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Conformation and Dynamic Aspects of Poly(γ-*n*-octadecyl L-glutamate) in the Solid State and Liquid-Crystalline State As Studied by Variable-Temperature ^{13}C CP/MAS NMR Spectroscopy

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ABSTRACT: ^{13}C CP/MAS NMR experiments are carried out for poly(γ-*n*-octadecyl L-glutamate) as a function of temperature, in order to elucidate dynamic and conformational features in the solid state and liquid-crystalline state. From these experimental results, it is found that the main chain of the polymer takes on a right-handed α-helical conformation within the temperature range from 27 to 100 °C, while long *n*-alkyl side chains take on an all-trans zigzag conformation in the crystalline state at room temperature and are in a mobile state above 35 °C. Further, it is found that at about 40 °C the α-helical main chain in the liquid-crystalline phase is undergoing molecular motion at a frequency of ca. 60 kHz.

Introduction

Recently, Watanabe et al.[1] have reported that in a series of α-helical poly(L-glutamates) with *n*-alkyl side chains of various lengths (*n* (number of carbon atoms in the alkyl group) = 4–18), *n*-alkyl side chains longer than *n* = 10 form a crystalline phase composed of paraffin-like crystallites together with the α-helical main chain packing into a characteristic layer structure. The polymers form thermotropic cholesteric liquid crystals by the melting of the side-chain crystallites. In order to investigate the structure and dynamics of these thermotropic cholesteric liquid crystals, it is important to collect detailed information about the main-chain and side-chain structures and motions at various temperatures.

It has been demonstrated that ^{13}C cross polarization/magic angle spinning (CP/MAS) spectroscopy is a very powerful tool for structural analysis of polymers in the solid state.[2] In a previous paper,[3] it was reported that, from the observation of ^{13}C NMR chemical shifts in the solid state, the main chain of poly(γ-*n*-alkyl L-glutamate) assumes a right-handed α-helical conformation irrespective of side chain length and that in the side-chain crystallites the *n*-alkyl chain assumes an all-trans zigzag conformation.[3] In these studies, ^{13}C CP/MAS experiments have been carried out only at room temperature. If ^{13}C CP/MAS NMR experiments can be done as a function of temperature, such experiments may present the potential for detailed insight into the molecular structure and dynamics of these polymers in the solid state and liquid-crystalline state.

The purpose of this work is to investigate the structure and dynamics of poly(γ-*n*-octadecyl L-glutamate) with a long *n*-alkyl chain in the solid state and liquid-crystalline state as a function of temperature.

Experimental Section

Materials: Poly(γ-*n*-octadecyl L-glutamate) (PG-18, where the number of carbon atoms in the *n*-alkyl group follows the letters PG) was synthesized by ester-exchange reactions between poly(γ-methyl L-glutamate) (M_v = 100 000) and *n*-octadecyl alcohol as described in a previous paper.[1] The complete replacement of methyl groups by *n*-alkyl groups was confirmed by the ^{1}H NMR spectra. The film of PG-18 was prepared by casting the solution from chloroform at room temperature.

Measurements. ^{13}C CP/MAS NMR spectra were measured by means of JNM-GX270 NMR (67.5 MHz) with a variable-temperature (VT) CP/MAS accessory at temperatures from room temperature (27 °C) to 100 °C. The sample (ca. 200 mg) was contained in a cylindrical rotor made of ceramic materials and spun at 4.5–4.8 kHz. Contact time is 2 ms and repetition time 5 s. Spectral width and data points were 27 kHz and 8K, respectively. ^{1}H field strength was 1.6 mT for both the CP and decoupling process. The number of accumulations was 200–400. ^{13}C chemical shifts were calibrated indirectly through external adamantane (29.5 ppm relative to TMS).

Results and Discussion

In Figure 1 is shown the ^{13}C CP/MAS NMR spectrum of PG-18 at room temperature. Assignment of peaks for the CO(amide), CO(ester), C_α, and C_β carbons is straightforward in view of reference data for poly(γ-benzyl L-glutamate) as examined previously.[3] As for the C_γ car-

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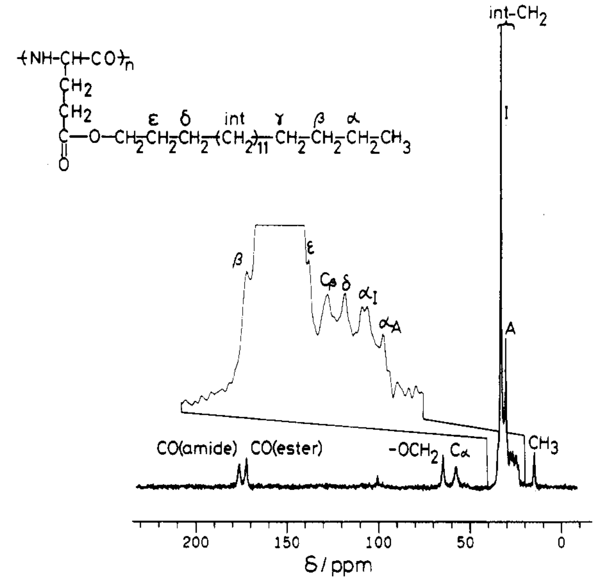

Figure 1. ^{13}C CP/MAS NMR spectrum of poly(γ-*n*-octadecyl L-glutamate) at room temperature. Peaks in the vicinity of 30 ppm are expanded. Assignment of each peak is done by reference data of poly(γ-benzyl L-glutamate) and *n*-alkanes in the solid state (see the text).

bon, the peak cannot be identified at low temperature because of the overlap with the interior CH$_2$ carbon peak, but at high temperature it clearly appears due to the upfield shift of the interior CH$_2$ carbon peak. The assignment of *n*-alkyl peaks is performed by reference data on *n*-alkanes as determined by VanderHart.[4] The main peak and small peak for the interior CH$_2$ carbons are designated by I and A, respectively. Peak I is ascribed to the all-trans zigzag conformation in the crystalline state, while peak A arises from the CH$_2$ carbons in the noncrystalline state, as described below.

It has been demonstrated that the ^{13}C chemical shifts of the CH$_2$ carbons in alkanes depend on the conformation and crystal structure[4-9] and that ^{13}C chemical shifts of CO(amide) and C$_\alpha$ carbons in polypeptides also depend on the main-chain conformation.[10-22] Therefore, much structural information about the main chain and side chain of PG-18 can be extracted from the observation of ^{13}C NMR chemical shifts.

At room temperature (27 °C), ^{13}C chemical shift values of CO (amide) and C$_\alpha$ carbons are 176.0 and 57.6 ppm, respectively. These values are characteristic for the right-handed α-helix conformation as shown in poly(γ-benzyl L-glutamate).[10] Also, ^{13}C chemical shifts of C$_\beta$ and CO (ester) carbons coincide with those of poly(γ-benzyl L-glutamate). This means that the inner part of side chain has the same conformation as poly(γ-benzyl L-glutamate). The peaks for the outer part of side chain appear in the vicinity of 30 ppm.

The ^{13}C chemical shift data of *n*-alkanes, cyclic alkanes, and polyethylene can be significantly used to discuss the conformation and crystal structure of the side chain CH$_2$ carbons.[4-9] It is known that the CH$_2$ carbon in alkanes appears at high field by 4–6 ppm if any carbon atom three bonds away is in a gauche conformation, rather than in a trans conformation.[23] In fact, the CH$_2$ carbons of cyclic alkanes and *n*-alkanes in liquid or solution and those of polyethylene in a noncrystalline state appear at higher field by 2–3 ppm than that in the crystalline state.[4-9] At 27 °C, the intense peak I and small peak A appear at 33.4 and 30.6 ppm, respectively. From the reference data on *n*-alkanes and polyethylene,[4,24] it is seen that peak I arises from the CH$_2$ carbons in the all-trans zigzag conformation and in the crystalline state (orthorhombic form) and that peak A arises from the CH$_2$ carbons in the noncrystalline state.

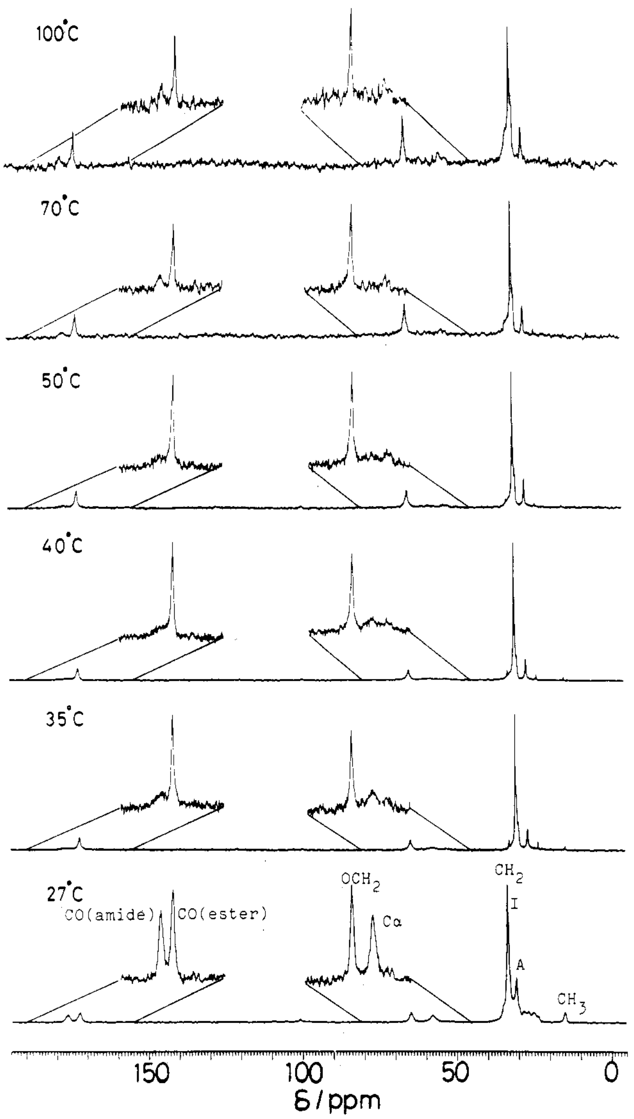

Figure 2. ^{13}C CP/MAS NMR spectra of poly(γ-*n*-octadecyl L-glutamate) as a function of temperature. The main-chain carbon peaks are expanded.

In Figure 2 are shown ^{13}C NMR spectra of PG-18 as a function of temperature and ^{13}C chemical shift values are listed in Table I. The *n*-alkyl CH$_2$ peaks are found to change observably as the temperature is increased, as shown in Figure 2. Peak I disappears above 35 °C and the intensity of peak A increases noticeably. This phenomenon is associated with the melting of side-chain crystallites.[1] When the temperature is further increased, peak A moves gradually upfield from 30.6 to 30.2 ppm. As indicated by the γ-effect concept,[23] the ^{13}C chemical shift moves upfield as the gauche population is increased due to an increase of temperature. Therefore, the above-mentioned upfield shift from 30.6 to 30.2 ppm means that the gauche population is increased as the temperature is increased. Such behavior is also identified in the case of the α-CH$_2$, β-CH$_2$, and CH$_3$ carbons.

Next, we are concerned with the temperature dependence of the line shape, intensity, and chemical shift for the main-chain carbons. An interesting feature is shown by these peaks. A progressive broadening of the CO (amide) and C$_\alpha$ peaks is observed. At about 40 °C, the peaks are broadened to the point of disappearing from the

Table I
^{13}C NMR Chemical Shifts of Poly(γ-*n*-octadecyl L-glutamate) at Various Temperatures

	^{13}C NMR chemical shift/ppm													
								β-CH_2[a]		interior CH_2[a]		α-CH_2[a]		
temp/°C	CO(amide)	CO(ester)	OCH_2	C_α	C_γ	C_β	δ-CH_2	C	A	C	A	C	A	CH_3
27	176.0	172.1	64.7	57.6		28.0	26.6	34.7		33.4	30.6	25.2	23.5	14.7
35		172.0	64.6	57.6			26.7		32.7		30.5		23.4	14.5
40		172.0	64.6		31.5		26.7		32.6		30.5		23.3	14.5
50		171.9	64.7		31.3		26.6		32.6		30.4		23.3	14.5
70	176.0	171.9	64.7		31.6		26.6		32.5		30.3		23.2	
100	176.0	171.8	64.7		31.5		26.7				30.2			

[a] C and A indicate the crystalline and noncrystalline states, respectively.

spectrum. As suggested by Lyerla et al.,[25] the broadening phenomenon can be explained on the basis that the reorientation rate of the main chain in the liquid-crystalline state becomes insufficient to average dipolar interaction with protons. This reduces the efficiency of the radiofrequency (rf) decoupling and leads to a maximum line width of the carbons when the molecular motion occurs at the frequency corresponding to the amplitude of the proton decoupling field (about 60 kHz for this experiment). Therefore, it can be said that the main chain is undergoing reorientation at a frequency of about 60 kHz. At temperatures above 50 °C, the main-chain carbon peaks become narrow and reappear in the spectra. This indicates that the efficiency of the rf decoupling is increased. In addition, the ^{13}C chemical shifts of the CO(amide) and C_α carbons are approximately independent of temperature. This means that the main chain assumes a right-handed α-helix at least within the temperature range from 27 to 100 °C. From these results, it can be said that the α-helical main chain is undergoing reorientation at a frequency of about 60 kHz in the liquid-crystalline phase (at about 40 °C).

Let us look carefully at the temperature change of other carbon peaks. As seen from Figure 2, the intensity of the CH_3 carbon peak becomes weak as the temperature is increased, and the peak then disappears above 70 °C. In addition, the α-CH_2 and β-CH_2 peaks also disappear at 100 °C. The disappearance of these peaks may be explained as follows. At high temperature the outer side-chain group may have a minimum in its proton $T_{1\rho}$ value and this results in an extremely weak ^{13}C peak through cross polarization since the proton is undergoing rapid reorientation before polarization transfer has proceeded to a significant degree. Because of this, the signal-to-noise level for the spectrum at 100 °C becomes lower than that at lower temperature. On the other hand, the OCH_2, CO(ester), δ-CH_2, and C_γ carbons in the side chains give sharp peaks at 100 °C. At 35 °C, the δ-CH_2 carbon has the highest intensity among them. As the temperature is further increased, the intensities of the OCH_2 and CO(ester) carbons become intense, and at 100 °C they are stronger than the δ-CH_2 peak. This indicates that the δ-CH_2 peak intensity passes through a maximum, while the OCH_2 and CO(ester) peak intensities are in the vicinity of the maximum. Therefore, it is suggested that the motion of the δ-CH_2 carbon is faster than that of the OCH_2 and CO(ester) carbons. As for the C_β carbon, the behavior of its peak intensity is similar to that of the main-chain carbons. From this, it can be said that the mobility of the C_β carbon is of the same degree as that in the main-chain carbons.

From the above results, the following can be concluded. The main-chain conformation of PG-18 assumes a right-handed α-helix within the temperature range from 27 to 100 °C. On the other hand, the side-chain conformation changes more abruptly between 27 and 35 °C. This phenomenon is associated with the melting of side-chain crystallites. In the liquid-crystalline state, the α-helical main chain is undergoing reorientation at a frequency of about 60 kHz, and the motion of the side-chain carbons becomes fast like that of liquid *n*-alkanes.

Registry No. PG-18 (SRU), 98540-59-1; PG-18 (homopolymer), 111265-56-6.

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