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Rigid-Rod Polyesters with Flexible Side Chains Based on 1,4-Dialkyl Esters of Pyromellitic Acid and 4,4′-Biphenol. 5. High-Resolution ^{13}C NMR Studies for Crystalline and Liquid Crystalline Layered Phases

Masato Sone, Brian R. Harkness, Hiromichi Kurosu, Isao Ando, and Junji Watanabe*

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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ABSTRACT: Rigid-rod aromatic B–C*n* polyesters with long alkyl side chains, composed of 1,4-dialkyl esters of pyromellitic acid and 4,4′-biphenol, form two distinct types of crystalline phases, K1 and K2, depending on the length of alkyl side chain. These crystalline phases are characterized by a layered structure, in which the aromatic main chains are packed into a layer with the side chains crystallized in the space between the layers. The detailed structures for these two crystalline phases were studied by ^{13}C solid-state NMR spectroscopy from which it was found that there are remarkable differences in the main-chain conformation and in the packing structure of the side chains. In the K1 crystal formed by the B-C*n* polymers with shorter side chains, the aromatic main chain assumes a twisted conformation with the side chains packed into an orthorhombic lattice. In contrast, in the K2 crystal of the longer side-chain B-C*n* polymers, the main chains assume a coplanar conformation with the side chains packed into a triclinic lattice. The NMR studies have also been extended to the two types of layered mesophases, LC-1 and LC-2, formed by these polymers. In these phases, the side chains are molten, with the main chains in the LC-1 and LC-2 phases assuming conformations similar to those in the K1 and K2 crystals, respectively. FPT-INDO calculations for the conformational energy have shown that the coplanar conformation in the K2 and LC-2 phases is strongly disfavored whereas the twisted conformation is stable. It is believed that the disfavored coplanar conformation observed in the K2 and LC-2 phases is forced by the layered segregation of the aromatic main chains and the long aliphatic side chains.

Introduction

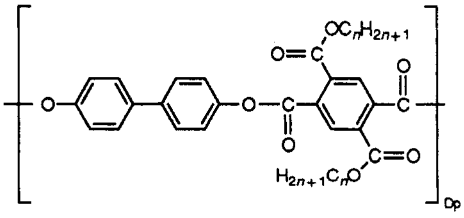
Over the past several years, there has been a considerable amount of effort directed toward the study of rigid-rod polyesters with long flexible side chains as a consequence of their ability to form thermotropic liquid crystalline phases.[1–18] Prior to and concurrent with these studies it was demonstrated that rigid-rod polymers with long alkyl side chains such as poly(γ-octadecyl L-glutamate) can form thermotropic cholesteric, smectic, and columnar phases.[19–23] Rigid-rod aromatic polyesters with long flexible alkyl side chains form thermotropic phases, but in this case they exhibit novel layered structures.[1–18] These layered structures are characterized by a lateral packing of the aromatic main chains into layers, with the fluidlike alkyl side chains occuping the space between the layers. It has been postulated that the driving force for the adoption of such a structure is a type of microphase separation of the aliphatic and aromatic domains. In these layered structures, the liquid crystallinity is the result of a partial or total lack of positional order with respect to the main-chain packing within the layers and also by the fluidlike disordered alkyl side chains between the layers.[6,17] The crystalline phases that develop from the layered mesophases also have a layered structure. In this case, X-ray studies have shown that the main chains and side chains crystallize in a cooperative fashion.[12,17]

In these layered structures, it is of interest to determine how the aromatic main chains are packed into a monolayer. Since the main chains are accommodated within the confined space of a monolayer, their conformation is presumed to be different from that observed in aromatic polymers without side chains. Furthermore, the main-chain conformation may also be affected by how the surrounding alkyl side chains are accommodated into the space between the layers. In fact, several types of layered crystals and mesophases have been observed with different packing modifications,[7–9,17] suggesting a plurality of aromatic main-chain conformations.

The objective of this work has been to examine the main-chain and side-chain conformations in the layered crystals and mesophases of the B-C*n* polyesters, through the use of high-resolution solid-state ^{13}C NMR. Furthermore, an attempt has been made to interpret these spectra and estimate the polymer conformation by considering the ^{13}C NMR shielding constants and performing total energy calculations using the FPT (finite perturbation theory) method within the INDO framework.[24,25]

Experimental Section

The synthesis of B-C*n* polyesters (*n*, the carbon number of the alkyl side chain) has been described in a previous report.[10] Here,



n = 6, 8, 10, 12, 14, 16, 18

the B-C*n* polyesters with *n* = 6–18 were employed.

^{13}C MAS NMR spectra were recorded on a JNM GSX-270 NMR spectrometer operating at 67.8 MHz with cross polarization/magic angle spinning (CP/MAS) and variable-temperature (VT) accessories. Samples were contained in a cylindrical rotor composed of zirconia with an O-ring and spun at speeds up to 4.0 kHz as controlled by a spinning controller. The contact time

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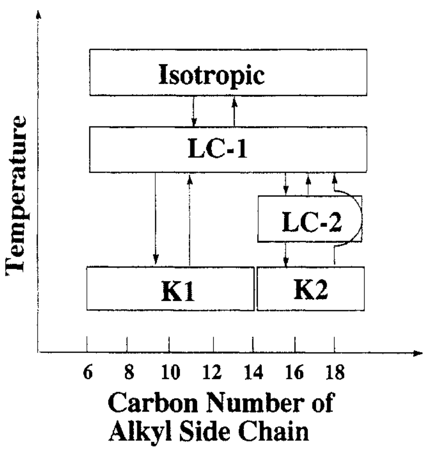

Figure 1. Schematic illustration of thermotropic phase behavior in B-C*n* polyesters.[17]

was 2 ms, and the repetition time was 3–6 s. The ^1H radiofrequency (rf) field strength was 60 kHz. Spectra were observed by the accumulation of 500–1000 scans so as to achieve a reasonable signal-to-noise ratio. The ^{13}C chemical shifts were calibrated indirectly with adamantane as the external standard (29.5 ppm relative to tetramethylsilane). ^{13}C MAS NMR spectra for the crystalline phases were observed by the CP/MAS method, while those for the liquid crystalline and isotropic phases were observed by the gated decoupling/MAS method.

The ^{13}C NMR shielding constant and the total energy calculations for the model compounds were performed using the INDO method incorporated with the FPT method.[24,25] The negative sign of the calculated ^{13}C NMR shielding means deshielding. The bond lengths and bond angles of a model compound as described by Coulter and Windle[26] are shown later in Figure 8. The calculations were carried out as a function of the torsion angles by using a SUN SPARC station 2.

Results and Discussion

1. Thermotropic Phase Behavior and Phase Structure of the B-C*n* Polyesters. In our previous studies,[10,13,17] we reported that the B-C*n* polyesters form two layered crystals (K1 and K2) and two liquid crystalline phases (LC-1 and LC-2). The phase behavior depends on the side-chain length as depicted in Figure 1.

In the layered K1 and K2 crystalline phases, the aromatic main chains are in a fully extended conformation with a repeat length of 16.6 Å and these are regularly packed within a layer. In addition, the side chains are also in a crystalline state between the layers. The X-ray pattern is indicative of a crystal structure with three-dimensional order,[17] which demands that the positional correlation between adjacent layers is maintained through the side-chain crystals. Thus, the crystal structure is likely built up by a close coupling of main-chain crystals and side-chain crystals. It is interesting to note that the main chains in the K1 and K2 crystals are packed in a different manner. For the K1 crystal, which is formed from the B-C*n* polyesters with side chains shorter than $n = 12$, the lateral packing distance of the main chains within a layer is 4.6 Å, but this reduces to 3.45 Å for the K2 crystal in the B-C*n* polyesters with side chains longer than $n = 16$. The polyester B-C14 has been found to have characteristics of both types of crystalline phases depending on the crystallization temperature.[18] The packing distance of 4.6 Å in the K1 crystal is reasonable for the main chains in a stable twisted conformation. In contrast, the short spacing of 3.45 Å in the K2 crystal indicates an unusually dense packing of the main chains that requires a conformation in which all the phenyl rings adopt a coplanar arrangement.[17]

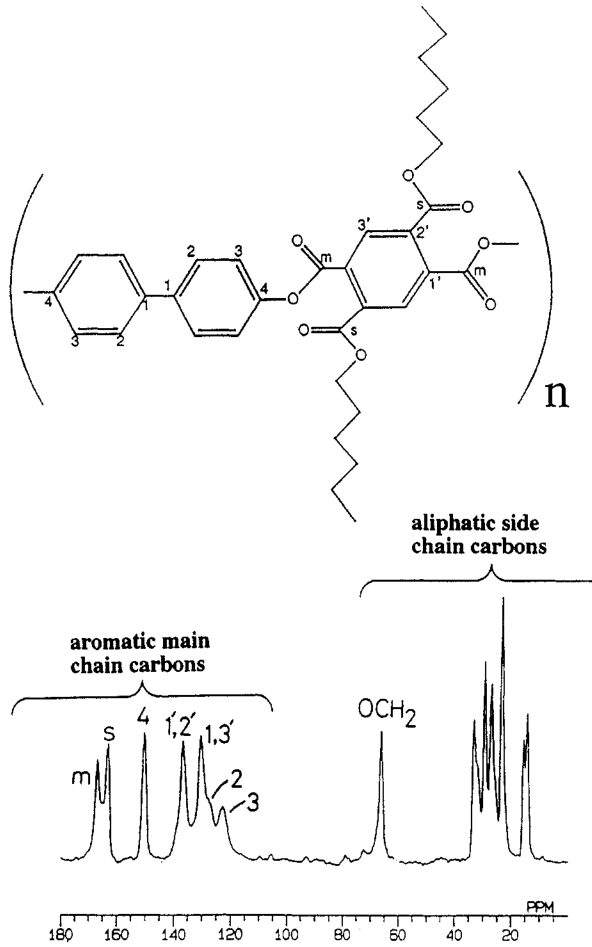

Figure 2. ^{13}C TOSS CP/MAS spectrum as observed for the crystalline phase of B-C6 with peak assignments.

The LC-2 phase, the lower temperature mesophase, also has a layered segregated structure similar to that of the crystalline phase although its fundamental structure is remarkably altered in several aspects from the crystal structure. The main chains are still in an elongated conformation (a repeat length of 16.6 Å) as in the crystalline phase, but they are packed into a layer having positional order only along the chain axis but not in the lateral direction. The side chains placed between the layers are in a molten state, which gives rise to the liquid crystalline fluidity of the phase. This type of liquid crystalline phase appears only for the B-C*n* polyesters in which the alkyl side chains are longer than $n = 14$ (see Figure 1).

The LC-1 phase, the higher temperature mesophase observed for all specimens, displays a nematiclike optical texture, but a classic nematic phase cannot be postulated because it still exhibits a lateral packing spacing as large as that in the LC-2 phase. A biaxial nematic phase has been tentatively proposed such that the layers are retained, but there are frequently irregularities in their packing.

This paper begins with an analysis of the main-chain and side-chain conformations in the layered K1 and K2 crystals, and in subsequent sections this is extended to measurements of the layered LC-1 and LC-2 mesophases.

2. ^{13}C NMR Studies of the Layered K1 and K2 Crystals. The solid-state ^{13}C NMR spectra of these polymers in the aromatic and carbonyl regions were found to be rather complicated due to a large number of side bands resulting from the large anisotropy of the individual shielding tensors.[25] In order to eliminate the side bands, thus simplifying the spectra, total suppression of side-band (TOSS) spectra was recorded. A typical example is shown in Figure 2 for B-C6 in the crystalline state. Here,

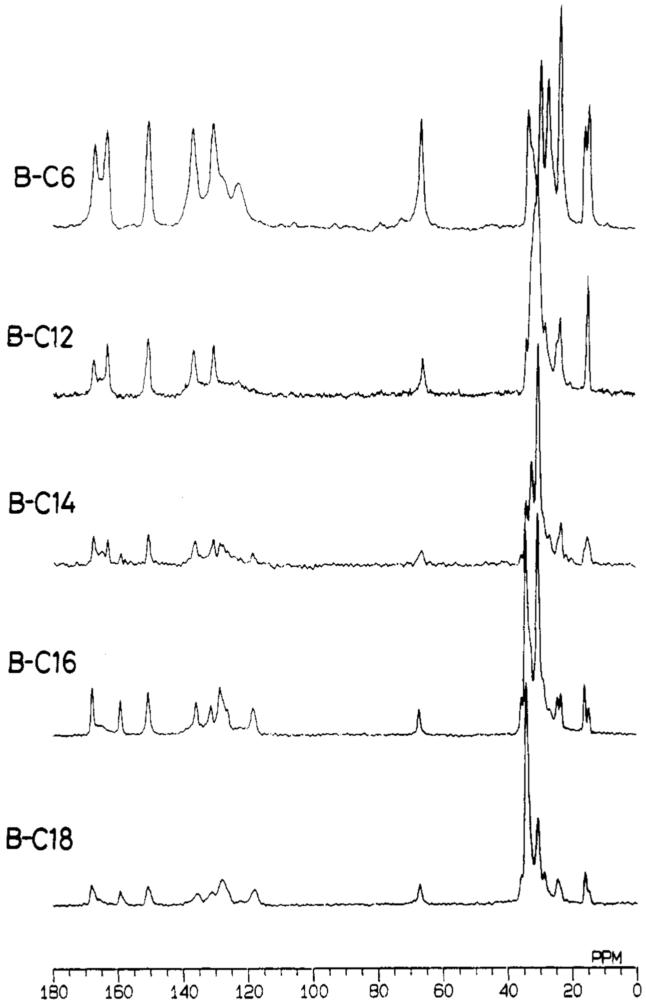

Figure 3. ^{13}C TOSS CP/MAS NMR spectra of B-C*n* polyesters in the crystalline state.

the peaks in the region of 100–180 ppm can be assigned to the aromatic main-chain carbons and the peaks in the region of 10–80 ppm to the aliphatic side-chain carbons.

The clear resolution of the component carbon atom signals is extremely advantageous in attempting to elucidate the conformation of the polymer in the two different crystalline phases, K1 and K2 phases. Figure 3 shows ^{13}C TOSS CP/MAS spectra for B-C*n* polyesters in the crystalline state as obtained by annealing for 1 week at 80 °C. According to these spectra, the two types of crystalline modifications are different with respect to their main-chain conformations and intermolecular interactions. It is interesting to note here that the B-C14 polyester exhibits an NMR spectrum characteristic of both crystalline forms and thus its crystalline phase is bimorphic. These results agree with X-ray diffraction data.[17,18]

In order to obtain information concerning the conformation of the polymer, it is first necessary to accurately assign the peaks in the ^{13}C NMR spectrum. To accomplish this, the NMR spectra of the crystalline polymers were measured using the dipolar dephasing method with a delay time of 60 μs, a typical example of which is shown in Figure 4 for the K1 crystal of B-C12 and the K2 crystal of B-C16. These data, together with the reference data,[27-29] allow a well-defined assignment of the chemical shifts, which are given in Figure 2 and summarized in Tables 1 and 2. According to these tables, there are three distinct differences between the chemical shifts for the K1 and K2 crystals. First, the chemical shifts for the higher field carbonyl carbon atoms of the pyromellitic ester moiety are different. Second, the number of aromatic carbon peaks are different. Third, the aliphatic signals indicate that there are differences in the state of the alkyl side-chain crystals. Thus, we can come to a preliminary conclusion that two crystals are different in the conformation of the pyromellitic ester, biphenyl, and alkyl side-chain moieties.

2.1. Main-Chain Conformation. At first, we shall focus on the main-chain conformation. In order to discuss the relationship between the main-chain conformation and chemical shifts, the possibility of intermolecular interactions between neighboring aromatic main chains that can contribute to the chemical shift values must be taken into consideration. In this aromatic polymeric system, electrostatic interactions may occur. In fact, it has been found that a charge-transfer complex is formed between neighboring biphenyl and the pyromellitic ester moieties in both the layered crystals and mesophases.[13] Simmons and Natansohn,[30] however, have reported that even strong charge-transfer complex formation without conformational change results in ^{13}C NMR chemical shifts of about 1 ppm. Thus, we have concluded that the chemical shift behavior is mainly influenced by the conformation of the aromatic main chains and the influence of intermolecular interactions on the ^{13}C NMR chemical shift values can be considered as being negligible.

Conformation of the Pyromellitic Ester Moiety. Figure 5 shows schematically the ^{13}C NMR chemical shifts with their assignments for the carbon atoms of the pyromellitic ester moieties as measured for the K1 and K2 crystals. Two sharp peaks due to the main-chain and side-chain carbonyl carbons in the K1 crystals are observed at 167.5 and 163 ppm, respectively, whereas in the K2 crystal they appear at 167.5 and 159 ppm. The two aromatic carbons, C1′ and C2′, are observed as a single sharp peak at 136 ppm in the K1 crystal, but in the K2 crystal they are split into two sharp peaks at 131 and 136 ppm with equivalent intensities. The aromatic carbon C3′ is observed at 130 ppm in both crystals. These results indicate that there is a remarkable difference in the conformation of the pyromellitic ester moieties between the K1 and K2 crystals.

As shown in Figure 6, four plausible conformations can be considered for the pyromellitic ester moieties under the reasonable assumption that the ester groups are coplanar with the aromatic moiety.[26,31] These conformations can be classified into two groups as follows. In models i and iii, a 180° rotation about an axis (a dashed line in Figure 6) drawn between the C1′ and C2′ atoms fails to superimpose the carbonyl functionalities, resulting in the C1′ and C2′ carbon atoms experiencing different electronic environments with different chemical shifts. In contrast, superpositioning is possible in models ii and iv. Hence, the electronic environment (or the chemical shift) for C1′ and C2′ should be the same. Of these two confomrations ii and iv, conformation iv can be eliminated as a possibility because of the steric hindrance between the carbonyl oxygen atoms which would be forced to occupy positions in which the intermolecular distance is less than that required to accommodate the van der Waals radii.

As compared with the observed data, the pyromellitic ester moieties in the K1 crystal can be postulated to assume conformation ii. This conclusion is in agreement with the solution-state ^{13}C NMR study of benzenepolycarboxylic acids by Bruck and Rabinovits,[27] in which the pyromellitic acid moieties in DMSO solution assume conformation ii, with the C1′ and C2′ carbons appearing as a single peak at 135.3 ppm. The conformation of the pyromellitic ester moieties in the K2 crystal is believed to be either

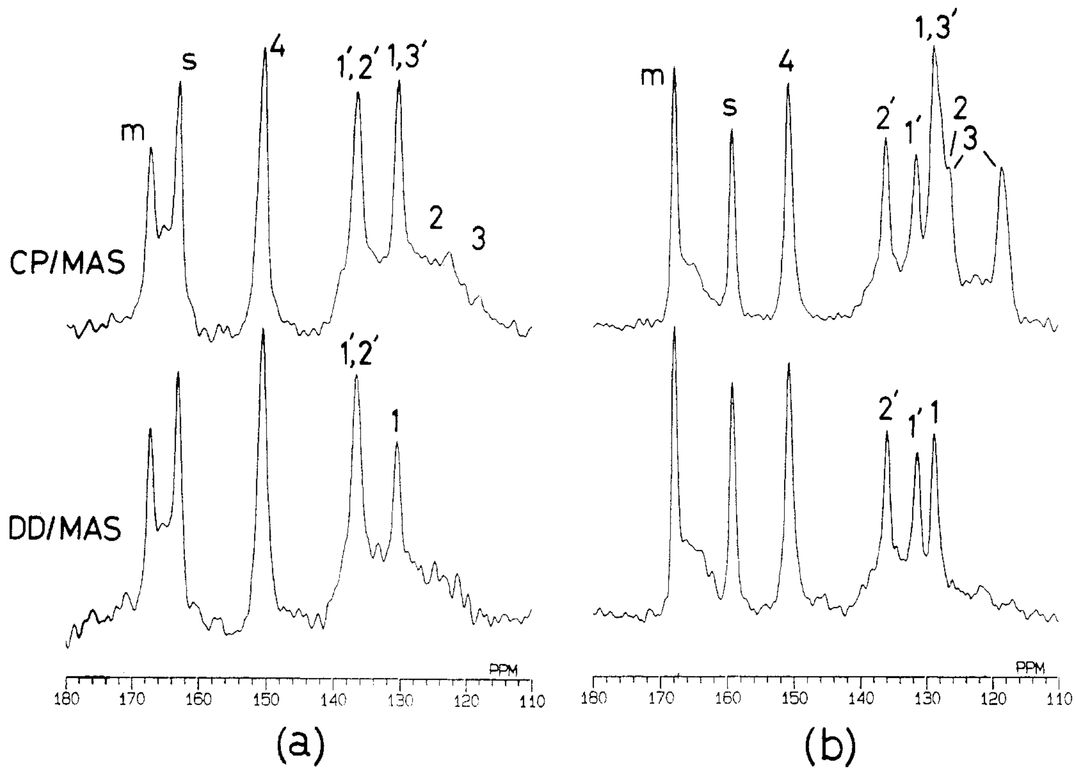

Figure 4. Expanded aromatic region of the ^{13}C MAS spectra for the two typical B-C*n* crystals using CP and dipolar dephasing (DD) methods: (a) the K1 crystal of the B-C12 polyester and (b) the K2 crystal of the B-C16 polyester.

Table 1. Observed ^{13}C NMR Chemical Shifts for the Aromatic Carbons of the B-C*n* Polyesters in the Crystalline State

	obsd ^{13}C NMR chemical shift (ppm)									
	C=O									
	m[a]	s[b]	C4	C2'	C1'	C3'	C1	C2	C3	
B-C16 soln[c]	165.6	164.7	150.2	134.6		130.0	130.0	128.3	121.5	
K1 crystal										
B-C6	167.5	163.5	150.7	136.1		130.0	130.0	128.0	122.8	
B-C12	167.3	163.2	150.5	136.5		130.4	130.4	128.0	122.6	
B-C14	167.3	163.2	150.5	136.5		130.4	130.4	128.0	122.6	
K2 crystal										
B-C14	167.6	158.8	150.6	136.0	131.5	130.0	128.0	128.0	126.2	117.8
B-C16	168.0	159.2	150.7	135.9	131.4	130.3	128.5	127.8	126.4	118.5
B-C18	168.1	158.2	150.9	135.6	131.0	130.1	128.1	128.1	126.2	118.4

[a] m, in the main chain. [b] s, in the side chain. [c] CDCl$_3$ solution.

Table 2. Observed ^{13}C NMR Chemical Shifts for the Aliphatic Carbons of the B-C*n* Polyesters in the Crystalline State

	obsd ^{13}C NMR chemical shift (ppm)						
		interior		α		methyl	
	COOCH$_2$	cryst	arom	cryst	arom	cryst	arom
B-C16 soln[a]	66.8		29.7		22.7		14.1
K1 crystal							
B-C6	66.3				23.4	15.7	14.4
B-C12	65.8	32.0	30.4		23.4		14.7
B-C14	66.3	32.3	30.3		23.2		15.0
K2 crystal							
B-C14	67.3	33.9	30.3	24.6	23.2	16.1	14.8
B-C16	67.3	34.3	30.5	24.6	23.5	16.1	14.8
B-C18	67.1	34.2	30.7	24.6	23.5	16.1	14.9

[a] CDCl$_3$ solution.

conformation i or iii. INDO calculations of a model compound indicate that conformation iii is more stable than conformation i and so may represent the conformation of the pyromellitic ester moiety in the K2 crystal.

Conformation of the Biphenyl Moiety. Figure 7 illustrates the observed ^{13}C chemical shifts with their assignments for the carbons of the biphenyl moieties in the K1 and K2 crystals. A difference in the conformation of the biphenyl moieties in the two crystals is apparent. Both crystals show the same chemical shifts at 128 and

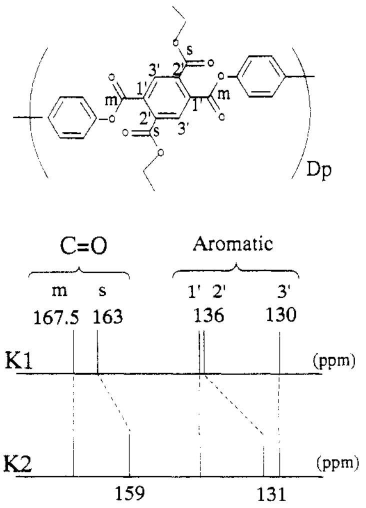

Figure 5. Diagram of the observed ^{13}C chemical shifts for the carbons of the pyromellitic ester moiety in the K1 and K2 crystals.

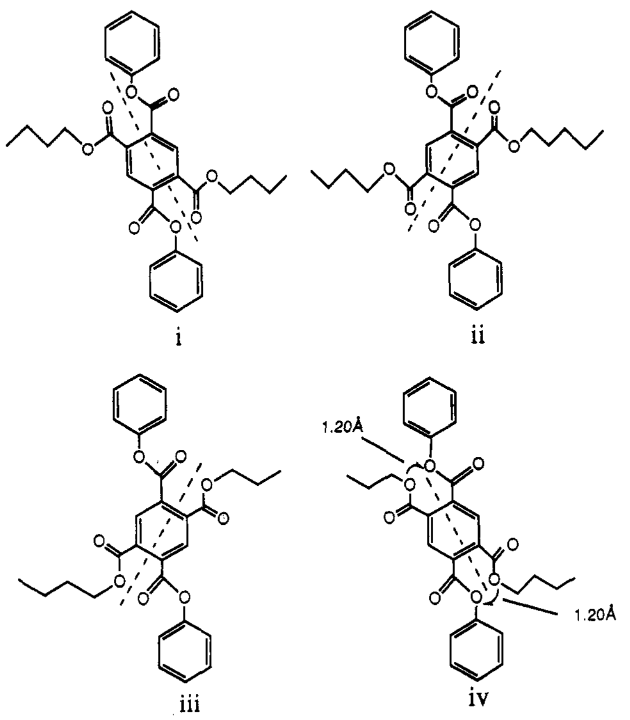

Figure 6. Four possible conformations for the pyromellitic ester moieties of the B-C*n* polyester.

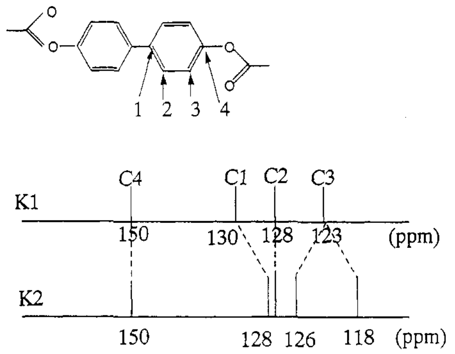

Figure 7. Diagram of the observed ^{13}C NMR chemical shifts of the carbons in the biphenyl moiety in the K1 and K2 crystals.

150 ppm for the C2 and C4 carbons, respectively, but the values for the C1 and C3 carbons are remarkably different (130 ppm for the C1 carbon and 123 ppm for the C3 carbon in the K1 crystal; 128 ppm for the C1 carbon and 126 and 118 ppm for the C3 carbon in the K2 crystal).

It is known that the two phenyl rings of the biphenyl moiety can rotate around the linking bond. It is also well-known that the most stable conformation for the biphenyl group is one in which the phenyl rings are twisted relative to each other. In addition, such a twisted conformation is preferred in solution and the isotropic melt.[32,33] The chemical shifts determined for the isotropic solution and melt of B-C16 are listed in Table 1 and lately in Table 4. It is interesting to note that these chemical shifts are quite similar to those in the K1 crystal. This leads to the simple conclusion that the biphenyl group in the K1 crystal assumes a twisted conformation as in solution and the isotropic melt and dictates that in the K2 crystal the biphenyl group assumes as anomalous conformation.

This conclusion is consistent with that deduced from the X-ray observation, according to which the molecular distance of 3.45 Å between neighboring main chains within a layer is unusually short in the K2 crystal relative to the value (4.7 Å) in the K1 crystal.[17] The latter value can be expected for a twisted conformation, but the former value, corresponding to the van der Waals radius of the phenyl ring, can be accounted for only by a coplanar arrangement of the aromatic groups. It is therefore proposed that the difference in the chemical shift values, especially for the C1 and C3 carbons between K1 and K2, is due to this conformational difference.

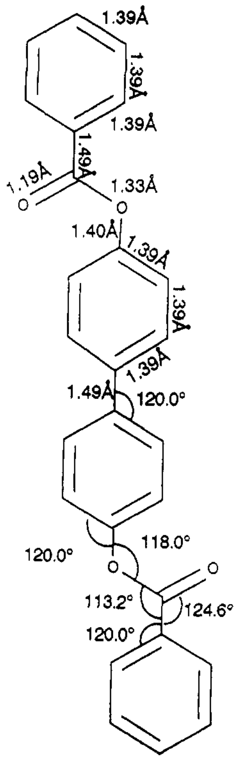

Figure 8. Model compound and the geometric parameters for the FPT-INDO calculation.

To test this hypothesis, the INDO calculations of the total energy and ^{13}C NMR shieldings for the model compound of Figure 8 were performed as a function of the two torsion angles, Φ and Ψ, which correspond to the angles between the two phenyl rings in the biphenyl moiety and between the phenyl rings of the biphenyl and pyromellitic moieties, respectively (refer to Figure 9). The geometric parameters given in Figure 8 are based upon X-ray diffraction data of aromatic ester compounds.[26] In performing the calculation, it was hypothesized that the carbonyl group and aromatic group of the pyromellitic ester moiety are coplanar.[26,31] Furthermore, it was presumed that the two pyromellitic ester moieties surrounding the biphenyl groups lie on the same plane, as shown in Figure 9. This is based upon X-ray data which indicates that the repeat distance along the chain axis corresponds to the length of the repeat unit in the polymer.[17] Under these assumptions, the calculations can be performed such that the torsion angles Φ and Ψ are varied under the condition of $\Phi = 2\Psi$ (refer to Figure 9).

Figures 10 and 11 show the variations of the total energy and the calculated ^{13}C NMR shieldings with the torsion angle Ψ, respectively. It is apparent from Figure 10 that the twisted conformation with $\Phi = 120°$ and $\Psi = 60°$ is the most stable. It should be noted here that these values of Φ and Ψ are approximate to those which have been evaluated for the most stable conformations.[26,31–33] Furthermore, this figure also indicates that the coplanar conformation ($\Phi = \Psi = 0°$) is very unstable, being approximately 20 kcal/mol less stable than the most stable twisted conformation. Thus, the coplanar conformation expected for the K2 crystal is strongly disfavored.

From Figure 11, on the other hand, one can find that the ^{13}C chemical shifts strongly depend on the torsion

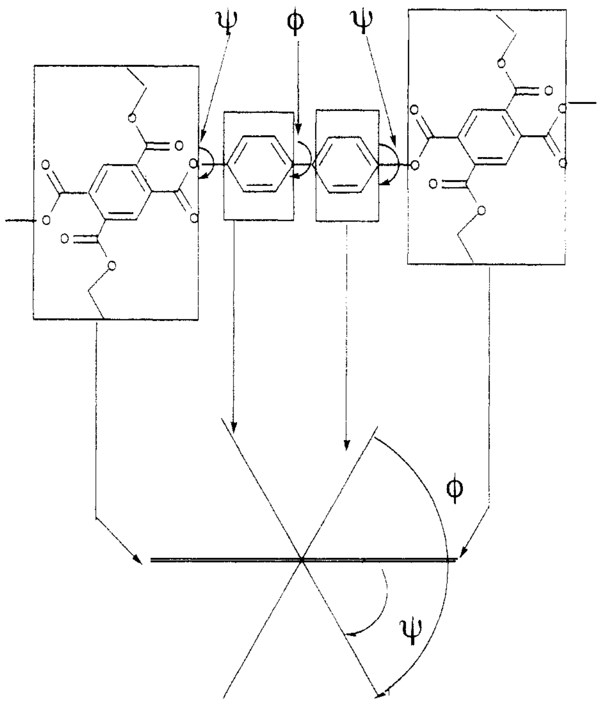

Figure 9. Torsion angles, Φ and Ψ, defining the relative twist between aromatic groups in the main chain.

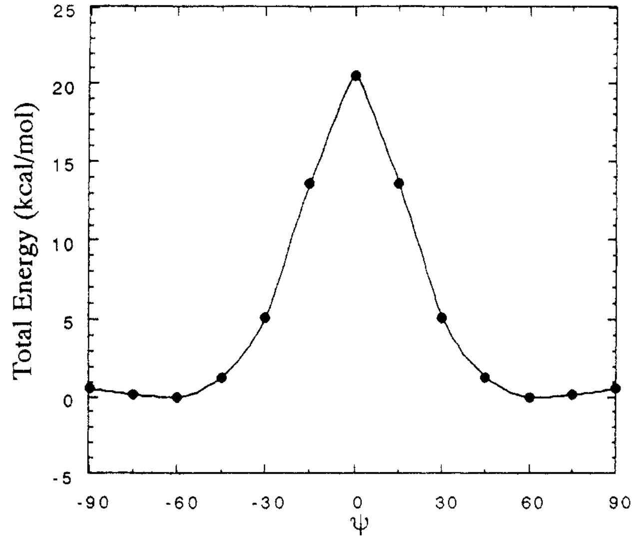

Figure 10. Calculated total energy as a function of the relative torsion angle, Ψ, under the condition $\Phi = 2\Psi$.

angle Ψ so as to allow the deduction of the conformation based upon these values. The difference in the chemical shifts between the most stable twisted conformation and the anomalous coplanar conformation is striking. When Ψ decreases from 60° to 0°, that is, when the conformation changes from the twisted form to the coplanar one, the C3 carbon signal undergoes a large splitting into two distinct components at higher and lower field and the C1 carbon peak shifts to a higher field. Moreover, with this conformational change, the C4 carbon peak does not change position and the C2 carbon peak undergoes only a slight splitting into two components. As compared with the observed data in Figure 7, this trend in the calculated ^{13}C NMR shieldings qualitatively corresponds to that observed experimentally. Thus, the FPT-INDO calculations support our suggestion that the main chain in the K1 crystal assumes a twisted conformation, while in the K2 crystal all of the aromatic rings of the main chain are in a nearly coplanar arrangement.

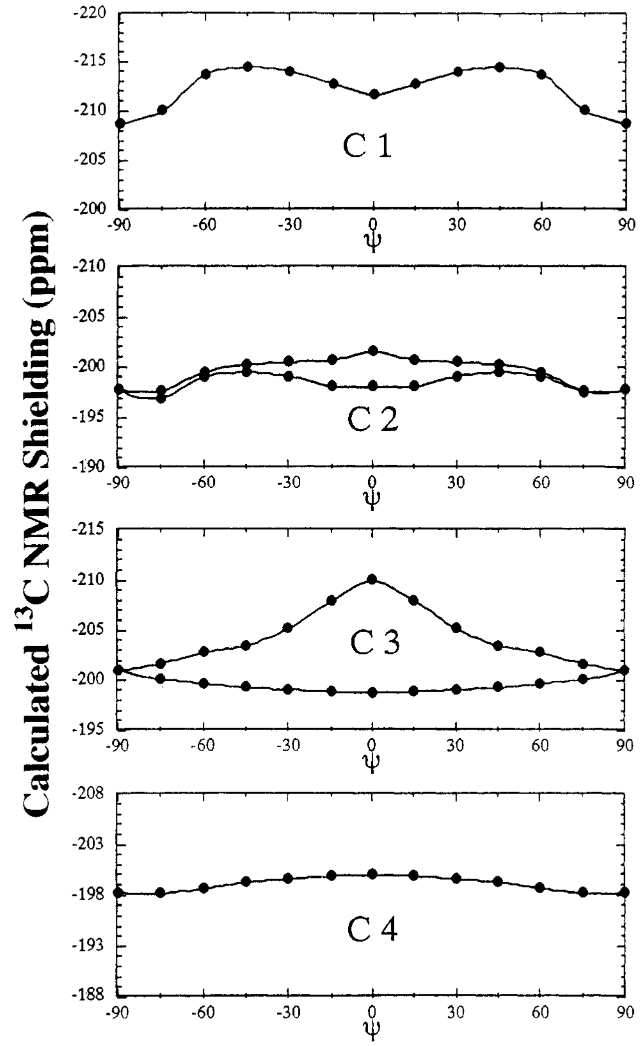

Figure 11. Calculated ^{13}C NMR shieldings of the carbons of the biphenyl moiety as a function of the relative torsion angle, Ψ, under the condition $\Phi = 2\Psi$. The negative sign indicates deshielding.

Recently, Tashiro et al.[34] have reported that Raman spectroscopy is an effective method for examining the conformation of biphenyl groups based upon the detection of a Raman active band at about 420 cm^{-1} which appears for the twisted form of the biphenyl group but is absent in the coplanar form. Our observations of the Raman spectra for the K1 and K2 crystals have supported the conclusion based upon the NMR studies. The results will be reported in more detail in a future paper.[35]

In Figure 12 are illustrated the two distinct conformations of the aromatic main chains in the K1 and K2 crystals which are deduced from the overall data.

2.2. Conformation of the Alkyl Side Chain. Figure 13 shows the expanded aliphatic region of the ^{13}C CP/MAS spectra for the K2 crystal of B-C16 and the K1 crystal of B-C12. The assignment of n-alkyl peaks is performed by reference data on n-alkanes as determined by VanderHart[36] and the observed chemical shifts are summarized in Table 2.

Ishikawa et al.[37] have analyzed the crystalline phases of polymethylene by high-resolution solid-state ^{13}C NMR spectroscopy. A similar analysis has been performed for the crystals of the alkyl side chains in poly(γ-octadecyl L-glutamate).[38] According to these studies, the signals for the methylene carbon atoms loaded in the interior of the chain appear at 32.8, 34.2, 33.2, and 30.5 ppm when these are in orthorhombic crystal, triclinic crystal, rotator,

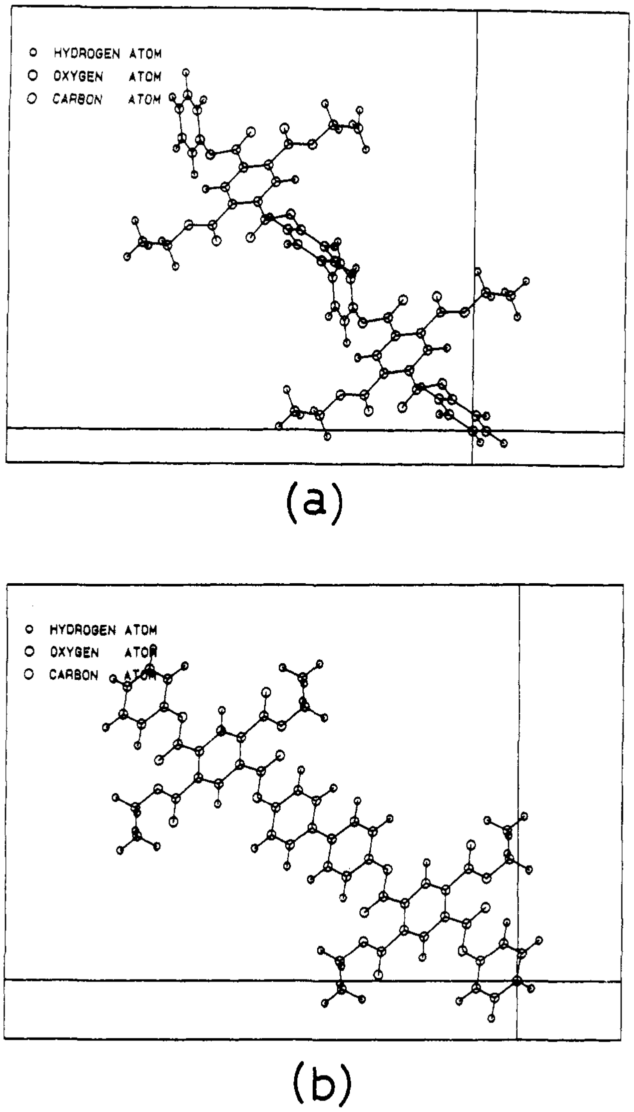

Figure 12. Chain conformations in (a) K1 and (b) K2 crystals according to the FPT-INDO calculation.

and amorphous phases, respectively.[37] The present results show that the methylene carbon atoms in the interior of the alkyl side chain in the K2 crystal of B-C16 appear at 30 and 34 ppm (see Table 2). In the K2 crystals, hence, the alkyl side chains crystallize into a tricilinic form, although the amorphous part is also included to some extent. The triclinic crystalline form in the K2 crystal is supported by X-ray diffraction studies.[18] On the other hand, the K1 crystal of B-C12 shows the main peak at 30 ppm, which is overlapped by a small peak at 32 ppm. The side-chain crystallization, thus, is not well progressing in this crystalline phase because of the short length of the side chain.

3. ^{13}C NMR Studies for LC-1 and LC-2 Mesophases. First, we shall focus on the side-chain conformation in the mesophases. The expanded aliphatic region of the ^{13}C NMR spectra for the B-C16 polyester in the LC-2 phase together with the isotropic phase is shown in Figure 14. The ^{13}C chemical shifts are listed in Table 3. The chemical shift values clearly show that the aliphatic side chains are in a molten state and fluidlike in the LC-1 and LC-2 phases as well as in the isotropic phase. Furthermore, it is apparent from Figure 14 that in the liquid crystalline phases the half-widths of the O–CH$_2$ and δ-CH$_2$ carbon atoms, which are near the main chain, are larger than those of other carbons, although in the isotropic phase the widths of all the aliphatic carbons are almost the same. These differences are believed to originate from inhomogeneities in the molecular motion of the alkyl side chains. Therefore, in the layered liquid crystals, the aliphatic carbons near

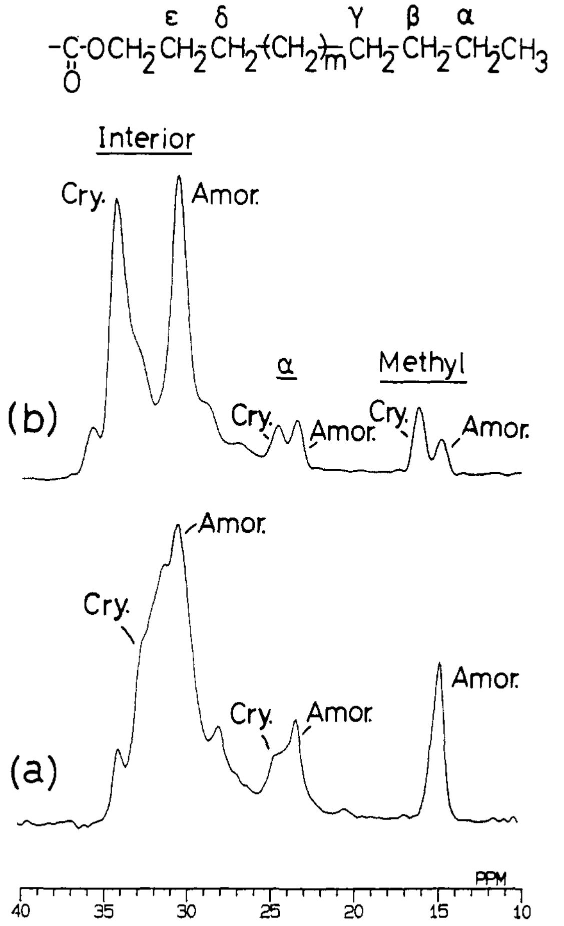

Figure 13. Expanded aliphatic region of the ^{13}C CP/MAS spectra for (a) the K1 crystal of B-C12 and (b) the K2 crystal of B-C16.

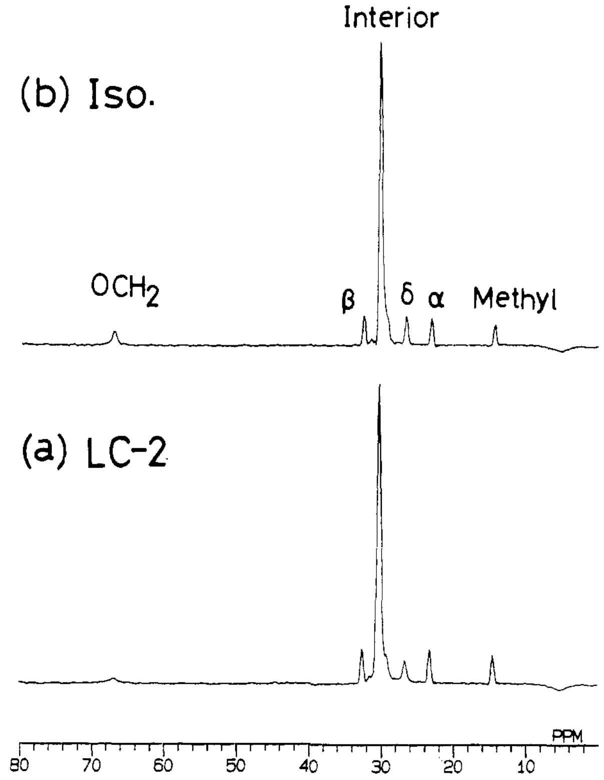

Figure 14. Expanded aliphatic region of the ^{13}C MAS spectra for (a) LC-2 and (b) isotropic phases of B-C16, as observed by the gated decoupling/MAS method.

Table 3. Observed ^{13}C NMR Chemical Shifts for the Aliphatic Carbons of the B-C16 Polyesters at Various Temperatures

	obsd ^{13}C NMR chemical shift (ppm)								
			interior			α		methyl	
temp (°C)	$COOCH_2$	β	cryst	arom	δ	cryst	arom	cryst	arom
25 (K2)	67.3	35.9	34.3	30.5	28.7	24.6	23.2	16.1	14.8
96 (LC-2)	67.0	32.7		30.5	26.7		23.4		14.6
148 (iso)	67.0	32.3		30.1	25.5		23.0		14.3

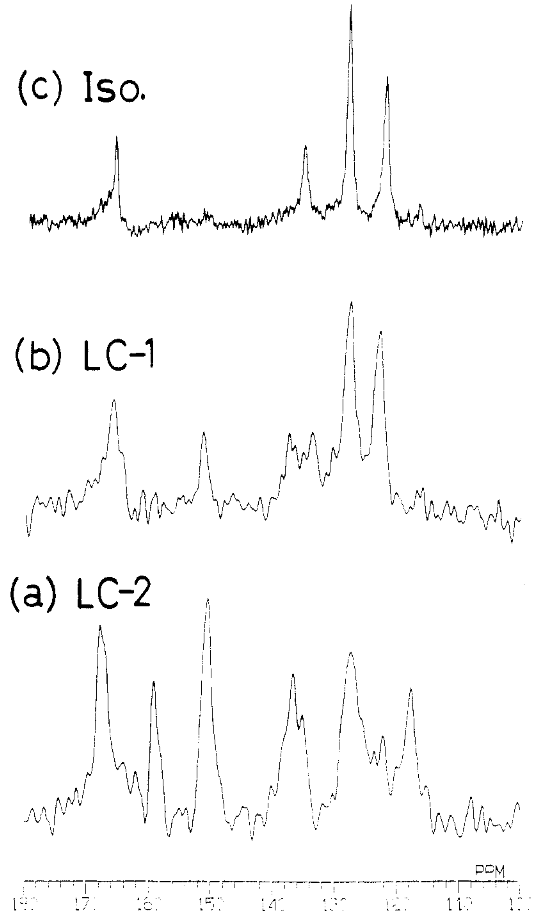

Figure 15. Expanded aromatic region of the ^{13}C MAS spectra for (a) the LC-2 of B-C16 as observed by the CP method and (b) the LC-1 of B-C12 and (c) the isotropic phase of B-C16 as observed by the gated decoupling/MAS method.

the main chain have less mobility than the other carbons. The formation of the layered structure is believed to restrict the molecular motion of the aliphatic carbon atoms near the main chains.

Figure 15 shows an expansion of the aromatic region of the spectra for the LC-1 (B-C12), LC-2 (B-C16), and isotropic phases (B-C16). The chemical shifts are listed in Table 4. Although the spectra are somewhat broad compared to those in the crystalline phases, we can reach the conclusion that the chemical shift values of LC-1 and LC-2 are similar to those of the K1 and K2 phases, respectively. This is especially evident in the spectra of the LC-2 and K2 phases which are identical, indicating that in this liquid crystalline phase all the aromatic groups are on a coplane, with the pyromellitic ester functionalities situated asymmetrically about an axis drawn between the C1′ and C2′ carbons. In the LC-1, the twisted conformation as in the K1 crystal can also be assumed according to the rough correspondence of the chemical shift values although a significant difference in the chemical shifts of the carbonyl carbons is observed (compare Tables 1 and 4). This difference may result from a greater degree of molecular motion of the main chain and side chains in the mesophase.

Concluding Remaks

High-resolution solid-state ^{13}C NMR spectra have provided detailed information about the main-chain and side-chain conformations in the crystalline and liquid crystalline phases of the B-C*n* polyesters. In the K1 crystal, the biphenyl moieties assume a twisted conformation. In addition, the phenyl rings of the biphenyl and pyromellitic moieties are also twisted about the ester bond. In the K2 crystal, in contrast, all the aromatic rings in the main chain are on the same plane and the side chains are packed into a triclinic lattice. In the LC-2 phase, the main-chain conformation is the same as that in the K2 crystal although the side chains are in a molten state. In the LC-1 phase, on the other hand, the main-chain conformation is similar to that observed in the K1 crystal.

FPT-INDO calculation as well as the reference data indicates that the twisted main-chain conformation in the K1 and LC-1 phases is the most stable while the coplanar conformation in the K2 and LC-2 phases is to be strongly disfavored. When considering that the K2 and LC-2 phases arise from the B-C*n* polyesters with side chains longer than $n = 14$, it is obvious that the anomalous coplanar conformation is the result of the long alkyl side chains segregating in the space between main-chain layers. On this point, the results obtained in a previous study[17] are interesting, in which the thermal stability of the K1 and K2 crystalline phases, i.e., the melting temperature, is remarkably altered by the side-chain length. The melting temperature drops significantly with an increase of *n* from 6 to 10 but then increases again with a further increase of *n*. The two distinct regions identified in the phase diagram are obviously related to the crystal structures or the polymer chain conformation. The decreasing region, observed for the shorter side-chain B-C*n*, corresonds to the lowering of the thermal stability of the K1 crystal, showing that its crystal structure is determined mainly by the polymer backbone with a perturbation by the shorter side chains. On the other hand, the regime of increasing thermal stability, observed in the longer side-

Table 4. Observed ^{13}C NMR Chemical Shifts for the Aromatic Carbons of the B-C*n* Polyesters in the Various States

	obsd ^{13}C NMR chemical shift (ppm)								
	C=O								
	m[a]	s[b]	C4	C2′	C1′	C3′	C1	C2	C3
iso (B-C16)	165.7	164.2	150.8	134.8	134.8	130.3	130.3	128.2	121.9
LC-1 (B-C12)	165.7	165.0	150.7	137.0	134.0	130.3	130.3	128.2	122.6
LC-2 (B-C16)	168.1	158.2	150.7	136.6	131.0	130.0	128.6	128.6	126.0, 118.0

[a] m, in the main chain. [b] s, in the side chain.

chain polyesters, corresponds to an enhancement of the thermal stability of the K2 crystal. The structure in the K2 crystal, hence, is strongly dominated by the crystallization of the long alkyl side chains. This may result in the anomalous coplanar conformation of the backbone and hence an anomalously dense packing of the backbones within a layer, although we cannot give a clear answer as to why the coplanar conformation is still retained even in the LC-2 mesophase in which the side chains are in a molten state.

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