Crystal Structure of 20-Methyl-Nonatriacontane $((C_{19}H_{39})_2CHCH_3)$ and Its Compatibility with Nonatriacontane $(C_{39}H_{80})$

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We synthesized a branched *n*-alkane sample M39 with a carbon number of the main chain n = 39 with the methyl group at the middle of the chain, and studied its crystalline structure and also compatibility with the corresponding linear homologue of C39. Results of SEM, DSC, X-ray diffraction, IR absorption, and Raman scattering measurements on solution-grown crystallized sample (SG-M39) and bulk-crystallized sample (BK-M39) reveal along with computer simulation that a triclinic type of crystal belonging to the space group $P\overline{1}$ is predominantly realized in BK-M39, whereas an orthorhombic type of $P2_12_12_1$ is found to be coexistent for SG-M39 crystal. The phase diagram is constructed for the BK-M39/C39 binary system, which shows that the system does not form a solid solution and the respective molecules with a small amount of contaminant of another component develop their own crystal structures separately over the entire range of molar fraction of M39 from 0.05 to 0.95 studied.

Introduction

Polyethylene (PE) is known to have various lengths of branches depending on catalysts used for polymerization along with different molecular weight distributions from the most probable one to a very broad one with a ratio of weight-average to number-average molecular weight as large as 20.¹⁻⁴ Branched groups and chain ends are both considered as defects to hinder formation of a chain-folded single crystal. Nevertheless, it has been long believed that such short branches as the methyl or the ethyl group are mainly incorporated into lamellae of PE crystals.

Ouite recently it became clear from a morphological study on two branched alkanes of high purity, C₉₆H₁₉₃CHRC₉₄H₁₈₉ with R being methyl or butyl, that such short branches are rejected to the lamellar surface and eventually affect molecular deposition on the crystal growth face so as to take a once-folded chain conformation.⁵⁻⁷ The branching effect was further studied on asymmetric methyl-branched alkane C₁₉₁H₃₈₃CH(CH₃)- $C_{99}H_{199}$ by the same group.⁸ They showed that the sample can be crystallized in two different semicrystalline forms depending on crystallization temperature, which on further cooling transform to a double layer and a triple layer crystalline structure, respectively. In both structures, the methyl branches are found to be always located on the lamellar interface, and the whole main chain took the extended conformation in the double layer structure, whereas the longer part of the chain was once-folded at the position of the methyl branch in the triple one. Thus topological restriction brought by introduction of the methyl

branch is likely to influence the crystallization kinetics as well as the equilibrium crystalline structure.

As the main chain carbon number *n* decreases, alkanes tend to crystallize, taking the extended chain conformation as the energetically most favored one. In this case, introduction of small functional groups such as the carbonyl or hydroxyl group at the middle of the main chain hardly disturbs the crystalline structure of their linear homologues. In earlier studies, this was proved indeed to be the case. 9^{-18} The subcell structure was the same for all samples examined, and their melting temperatures became higher than those of the linear homologues because of dipole-dipole interaction or hydrogen bonding, whereas the solid-solid-phase transitions characteristic of pure linear alkanes disappeared.¹⁹⁻²⁴ On the other hand, attachment of bulky side groups such as hydrocarbons or aromatic compounds without having any specific interaction to the center of the main chain does not contribute to stabilization of the crystal structure but greatly impedes crystallization kinetics with an increase in a size of the branch. In an extreme case, the main chain might fold so that the bulky side groups may be rejected on the lamellar interface, or the sample cannot crystallize any more but might become a glass-forming material. Thus it seems meaningful to perform a systematic study on effects of a branch size on solid structures of alkanes that contain branches with various lengths in the center of an otherwise linear chain taking the extended conformation in the crystalline state.

In this paper, we report results on the methyl-branched alkane M39 with n = 39 obtained from SEM, DSC, X-ray diffraction, Raman scattering, and IR absorption measurements as well as computer simulation. We find that M39 crystallizes as an extended chain with the methyl group being inside the lamellae and the crystals obtained with the solution-grown and bulk-

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SCHEME 1



crystallization methods both exhibit polymorphs taking two different crystalline structures belonging to the space groups P1 and $P2_12_12_1$. The difference between them is that an orthorhombic type of crystal structure is mainly formed for the solution-grown M39, whereas a triclinic type of crystal structure is dominantly realized in the bulk-crystallized M39. The crystalline structures determined in this work are in appearance similar to the double layer structure of C₁₉₁H₃₈₃CH(CH₃)C₉₉H₁₉₉ proposed by Ungar et al.⁸ where all long alkane chains take extended conformation, but are unique for packing of the central methyl branch in cooperation with end methyl groups, which gives rise to staggered alignment between the neighboring extended chain with the relative translation of a half main chain length. Compatibility between M39 and its linear homolouge C39 is also examined from DSC measurements, which indicate that the respective molecules, allowing a small amount of contamination of another component, tend to develop their own crystal structures separately over the entire range of molar fraction of M39 from 0.05 to 0.95 studied.

Experimental Section

Materials. The long chain *n*-alkane with a branch at the middle, 20-methyl-nonatriacontane $((C_{19}H_{39})_2CHCH_3)$ denoted M39, and the corresponding linear *n*-alkane C39 were used for this investigation. The branched alkane was synthesized through ketene dimerization and Grignard reactions using the corresponding carbonic acid chlorides free from other homologues. Details of synthesis are reported elsewhere.²⁵ As is shown in Scheme 1, carboxylic acid chloride (**2**) synthesized from corresponding carboxylic acid (**1**) (SIGMA Co., purity; minimum 99.0%) and thionyl chloride in argon atmosphere was further reacted in ether solution with tertiary amine to obtain alkyl ketene dimer (**3**). Symmetrical ketone (**4**) with a carbonyl group at the middle of the main chain was easily obtained from hydrolysis of (**3**). C39 was synthesized by reducing the corresponding ketone (**4**) using the Wolff–Kishner method.²⁶

Tertiary alcohol (6) was synthesized through the product (5) of the meso compound from symmetrical ketone (4). Powders of symmetrical ketone (4) were poured into 3 M *tert*-butyl ether solution of a Grignard reagent (CH₃-MgBr; Aldrich Co.) and

reacted in a nitrogen atmosphere at room temperature for 24 h. Hydrolysis of the solution of (5) by dropwise addition of aqueous solution saturated with ammonium chloride yielded the product (6).²⁷ After evaporation of solvent the product was confirmed as a tertiary alcohol (6) from IR measurement and gas chromatography. The tertiary alcohol (6) was reduced in a water/ethyl alcohol mixture containing iodine and phosphorus as reducing agents for 24 h at room temperature. In this reaction, however, a double bond was occasionally introduced as a result of a side reaction in the main or the side chain through an intermediate stage of carbocation generation; thus the additional hydrogenation reaction became necessary for conversion of the double bond into the single one (reaction $(7) \rightarrow (8)$) adding hydrogen molecules in an autoclave. Products obtained were finally purified with elution and recrystallization through a silica column using hexane as solvent.

After solubility tests of pure C39 and M39 using several organic solvents, we chose toluene and butanone for solutiongrown crystallization of C39 (SG-C39) and M39 (SG-M39) respectively, because each solvent is not a bad solvent to C39 and M39 and crystallization took place at around room temperature. It is to be noted that we could not obtain a crystallized M39 sample from 3% toluene solution at a temperature as low as 250 K. Bulk-crystallized C39 and M39 denoted BK–C39 and BK-M39, respectively, were prepared with a slow cooling rate of 2.0 K/h from the melt at 120 °C. Eight binary M39/C39 samples with a molar fraction f_m in the range 0.05–0.95 were prepared from respective homogeneous solutions of C39 and M39 in hexane by evaporating the solvent on a hot plate and then slowly cooling to ambient temperature.

Homologous purities of C39 and M39 were determined by a capillary gas chromatograph (GC-14A, Shimazu) as 99.9% and 99.6% respectively. The density was measured with a Gay–Lussac pycnometer as 0.944 g cm³ for SG-C39 and 0.915 g cm³ for SG-M39.

Methods. SEM was made for morphology observation of SG-C39 and SG-M39 at room temperature with JSM-T100 (Nihondenshi). DSC measurements were performed using a calorimeter (DSC-8240B with a TAS-100 controller, Rigaku) for SG- and BK-M39, SG-C39, and C39/M39 binary mixtures from 293 to 393 K. The standard heating rate of 1.0 K min⁻¹ was employed under dry nitrogen atmosphere for a sample mass of about 1.0 mg. The heating rate dependence was examined for several samples of the M39/C39 system chosen randomly and was found negligible. Temperature calibration was performed using indium (In) and also shorter *n*-alkanes with known equilibrium melting temperatures. The heat of transition or fusion was calibrated using In and gallium.

The X-ray diffraction measurements were performed for SG and BK samples of C39 and M39 with a diffractometer using Ni-filtered Cu Ka radiation (Rigaku, Geigerflex 2027) at room temperature. Structural changes in respective crystals with increasing T were studied from room temperature to T just below the melting temperature of SG-M39 at twelve or fifteen temperatures. Raman spectra were obtained for SG-C39 and SG-M39 samples with an NR-1800 Raman spectrometer (Japan Spectroscopic Co). A beam line with 514.5 nm of wavelength from an argon ion laser was used as an excitation light source. IR spectra were obtained at room temperature using a FT-IR spectrometer (FTS-6000, Bio-Rad) with 64 scans at a resolution of 2 cm^{-1} . To find the energetically most stable crystal structure, a commercial software Polymorph Predictor, a module of Cerius² (version 4.0, Accelrys Inc.), was used. The unit cell parameters of the crystal structural models obtained were slightly







modified so that they may give better reproduction of X-ray diffraction data measured at room temperature keeping essential features of the structure unchanged. These modified structures were minimized again under the assumption of rigid body molecules.

Results and Discussion

Crystal Structure of M39. *Direct Observation.* Figure 1 shows SEM photographs of (a) SG-C39 and (b) SG-M39. C39 forms a typical lozenge shape of thin single crystal mat for which the crystal grows along the (110) plane. In contrast, M39 takes a needlelike crystal different from C39, indicating that the attachment of the methyl residue to the middle of the main chain significantly affects a mechanism of crystal growth. The difference shall be discussed later after the crystalline structure of M39 is determined. Because the M39 crystal was obtained as fine powders, it was not possible to use a four-circle X-ray diffractometer to determine the crystal structure.

Thermal Behaviors. Figure 2 shows DSC curves of SG-C39, SG-M39, and BK-M39. BK-C39 gave a DSC curve with almost the same characteristic feature as SG-C39. The curve of C39 unambiguously exhibits the B and C solid—solid–phase transitions at 333 and 341 K, respectively, and a sharp melting peak at 353 K. On the other hand, melting peaks observed for SG-and BK-M39 are quite broad as compared with the peak of C39, and their melting temperatures T_m are 331.4 and 330.7 K, respectively, being lower by more than 20 K in comparison with T_m of C39. Lowering of T_m and broadening of the



Figure 2. DSC curves of C39, SG-M39, and BK-M39. The weight of the samples used is 1.0 mg, and the scanning rate, 1.0 K min^{-1} .



Figure 3. X-ray diffraction profiles of BK-M39, SG-M39, and C39 at room temperature.

endothermic peak are undoubtedly related so that M39 could not form the single crystal but was forced to take a more or less disordered crystal due to a difficulty of M39 molecules in achieving close parallel chain packing. A small dip is observed in the DSC curve near the bottom of the BK-M39 data. Repeated measurements, however, showed that the position of the dip on the temperature axis as well as its depth varied every run. At present we have no explanation why this kind of distortion is observed for the BK-M39 sample.

X-ray Diffraction Profiles. Figure 3 shows X-ray diffraction profiles of SG-M39 and BK-M39 measured at room temperature, and also that of SG-C39 for comparison in a range of diffraction angle 2θ from 3° to 40°. SG-C39 gives a sequence of sharp diffraction peaks over a wide diffraction angle range corresponding to (00*l*) reflections of the long spacing with even number of *l* along the main chain *c* axis as well as two peaks at $2\theta = 21.5^{\circ}$ and $2\theta = 23.8^{\circ}$ from the (110) and (200) planes characteristic of linear alkanes with odd carbon number at room temperature, i.e., of the A structure.²² On the other hand, only a small number of broad diffraction peaks are observed in the



Figure 4. Changes in X-ray diffraction profiles induced by heat treatment. (a) SG-M39: (1) 298.3 K, (2) 313.1 K, (3) 327.6 K, and then cooled to (4) 297.6K. (b) BK-M39: (1) 294.6 K, (2) 312.1 K, (3) 327.4 K, and then cooled to (4) 294.6K.

low diffraction angle region for the M39 samples, and corresponding intensities are very low, especially for BK-M39. This is not an unexpected result for a powder-like crystal, whereas broadness of the peaks might be due to superposition of two or even three peaks. Even though the presence of these low angle peaks must be taken into account in determining their crystalline structures, the X-ray diffraction measurement after all does not permit accurate determination of the long spacing *L*, and it remains uncertain whether the main chain of M39 is fully extended or once folded due to presence of the bulky methyl group.

SG-M39 gives three strong peaks at around $2\theta = 19.3^{\circ}, 21.1^{\circ}$, and 23.5° with the largest intensity at $2\theta = 21.1^\circ$, of which the peak at $2\theta = 19.3^{\circ}$ is a new one with the spacing d = 0.458nm not present for the orthorhombic type of the subcell structure as C39 and the peak at $2\theta = 23.5^{\circ}$ appears to have a shoulder at $2\theta = 23.0^{\circ}$. On the other hand, the sample gives two weak peaks at $2\theta = 35.9^{\circ}$ and 39.6° close to the positions where peaks from (020) and (310) reflections are observed for C39. These results lead to supposition that the SG-M39 crystal may be polymorphous. BK-M39 also gives three strong peaks at around $2\theta = 19.3^{\circ}$, 21.1°, and 23.1° with the largest intensity at $2\theta =$ 19.3°, but no peaks at higher 2θ . Three main peaks imply that the unit cell of BK-M39 is presumably a triclinic or a monoclinic form, but we surely need to collect more information using other experimental techniques to determine a type of the crystal lattice and unit cell parameters, and also to examine a possibility if BK-M39 might be polymorphous as SG-M39.

Because not only X-ray diffraction patterns but also DSC peaks are broad for M39 samples, changes in diffraction profiles with raising T were studied at twelve temperatures from room temperature to T just below respective melting points and also at room temperature after the samples were cooled. Parts a and b of Figure 4 show X-ray diffraction patterns at four selected temperatures for SG-M39 and BK-M39, respectively. As is clear from the figure, thermal treatments appear to have influenced

the patterns in different manners. For SG-M39, two peaks at $2\theta = 19.3^{\circ}$ and 21.1° remain essentially at the same positions with a rise in *T*, whereas the shoulder observed for the broad peak at $2\theta = 23.5^{\circ}$ of the virgin sample (1) at T = 298.3 K tends to be split as an independent peak with increasing temperature and this new peak at $2\theta = 23.2^{\circ}$ is irreversibly maintained after the sample is cooled to T = 297.6 K in profile 4. Furthermore, comparison profiles 4 and 1 indicates that intensities at $2\theta = 21.1^{\circ}$ and 23.5° measured with peak height noticeably increased with this heat treatment. Thus it seems plausible that the broad endothermic peak of SG-M39 shown in Figure 2 is related to formation of a rather distorted crystal lattice with the solution-grown method or disordering of molecular alignment brought by competitive formation of two different crystalline structures, or to the both.

In the X-ray diffraction patterns of BK-M39 shown in Figure 4b, on the other hand, three characteristic peaks simply shift to the lower θ with raising temperature probably due to thermal expansion and, after annealing, they return to almost the same angles with the peak shapes unchanged. There appears to be no change in the crystal structure with increasing temperature before the melting point is reached, even though a dip was observed in the DSC curve in Figure 2.

Raman Scattering. The small-angle X-ray diffraction measurement on M39 samples did not provide information sufficient for determination of the long spacing *L*. Alternatively, conformation of the main chain or the chain length in the crystalline state can be unambiguously determined from Raman scattering measurement using vibration modes of the longitudinal acoustic mode (LAM), if the chain is depicted as a continuous elastic rod. The *j*th LAM frequency of the vibration, v_j , is given

$$v_i = (j/2cL)(E_c/\rho)^{1/2}$$
(1)

where c is the speed of light in the medium, E_c is Young's modulus of the chain in the solid state, ρ is the density, and j



Figure 5. Raman spectra from longitudinal acoustic modes (LAM) for SG-C39 and SG-M39.

is the vibration order (only odd numbers are Raman active). Figure 5 shows results of Raman scattering measurements on SG-M39 and SG-C39 at room temperature. Three peaks are clearly observed for SG-C39 at 62.6, 176, and 283 cm⁻¹, corresponding to the LAM modes with j = 1, 3, and 5, respectively. Stroble and Eckel pointed out, from Raman scattering experiments on linear alkanes C_nH_{2n+2} with $33 \le n \le 94$, that weak interlamellar forces result in an upward shift of v_j given by eq 1, and proposed an empirical equation²⁸

$$\nu_i = 2236j/(n-1.6) + 2.2/j \tag{2}$$

Equation 2 gives $v_1 = 62.0 \text{ cm}^{-1}$ for n = 39, which is in excellent agreement with the experimental value of $v_1 = 62.6$ cm⁻¹, and also $\nu_2 = 180$ cm⁻¹ and $\nu_3 = 299$ cm⁻¹, being slightly larger than the values measured. Three peaks are also observed for SG-M39 at 62.3, 176, and 285 cm⁻¹, which are in excellent agreement with corresponding v_i values of C39. Because C39 molecules are known to take the extended chain conformation, forming the orthorhombic type of crystal, we conclude that M39 molecules are not folded but extended so as to take the planar zigzag form in the solid state. In addition, close agreement of v_i values between C39 and M39 indicates that intermolecular interactions responsible for symmetrical longitudinal backbone vibration modes are almost the same for the two samples, even though the methyl group attached to the center of the main chain of M39 must be located inside the lamellae and is expected to perturb the chain packing to some extent.

IR Absorption. Results of X-ray diffraction measurement on SG-M39 have suggested that the structure of the subcell is likely to consist of two different types; one is a triclinic or a monoclinic type supposed to be identical to the BK-M39 case and the other an orthorhombic type. For the latter, the IR absorption band at 720 cm⁻¹ corresponding to the CH₂ rocking mode is known to be split into two components due to intermolecular interaction,



Figure 6. IR spectra for SG-C39, SG-M39, and BK-M39 in the CH₂ rocking mode region at 303.1K.

whereas there occurs no splitting for the former. We performed IR absorption measurements on powder samples of SG-C39, SG-M39, and BK-M39, which were carefully sandwiched between two KBr plates to minimize possible disturbances or alteration of crystalline structures of the fragile samples by applied pressure. It is to be noted that completely different IR spectra were indeed obtained for M39 samples prepared with such a conventional method that the samples are mixed well with KBr powder and then pressed to make the disk.

Figure 6 gives IR spectra of three samples in a relatively narrow wavenumber region of 700-750 cm⁻¹ at 303.1 K. The measurements were also made at elevated temperatures below respective $T_{\rm m}$'s, and essentially the same shape of the spectrum was obtained for each sample. The well split IR bands are seen in C39 as expected, but not for the two M39 samples. The spectrum of SG-M39 is broad, but a small peak is found at 730 cm^{-1} corresponding to the vibration mode parallel to the *a* axis intrinsic for the orthorhombic type of subcell structure and the peak at 720 cm⁻¹ is broader compared with the corresponding one of SG-C39. Similar trends were also observed for the CH₂ deformation mode at 1465 cm⁻¹. These IR results are in accord with X-ray diffraction profiles of this sample, indicating polymorphs composed of the orthorhombic and the triclinic or monoclinic subcells for SG-M39. The IR spectra of BK-M39 look broader toward the low wavenumber direction, which may be adressed to (1) more distorted chain packing in the local subcell size when M39 is bulk crystallized and (2) superpositions of the normal orthorhombic doublet and some additional band-(s) from another phase, or to the both. Issue 1 may be supported by that the molar enthalpy of fusion, $\Delta H_{\rm m}$, of BK-M39 is lowered to 114 kJ mol⁻¹ from the value of $\Delta H_{\rm m} = 120$ kJ mol⁻¹ of SG-M39 and both are much smaller than $\Delta H_{\rm m} = 146$ kJ mol^{-1} of SG-C39. Issue 2 comes from the observation of the shoulder in the spectra at around 730 cm⁻¹. We performed IR

measurement on the another sample BK-M39 obtained by melting of BK-M39 at T = 333.5 K slightly above $T_{\rm m}$ of BK-M39 and subsequently slow cooling to 303.1 K, and the result is shown in the same figure. Obviously, the heat treatment improved local chain packing so that the peak at 720 cm⁻¹ increased not only in intensity but also became sharper and furthermore the shoulder shifted to the lower wavenumber side with a decrease in intensity. Combining the two IR results mentioned above, we should consider that BK-M39 predominantly takes a triclinic or a monoclinic type of the crystalline structure with rather distorted local chain packing and may contain a small fraction of the orthorhombic type of the crystal as in SG-M39. However, we did not attempt to estimate the fraction, because of a drastic change in the spectra by heat treatment, lacking of a clear theoretical guide for decomposition, and poor resolution of 2 cm^{-1} of the instrument used.

Computer Simulation. X-ray diffraction, Raman scattering, and IR data described in previous sections strongly suggested that SG-M39 and probably BK-M39 are present in polymorphic forms, one being the orthorhombic one and another a triclinic or a monoclinic one, whereas the main chain takes the planar zigzag form. Owing to a small number of diffraction peaks, another technique such as computer simulation may be helpful for determining how extended main chains are aligned and how the central methyl groups are packed in cooperation with end methyl groups in respective unit cells. We performed computer simulation to find the energetically most stable crystalline structure choosing five space groups of $P2_1$, $P2_12_12_1$, $P2_1/c$, C2/c, and P1 as potential candidates for the M39 crystal. X-ray diffraction profiles were calculated from lattice parameters predicted for each space group and compared with those experimental curves shown in Figure 3. Two space groups of $P2_12_12_1$ and $P\overline{1}$ were found to reproduce experimental results fairly well, whereas others belonging to the monoclinic group failed to predict one or two main peaks at positions of 2θ observed.

Figure 7 illustrates the predicted molecular model belonging to the $P2_12_12_1$ space group whose unit cell dimensions are a =1.515 nm, b = 0.505 nm, c = 5.358 nm, and $\alpha = \beta = \gamma = 90^{\circ}$, and the density is 0.919 g cm^{-3} , being close to the experimental value of 0.915 g cm⁻³ obtained for SG-M39. The model predicts that the unit cell contains four M39 molecules as found for C39 taking the double layer structure, but the lattice parameters a, b, and c are different from a = 0.749 nm, b = 0.496 nm, and c = 5.197 nm of C39. The closest packing of end methyl groups at the interface in the C39 crystal gives rise to the relative translation of linear alkane molecules along the *a* axis in the upper and the lower layers; thus c becomes a double of the main chain length. In the M39 crystal, adjacent four extended chains surrounding one M39 molecule relatively translate by a half of the main chain length along the c axis to accommodate the central methyl group under cooperation of end methyl groups, which affect directions of chain planes of the next nearest neighbor chains, resulting in the unit cell with the large a, as illustrated in the projection on the a-b plane. According to this model, nevertheless, introduction of the central methyl group very slightly loosens the local chain packing to a similar extent along all three axial directions. The model illustrated in Figure 8 belongs to the P1 space group. The lattice parameters estimated for this triclinic type of crystal are a = 1.050 nm, b = 0.470 nm, c = 5.176 nm, $\alpha = 72.6^{\circ}$, $\beta = 68.0^{\circ}$, and $\gamma =$ 65.0° , and the density is 0.88 g cm⁻³. The unit cell contains two M39 molecules due to staggered alignment between adjacent chains with the relative translation of a half main chain



Figure 7. Molecular model of M39 simulated for the space group $P2_12_12_1$. a = 1.515 nm, b = 0.505 nm, c = 5.358 nm, $\alpha = \beta = \gamma = 90.0^{\circ}$.

length and chain planes of all molecules are oriented to the same direction. The triclinic structure proposed is different from those in even alkanes from $C_{10}H_{22}$ to $C_{26}H_{54}$.²⁹⁻³⁴ The number of molecules in the unit cell is 1 up to C22 and becomes 2 for C24 and C26. Typical values of lattice parameters below C22 are, for example, a = 0.483 nm, b = 0.429 nm, c = 2.482 nm, $\alpha = 67.8^\circ$, $\beta = 85.1^\circ$, and $\gamma = 72.5^\circ$ for C18 with the density of 0.929 g cm⁻³, and for C26, a = 0.767 nm, b = 0.526 nm, c= 3.528 nm, α = 68.4°, β = 83.6°, and γ = 83.0° with the density of 0.926 g cm⁻³. X-ray diffraction patterns shown in Figure 3 were indexed with the two molecular models and results are listed in Table 1. It is to be noted that, if unit cell structures given by the two models are realized in M39 crystals, intensities from (00l) reflections should be considerably lowered in comparison with those of C39. The orthorhombic model successfully predicts four peaks of SG-M39 at $2\theta = 21.1^{\circ}$, 23.5°, 35.9°, and 39.6°, and also two broad peaks at low angles as reflections from (002) and (004) planes but no peak to (003)



Figure 8. Molecular model of M39 simulated for the space group $P\overline{1}$. $a = 1.050 \text{ nm}, b = 0.470 \text{ nm}, c = 5.176 \text{ nm}, \alpha = 72.6^{\circ}, \beta = 68.0^{\circ}, \gamma = 65.0^{\circ}$.

 TABLE 1: Comparison of Diffraction Angles 2θ Measured

 with Those Calculated from Computer Simulation

			crystalline lattice simulated					
experimental			P	Ī	$P2_{1}2_{1}2_{1}$			
sample	$2\theta/\text{deg}$	d/nm	$2\theta/\text{deg}$	(hkl)	2/deg	(hkl)		
BK	3.2 (vw)	2.79			3.3	(002)		
	6.2 (vw)	1.36			6.6	(004)		
	19.3 (s)	0.459	19.5	(200)				
	21.1 (m)	0.421	21.6	(010)	21.1	(210)		
	23.1 (vs)	0.385	23.2	(210)	23.5	(400)		
SG	3.2 (w)	2.79			3.3	(002)		
	6.5 (vw)	1.35			6.6	(004)		
	19.3 (s)	0.458	19.5	(200)				
	21.1 (vs)	0.420	21.2	(010)	21.1	(210)		
	23.0 (s)	0.386	23.2	(210)				
	23.5 (s)	0.380			23.5	(400)		
	35.9 (m)	0.250			35.6	(020)		
	39.6 (vw)	0.228			39.9	(610)		

reflection consistently. The strong peak at $2\theta = 19.3^{\circ}$ and the shoulder at $2\theta = 23.0^{\circ}$ may be complemented by coexistence of the triclinic form approximately. Thus, we may be allowed



Figure 9. DSC curves of bulk-crystallized M39/C39 compared with those of C39, SG-M39, and BK-M39. The weight of the samples used is 1.0 mg, and the scanning rate, 1.0 K min⁻¹.

to conclude that SG-M39 is present in polymorphic forms, one being the orthorhombic one and another the triclinic one with approximate lattice parameters obtained from the simulation. Three strong peaks of BK-M39 at $2\theta = 19.3^{\circ}$, 21.1° , and 23.1° appear to be represented by the triclinic model. The model gives (002) and (003) reflections at $2\theta = 3.73^{\circ}$ and 5.60° , but no peak is seen at those angles. Instead, very weak and broad peaks are seen at $2\theta = 3.2^{\circ}$ and 6.5° , which are close to (002) and (004) reflections of the orthorhombic model whose main peak is located at $2\theta = 21.2^{\circ}$. Thus it seems legitimate to consider that the BK-M39 crystal is also present in polymorphic forms, taking the triclinic form predominantly and the orthorhombic one as a minor component.

The molecular models illustrated in Figures 7 and 8 have a characteristic feature that there exists no smooth flat interface where methyl groups are disclosed. Instead, all methyl groups are located inside the crystal, which gives rise to staggered alignment between neighboring extended chains. Thus it does not seem unreasonable to suppose that chain stacking along the main chain axis is quite difficult. It is also to be noticed that, in Figure 8, crystal growth along the *b* axis does not produce extra surface, whereas more extra surface energy is needed along the *a* axis. Anisotropy of rates of crystal growth along three directions may explain why a needlelike crystal has been obtained for M39 samples.

Compatibility of M39 with C39. Figure 9 shows eight DSC curves of the bulk-crystallized M39/C39 binary system (BK-M39/C39) with those of pure BK-M39 and C39. In the range of the molar fraction f_m of M39 from 0.05 to 0.80 studied, we observe the solid-solid-phase transitions characteristic of pure C39 followed by melting, and also another melting peak at a lower *T* close to the melting temperature of pure M39. It is ambiguous if the solid-solid-phase transition persists above $f_m = 0.80$, because of lowering of the melting temperature of the C39-rich phase. The phase diagram was constructed for BK-M39/C39 using peak temperatures on respective DSC curves



Figure 10. Phase diagram for bulk-crystallized M39/C39 system: (\bullet) solid-solid-solid transitions and melting of the C39-rich phase; (\bigcirc) melting of the M39-rich phase. The liquidus line is calculated from eq 3, and horizontal and dotted lines are empirically drawn.

excluding the endothermic curve at the higher melting temperature, to which the final melting temperature was used and is shown in Figure 10. In the figure, filled circles correspond to the transition and the melting points of the C39-rich phase and unfilled circles correspond to that of the M39-rich phase. The two solid-solid transition temperatures look to decrease very slightly with increasing f_m following empirically drawn dotted lines. Effects of a small amount of impurity on the DSC transition behaviors were studied using a homologous series of n-alkanes.35 Mixing of 0.5 mol % C26 into C27 did not affect the latter melting temperature as well as the transition temperature to the C structure, but lowered the transition temperature to the B structure by 1.7 K. Mixing of 0.8 mol % of C25 into C26 gave another independent solid-solid transition peak. Therefore it seems plausible that the amount of M39 contaminated in the C39-rich phase may be less than 1 mol %. On the other hand, the melting temperature $T_{m,M39}$ of the M39-rich phase remains constant independent of f_m excluding the data point given by the white circle at $f_{\rm m} = 0.10$ and the endothermic peaks are sharper than pure M39. These strongly suggest that $T_{\rm m,M39}$ should be regarded as the eutectic temperature. The triple point may be located as the point where the two solid lines in the figure tend to intersect. Because the melting point of pure BK-M39 sample is slightly but definitely lower than the eutectic temperature, this conclusion is ambiguous a little bit yet.

The melting point $T_{m,C39}$ of the C39-rich phase is appreciably depressed with increasing f_m . It is likely that the depression is caused by melting of the M39 component at elevated temperatures.³⁶ Because M39 and C39 are considered to mix athermally in the liquid state to a very good approximation and the C39rich phase is exclusively composed of pure C39, eq 3 was applied to examine the above presumption.

$$\ln f_{\rm c} = \Delta H_{\rm m,C39} * / R(1/T_{\rm m,C39} * - 1/T_{\rm m,C39})$$
(3)

Here $f_c = 1 - f_m$ is the molar fraction of C39 in the mixture prepared, $T_{m,C39}^*$ and $\Delta H_{m,C39}^*$ are the melting point and the molar enthalpy of fusion of pure BK–C39, and *R* is the gas constant. Substitution of measured $T_{m,C39}^*$ and $\Delta H_{m,C39}^*$ values



Figure 11. Heat of transition ΔH for the M39/C39 system as a function of $f_{\rm m}$: (\bullet) $\Delta H_{\rm C39}$ of the C39-rich phase; (\bigcirc) $\Delta H_{\rm M39}$ of the M39-rich phase.

 TABLE 2: Melting Temperatures and Heats of Transition for the M39/C39 System

			$\Delta H/{ m kJ}~{ m mol}^{-1}$						
M39 molar fraction	$\frac{T_{\rm m}}{\rm M39}$	/K C39	at T _{m,M39}	at T _{m,C39}	$A' \rightarrow B$	$B \rightarrow C$	total		
0		354.4		136	2	8	146		
0.05	331.5	354.1	7	124	2	7	139		
0.10	328.0	353.7	12	117	2	6	136		
0.20	331.6	353.0	24	103	4	7	138		
0.40	331.7	351.1	49	72	3	6	129		
0.60	331.8	348.2	76	47	3	5	130		
0.80	331.8	343.7	96	22	2		120		
0.90	331.9	337.9	111	4			114		
0.95	331.8	333.3	114	2			116		
1.00(BK)	330.7		114				114		
1.00(SG)	331.4		120				120		

into eq 3 gives the solid curve in Figure 10, which successfully reproduces the $f_{\rm m}$ dependence of $T_{\rm m,C39}$.

We calculated enthalpy ΔH associated with melting or the solid-solid-phase transitions from area of respective endothermic peaks on DSC curves for this system and results are given in Table 2 with values of two melting temperatures. Because ΔH of the A \rightarrow A' transition was only observed for pure C39 and was very small, it has not been listed. Total enthalpies ΔH of the binary system listed in the last column of Table 2 indicate that they tend to decrease almost linearly with an increase in f_m from $\Delta H_{m,C39}^* = 146$ kJ mol⁻¹ of pure C39 to $\Delta H_{m,M39}^* =$ 120 kJ mol⁻¹ of pure M39; thus ΔH may be given by

$$\Delta H = \Delta H_{\rm M39} + \Delta H_{\rm C39}$$

= $f_{\rm m} \Delta H_{\rm m,M39}^{*} + (1 - f_{\rm m}) \Delta H_{\rm m,C39}^{*}$ (4)

Here ΔH_{M39} is the enthalpy corresponding to the peak at $T_{m,M39}$ and ΔH_{C39} a sum of enthalpies due to melting and solid-solid transitions of the C39 component. Figure 11 shows dependences of ΔH_{M39} and ΔH_{C39} on f_m as unfilled and filled circles, respectively. The both quantities linearly vary with f_m over the entire range of $0.05 \le f_m \le 0.95$, which confirms the second equality in eq 4. The results establish that a great majority of C39 and M39 molecules are present separately in this binary system, taking crystal structures different from each other.

Two crystalline structures proposed for M39 appear considerably different. A closer look at Figures 7 and 8, however, suggests that molecules are aligned as a pair of extended chains at their closest distance with the methyl groups being arranged toward the same direction for the $P\overline{1}$ group and along the opposite direction for the $P2_12_12_1$. This may partially explain why the two crystalline structures appear to have almost the same melting temperature as seen on the DSC curves.

A final remark is concerned with an interrelationship between the branching effect on the crystal structure and the main chain length of alkane molecules. Ungar and Zeng have pointed out in their review⁸ that, because of the surface overcrowding effect, lamellar crystals of very long alkane chains cannot grow laterally without chain folding at the conventional experimental condition of 1 atm and also that introduction of a short branch to the center of the main chain facilitates chain folding at the branching point for sufficiently long alkanes and results in rejection of the branch to the lamellar surface. This does not seem to apply for symmetric branched alkanes with a carbon number of the main chain as low as 39, whose linear homologue exclusively takes a planar zigzag conformation in the crystalline state due to a heavy restriction that extra energy is needed for chain folding. As demonstrated in this work for the first time, main chains pack taking the extended conformation, whereas all central methyl branches are accommodated inside lamellae in cooperation with end methyl groups, which gives rise to staggered alignment between adjacent extended chains. We shall report that a similar crystalline structure is realized for symmetric branched alkanes with various long branches in a forthcoming paper. However, chain folding may take place for a highly symmetrical branched alkane such as a three- or four-arm star as the energetically most favorable state, even if the carbon number of the main chain is low, and this possibility should be definitely examined.

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