at 37°C transforms to the low-temperature β phase around 33°C when quickly cooled (Figure 1). This will certainly reduce the diffusivity of the intermixed region, resulting in a decrease in D .

Vacancy mechanism of the chain diffusion

The molecular diffusion in the crystal is considered to be due to the vacancy migration^{13,19}. The diffusion coefficient is determined by the product of the vacancy concentration and the mobility of the vacancy. The energy for the vacancy formation is of the order of the cohesive energy¹³. *n*-Alcohols, for example, have the end OH group, and have much higher cohesive energy than *n*-alkanes²¹. This implies that *n*-alcohol crystals should have much decreased vacancy population, with a consequent decrease in the chain diffusivity. We did similar experiments on the chain diffusion in a binary system of alcohols C_{17} – C_{18} , and as expected we found no intermixing at the junction.

Here we have only considered the transverse diffusion perpendicular to the chain axis, since quantitative measurement of the longitudinal diffusion is very difficult¹⁶. The vacancy population will make the same contribution to both the transverse diffusivity D_\perp and the longitudinal diffusivity D_\parallel . The difference in D_\perp and D_\parallel should originate from the mode of chain migration to the neighbouring vacant sites. The *n*-alkane molecules in the crystal have a very anisotropic rod-like shape;

therefore, we can expect a large difference in the chain diffusivity; the transverse diffusion seems to be much easier geometrically than the longitudinal diffusion (interlamella migration) along a very narrow channel in the crystal. If some interlamellar defects such as stacking faults are present, the high-energy interfacial region will hinder the interlamellar migration of the chains, thereby reducing the longitudinal diffusivity. The terraced structure observed in the upper surface junction¹⁶ is considered to have such an origin. The possibility of detecting the stacking fault by such a method is an interesting future application.

Our *in situ* measurement of the chain diffusion is based on a rather simple principle, but the analysis is not always easy. This is because the diffusion is in a two-phase system which have a moving boundary. In addition, other chemical factors such as the strong dependence of D_α on the concentration seriously complicate the problem. However, the present method enables *in situ* measurement for the very small system of a perfect single crystal, and provides interesting possibilities for future investigations.

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