NOTES

Polymorphic Transitions of *n*-Pentacosane Samples Purified by Gel Permeation Chromatography

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Recently, much attention has been paid to the phase transition behavior of *n*-alkane crystals. In odd *n*-alkanes, several kinds of solid-solid transitions generally precede melting or a hexagonal transition.[1-3] All the subcell structures of these intermediate phases are orthorhombic, identical with that of an orthorhombic form stable at room temperature.[1] It seems that there is some correlation between these solid-solid transitions and the disordering process of chain molecules in the crystals. For clarification of this, we continued the phase study for odd *n*-alkanes ranging from C23 to C43. (Hereafter, $n\text{-}C_nH_{2n+2}$ is abbreviated by Cn.) This note is concerned with our interesting finding obtained during the study that the homologous impurity has a profound effect on the polymorphic change in *n*-pentacosane (C25) crystals.

An early study on *n*-alkanes in 1931 already noted that 1% homologous impurity could be detected by the rotator transition temperature, but not by the melting point.[4] The impurity effect is anticipated to become more severe for the solid-solid transitions at lower temperature. The first thing to be considered in the phase study is how we could obtain samples as free as possible from homologues. Our strategy was to synthesize *n*-alkanes from well-characterized, short-chain starting materials.

Odd alkanes were prepared by following relatively simple procedures: Ketene dimers were made from aliphatic acid chlorides and hydrolyzed to make symmetrical ketones. They were then reduced to *n*-alkanes by the Wolff-Kishner method. A commercial sample of *n*-tridecanoic acid as the starting material for C25 contained about 0.4% homologues with carbon atoms of 11, 12, and 15. A synthesized sample of C25 was at last treated with concentrated sulfuric acid at 125°C and purified through an alumina column. Its purity determined by gas chromatography (GC) was 99.66%.

A GC examination of sample purity was made by a Shimadzu GC-4B equipped with a packed column of Silicone OV-17. In order to detect traces of impurity, the use of a glass column was preferable. In general, impurity detection of higher homologues in a sample was more difficult than that of lower ones. On analysis of C25, 0.02% was the limit of detection for C26.

DSC measurements were carried out by a Perkin-Elmer DSC-1B. DSC curves for the C25 sample are shown in Figure 1. The curve b was obtained on 1 mg sample with a scanning rate of 5 K min^{-1}. A measurement was also done on a sample of 4 mg (curve a). Both the samples were crystallized in bulk at a cooling
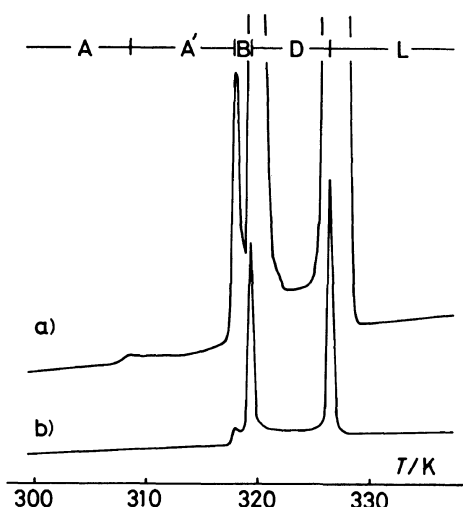
Figure 1. DSC curves of the synthesized sample of *n*-pentacosane, crystallized in bulk at 0.625 K min^{-1}. Heating rate of 5 K min^{-1}. Sample sizes of a) 4 mg and b) 1 mg.

rate of 0.625 K min^{-1}. Peak temperature was used as the transition temperature and temperature calibration of the instrument was done, using the melting peak position given by the reported value of 326.7 K.[10]

On the curve a, a small and relatively broad peak could be observed at 308.6 K, while not discernible on the curve b. This was repeatedly observed. The peak position suggests that it corresponds to a delta transition at 310.2 K, found by Snyder et al.[3] They did not, however, show DSC curves. The next peak at 318.0 K could be ascribed to the transition to phase B. Strobl et al. first found the phase for C33 and determined its crystal structure as monoclinic Aa.[1] In accordance with their designation of the phases, the intermediate phase between the orthorhombic phase (A) and phase B is hereafter called A′. Two large peaks on the curve b are due to the transition to the hexagonal phase (D) and the melting, respectively. Snyder et al. estimated the A′—B transition temperature at about 319 K, although this peak could not be separated from the D transition peak on DSC scans.[3] However, they confirmed the existence of phase B from IR

measurements. Ungar also reported that phase B for C25 was stable between 319.4 and 321.0 K.[9] Although the transition temperatures are higher than the values reported by us and by Snyder et al., the temperature interval of 1.5 K is identical with ours. The difference in the appearance of phase B may be interpreted in terms of a very samll difference in homologous impurity in the samples. The C25 sample used by Snyder et al. was one of API samples and had a purity of 99.8%, as determined by mass spectroscopy.[10]

In order to increase the purity of our sample, preparative gel permeation chromatography (GPC) was performed. Two columns of HF 2003 (20 mmϕ × 500 mm, Showa Denko) in tetrahydrofuran were used. One ml of 3% solution was injected successively at adequate time intervals. Elution volumes of neighboring homologues were within breadth of a peak of C25. Fractions were automatically collected according to the scheme shown in Figure 2a. Table I lists the contents of homologous impurity in some fractions. The preparative GPC technique is said to separate the homologues although its efficiency is not so high.

The sample purity was found to have a remarkable effect on the DSC behavior of the transitions (Figure 2b). The improvement of the purity by only 0.17% from the original to Fraction 3 and 4 made phase B disappear and the A—A′ transition temperature remarkably increase (Table I). It may be concluded that phase B is unstable for pure C25. Up to the present, why the homologues induce the appearance of phase B is not clear. One of reasons is a subtle change of stacking mode of end methyl planes in the C25 crystals.

The A—A′ transition temperature is remarkably affected by very small amount of the homologues. On Fraction 2, it was difficult to discern the transition peak on the DSC curve. This may arise from larger content of a long homologue in the fraction than the original. The effect of such a homologue was also observed by comparison of the phase behavior
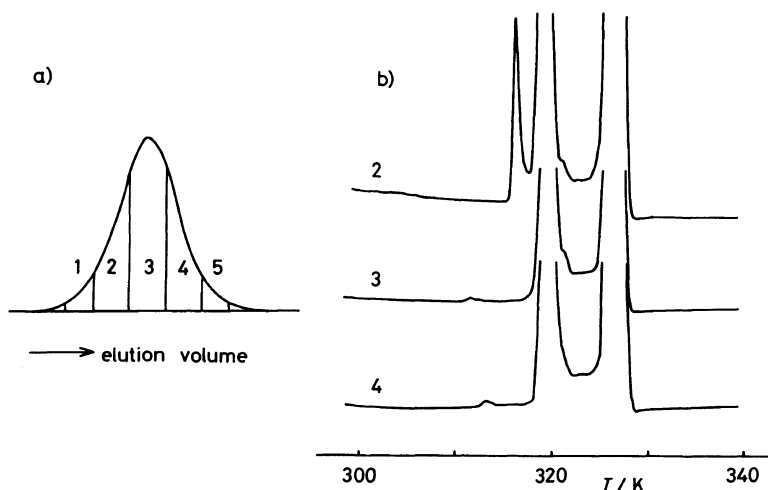
Figure 2. a) GPC elution curve for the sample of *n*-pentacosane and separating scheme for fractions. Numeral is the fraction number. b) DSC curves for the corresponding fractions crystallized in bulk at 0.625 K min⁻¹. Heating rate is 5 K min⁻¹. Sample size, 4 mg.

Table I. Contents of homologous impurity and transition temperatures for various samples of *n*-pentacosane

Sample	Homologous impurity/%		Transition temperature			(Type)[a]
	C24	C27	K			
Original	0.11	0.23	308.6 (A-A′)	318.0 (A′-B)	319.5 (B-D)	
Fraction 2	0.04	0.50		316.4 (A-B)	319.6 (B-D)	
Fraction 3	0.08	0.09	312.3 (A-A′)		319.8 (A′-D)	
Fraction 4	0.17		313.6 (A-A′)		320.1 (A′-D)	
Fraction III	0.10		314.2 (A-A′)		320.1 (A′-D)	

[a] Determined from DSC peak position, under the condition that all the samples have the same melting point of 326.7 K.

between Fractions 3 and 4. Overall impurity contents for both were the same, but Fraction 4 contained only a short chain homologue. This difference increased the transition temperature by 1.3 K. The molecular ends of long homologues, protruding from the end methyl planes, seemed to strain the crystals more strongly than vacancy did due to the short homologues. Further purification, as shown on Fraction III, one of refractionated samples of Fractions 3 and 4 together, indicated that the transition temperature further increased, while the rotator one of the A′—D remained unchanged. It may be concluded that the A—

A′ transition is intrinsic for pure C25 and locates near 314.2 K, although a sample perfectly free from homologous impurity has not been obtained yet. The value of 314.2 K is higher by 4.0 K than that reported by Snyder *et al.*[3]

The present work was carried out by using the DSC-1B instrument, whose sensitivity and stability were not high enough. The heating rate used was relatively high. In order to measure thermodynamic properties in near equilibrium, we begin to use a DSC instrument of heat flux type. Its high sensitivity at low rates of heating may enable us to study in detail the

complicated phase behavior of the chain crystals and the homologous impurity effect.

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