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Molecular Motion of the Main Chain for a Series of Poly(alkyl L-glutamate)s as Studied by ^{2}H NMR

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Abstract

^{2}H NMR measurements were carried out for a series of poly(alkyl L-glutamate)s (PALG) in which the ^{1}H of the amide group in the main chain is replaced by ^{2}H in order to investigate the mobility and motional mode of the main chain. At low temperature, the ^{2}H spectra were typical powder patterns which have three principal values. The temperature dependencies for the ^{2}H NMR spectra varied with the side chain length. For PALG with a short side chain length, $\Delta\nu_1$, $\Delta\nu_2$ and $\Delta\nu_3$ are almost constant in all temperature ranges. As the side chain length increases, the difference between the peaks and shoulders decreased with temperature. For PG-12-N-D, the peaks and shoulders are fused at high temperature in a liquid crystalline state. The mobility and molecular motion of the main chain is discussed based on the obtained ^{2}H NMR spectra.

Introduction

Poly(γ-n-alkyl L-glutamate)s (PALGs), in which the n-alkyl groups are introduced into the side chains of poly(L-glutamate) [1], show interesting features depending on the side chain length. The polymers with n-alkyl side chains longer than an n-decyl group form a crystalline phase composed of paraffin-like crystallites. This shows that the melt of the side chain crystallites induces a thermotropic liquid crystalline nature in the rigid α-helical main chain.

In general, the compounds that form liquid crystalline phases consist of both rigid and flexible parts. The phase behavior of the liquid crystalline polymers with the same mesogenic group is influenced by the flexible part. The mobility of the flexible part dominates the structure and dynamics of the liquid crystal. A knowledge of the molecular parameters such as molecular order and dynamics is of great interest for the applications of polymeric liquid crystals. Thus, in order to relate the physical properties of liquid crystals to their structural and dynamic behavior on a molecular level, the molecular order and mobility of the mesogenic and flexible parts must be characterized.

It has been reported that ^{13}C CPMAS NMR spectroscopy is a useful technique to characterize the structural and dynamic behavior of liquid crystalline polymers [2-5]. In a previous paper [6], VT CPMAS NMR measurements were carried out for a series of PALGs. For PALGs with short side chains, the mobilities and temperature dependence of the main chains are close to those of their side chains. As the number of carbon atoms in the side chain increases, the mobility of the side chain increases drastically with temperature. Therefore, for PALG with a long n-alkyl side chain, the mobility of the main chain is much slower than that of the side chain, especially at high temperature. This difference in mobility is one of the important factors for the formation of the liquid crystalline state. For the side chain carbons, from the ^{13}C chemical shift, information about the structure and molecular motion can be retrieved because individual carbon peaks are clearly separated. Long side chains form paraffin-like crystallites with an all-trans conformation at low temperature. In this state, the molecular motion is restricted. The molecular motion of the side chain with a long n-alkyl group in the liquid crystalline state or with a short n-alkyl group is similar to those of the amorphous phase of polyethylene or liquid paraffins. On the contrary, peaks for the main chain are almost disappeared because of their reorientational rate. The chemical shifts indicate that the

α-helix is maintained even at high temperature. However, the molecular motion of the main chain is not clear.

In this paper, selective labeling and ^2H NMR measurements were carried out for PALG in order to gain insight into the molecular motion of the main chain.

Experimental

Materials

Poly(γ-n-alkyl L-glutamate)s (PG-n, where n is the number of carbon atoms in the n-alkyl group) are synthesized by ester-exchange reactions between poly(γ-methyl L-glutamate) and the corresponding alcohols as described in a previous paper [6]. The selective labeling of ^1H in the amide group by ^2H is carried out using Chapman's method [7]. PG-n is dissolved in deuterated trifluoroacetic acid and this solution is stirred for 1 hour. The reaction mixture is poured into excess methanol. The obtained polymer is recrystallized with chloroform and methanol then dried. From the CPMAS NMR measurements, the obtained polymers took a right-handed α-helix conformation. For convenience, the deuterated sample is expressed by PG-n followed by N-D, such as PG-10-N-D.

Measurements

The ^2H solid state NMR spectra were measured with a quadrupole echo pulse sequence using a JNM-EX400WB (61MHz) NMR spectrometer at temperatures from -60 to 140°C.

Results and Discussion

In Fig.1a is shown the theoretical ^2H NMR spectrum in which the asymmetrical parameter, η, is 0.5. Separations, $\Delta\nu_1$, $\Delta\nu_2$ and $\Delta\nu_3$ have different values. If the symmetrical motion takes place, the molecular motion is reflected in the obtained spectrum as an axially symmetrical powder pattern. Fig.1b shows the ^2H NMR spectrum of PG-10-N-D at 40°C. This spectrum shows a typical powder pattern composed of inner peaks ($\Delta\nu_1$), shoulders ($\Delta\nu_2$) and outermost wings ($\Delta\nu_3$). Therefore, the molecular motion of PG-10-N-D at 40°C is restricted.

PLACE FIG.1 HERE

In order to investigate the molecular motion, it is important to determine the direction of the principal axis. In Fig.1c is shown the ^{2}H NMR spectrum of the 10% chloroform solution of PG-10-N-D. In this figure, two sharp ^{2}H peaks are observed. This indicates that all the N-D directions to the magnetic field in the sample are unique. In the magnetic field, it is known that PALG in the liquid crystalline state tends to orient to the magnetic field. The long axis of mesogenic α-helix becomes parallel to the magnetic field. This is confirmed by the ^{13}C NMR chemical shift by taking the principal axis of the chemical shift tensor into account [8]. The sample forms a nematic liquid crystal in the magnetic field. Splitting between the two peaks is about 250 kHz. This splitting corresponds to $\Delta\nu_3$. In the α-helix, N-D direction is almost parallel to the α-helix axis within 5°. The outermost wing in the ^{2}H NMR spectrum corresponds to the α-helix axis. The peak ($\Delta\nu_1$), and its shoulder ($\Delta\nu_2$) can be attributed to the axes perpendicular to the α-helix.

PG-4-N-D

In Fig.2 is shown the ^{2}H NMR spectra of PG-4-N-D as a function of temperature. As seen from this figure, it is found that typical powder patterns like Fig.1b are observed over the entire temperature range. In Fig.3 is shown the temperature dependencies of $\Delta\nu_1$ and $\Delta\nu_2$ obtained from Fig.2. As seen from Fig.3, $\Delta\nu_1$ and $\Delta\nu_2$ are almost constant in the observed temperature range. The typical powder pattern with $\eta \neq 0$ and an invariance of $\Delta\nu_1$ and $\Delta\nu_2$ mean that the exchanges between the principal axes do not occur, in other words, the molecuar motion is restricted. If certain molecular motions are taking place, changes should be observed for $\Delta\nu_1$ and $\Delta\nu_2$. From the ^{13}C CPMAS NMR spectra [6], the peak of the main chain carbons (carbonyl and C_α) decreased in intensity, but did not completely disappeared. If the disappearance of the CPMAS peak takes place during successive increases in the temperature, it means that the molecular motion with the rate close to the frequency of the dipolar decoupling (60 kHz for EX400WB) occurs. As the peak intensity decreased with temperature, a certain molecular motion is taking place. However, its mobility is much slower than the decoupling frequency. In this case, both from the ^{2}H and ^{13}C CPMAS NMR, while the molecular motion takes place in PG-4-N-D, the rate of the molecular motion in PG-4-N-D is much slower than several tens of kHz.

PLACE FIG.2 AND 3 HERE

PG-6-N-D and PG-8-N-D

The ^{2}H NMR spectra of both PG-6-N-D and PG-8-N-D showed similar temperature behaviors. In Fig.4 is shown the ^{2}H NMR spectra of PG-8-N-D as a function of temperature. As seen from Fig.4, it is found that typical powder patterns, $\eta \neq 0$, are observed at all temperatures. Therefore, the molecular motion of the main chain is restricted. Since wings are clearly observed in all spectra, exchanges between the α-helix axis and others do not occur in the measured temperature range. As for the inner peaks and shoulders, the inner peaks move to outside and the shoulder inside as the temperature increases. In Fig.5 is shown the temperature dependencies of $\Delta\nu_1$ and $\Delta\nu_2$. As seen from Fig.5, $\Delta\nu_1$ and $\Delta\nu_2$ increase and decrease, respectively, as the temperature increases. This indicates that a certain molecular motion which averages out between the principal axes perpendicular to the α-helix axes takes place. As the inner peaks and shoulders are not completely averaged, the motion may be slower than the difference between the inner peaks and shoulders. The difference between the inner peaks and shoulders is about 60 kHz. Therefore, the rate of molecular motion seems to be close to several tens of kHz. From the previous results for the ^{13}C CPMAS NMR [6], peaks for the main chain carbons (carbonyl and Cα) disappeared at high temperature. As mentioned above, the disappearance of the ^{13}C CPMAS peaks means that the rate of molecular motion is close to the frequency for dipolar decoupling, about 60 kHz. The rate for the molecular motion obtained from the ^{2}H NMR is in good agreement with that from the ^{13}C CPMAS NMR. Since the outer most wings are unchanged, the molecular motion occurring in these samples must reflect the experimental results. As described above, the outer most wings correspond to the α-helix axis. The molecular motion taking place in these samples does not mix the principal axis parallel to the α-helix axis with those perpendicular to the the α-helix axis. The molecular motion simultaneously averages the principal axes perpendicular to α-helix axis. The molecular motion derived from these obtained results is the rotation or vibration around the α-helix axis. For PG-6-N-D ~PG-8-N-D, this motion is activated as the temperature increased. The rate of this motion

increased and became close to several tens of kHz with temperature.

PLACE FIG.4 AND 5 HERE

PG-10-N-D and PG-12-N-D

In Fig.6 is shown the ^{2}H NMR spectra of PG-12-N-D as a function of temperature. As seen from Fig.6, it is noted that the existence of the outer most wings are confirmed even at 100°C. Similar to PG-4-N-D, PG-6-N-D and PG-8-N-D, this principal axis does not exchange with other axes in this sample. Both inner peaks and shoulders exist at low temperature. As the temperature increases, the inner peaks and shoulders moves to the outside and inside, respectively. At high temperature, the shoulder completely disappeared and these peaks are fused together. In Fig.7 is shown the temperature dependencies of $\Delta\nu_1$ and $\Delta\nu_2$. As the temperature increases, $\Delta\nu_1$ and $\Delta\nu_2$ gradually increase and decrease, respectively. These slow changes mean that the molecular motion increases step by step. At the temperature above 80°C, $\Delta\nu_2$ suddenly decreased and $\Delta\nu_1$ and $\Delta\nu_2$ become equal due to the disappearance of the shoulder peaks. As the wings are recognized in the spectra, the molecular motion occurring in PG-12-N-D is same as those in PG-6-N-D and PG-8-N-D, denoting the rotation or vibration around the α-helix axis. In PG-12-N-D at high temperature, the rate of molecular motion around the α-helix axis is faster than those in PG-6-N-D and PG-8-N-D. Peaks of the main chain obtained by ^{13}C CPMAS NMR completely disappeared at high temperature, which means the rate of molecular motion is close to the dipolar decoupling frequencey of 60 kHz. Since the difference between the inner peaks and shoulders is about 60 kHz and these peaks are completely averaged, the rate of the motion should be at least more than this frequency difference. If the rate is much faster than 60 kHz, the peaks of the ^{13}C CPMAS NMR spectra reappear. Taking these situations into account, the rate of molecular motion seems to be close or a little faster than 60 kHz.

At 140°C, the intensity of the wings decreased. This means that some kind of averaging for the principal axis parallel to the α-helix axis takes place. However, as seen in Fig. 6, two peaks, which are the averaged peaks between the inner peaks and shoulders are almost at the same position as that at 100°C. If overall averaging for the three principal axes takes places, the peak position should be the average of the three

principal values, the average of the inner peaks, shoulder and wings. From these results, in PG-10-N-D at 140°C, similar to PG-6-N-D and PG-8-N-D, the rotation or vibration around the α-helix axis provides the greatest contribution to the molecular motion. In addition, the fluctuation in the α-helix axis occurs with a much smaller contribution to the molecular motion.

PLACE FIGS.6 AND 7 HERE

From a series of ^{2}H NMR spectra, the molecuar motions of the main chain of the PALGs seem to be similar to each other. Conformation of the main chain is the right handed α-helix for all PALGs in the measured temperature range, which has been already confirmed by the ^{13}C chemical shift of the carbonyl and Cα. It is reported that this conformation is stable even at 230°C [5]. A similarity in the molecular motion arises from this common conformation. As the right handed α-helix is frequently likened to a rigid rod, it is reasonable that the most probable molecular motion is the rotation or vibration around the α-helix axis. For PALG with a short side chain like PG-4-N-D, the main chain can not move because the molecular motion of the side chain is not very fast and the amount of the side chain, the number of atoms in the side chain, is not significant. For PG-6-N-D and PG-8-N-D, the amount of the side chain and the rate of the side chain motion increased enough to activate the main chain molecular motion. However, these polymers do not form a liquid crystalline phase. Even though the side chain mobility increased, it is not enough for reordering of the main chains to form a liquid cyrstalline phase. For PG-10-N-D and 12-N-D, the side chain is mobile enough to reorder the main chain as mesogens.

From these results, it is found that the molecular motions of the main chain are common to all PALGs. The main chain can rotate or vibrate around the α-helix axis. As the temperature increases, the rate of rotation or vibration increases and the α-helix conformation remains unchanged.

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Figure Captions

Fig.1 (a) Theoretical ^{2}H NMR spectrum with η=0.5. (b) ^{2}H NMR of PG-10-N-D measured at 40°C. (c) ^{2}H NMR of 10% chloroform solution of PG-10-N-D.

Fig.2 ^{2}H NMR spectra of PG-4-N-D as a function of temperature.

Fig.3 Temperature dependencies of $\Delta\nu_1$ and $\Delta\nu_2$ for PG-4-N-D.

Fig.4 ^{2}H NMR spectra of PG-8-N-D as a function of temperature.

Fig.5 Temperature dependencies of $\Delta\nu_1$ and $\Delta\nu_2$ for PG-8-N-D.

Fig.6 ^{2}H NMR spectra of PG-10-N-D as a function of temperature.

Fig.7 Temperature dependencies of $\Delta\nu_1$ and $\Delta\nu_2$ for PG-10-N-D.

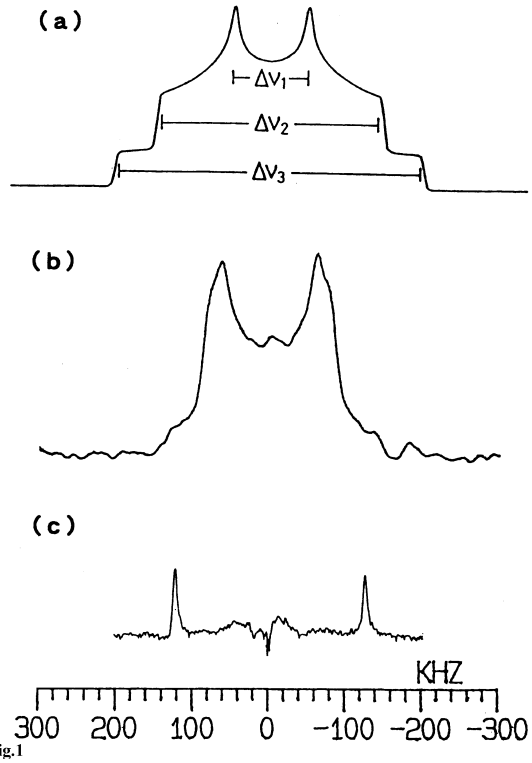
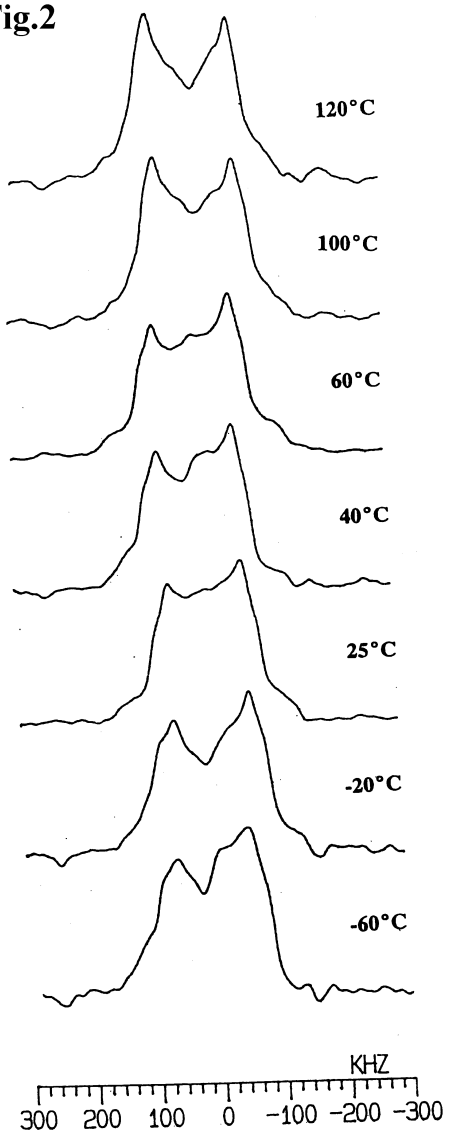
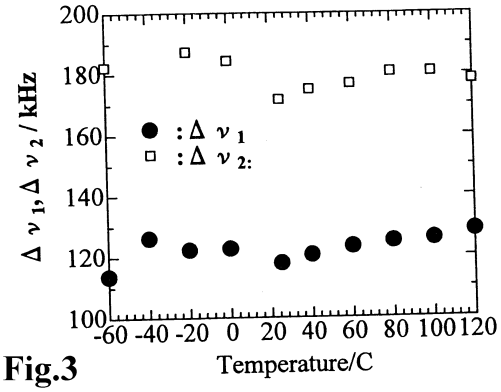


Fig.1

Fig.2

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180
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Δ ν 1, Δ ν 2 / kHz
● : Δ ν 1
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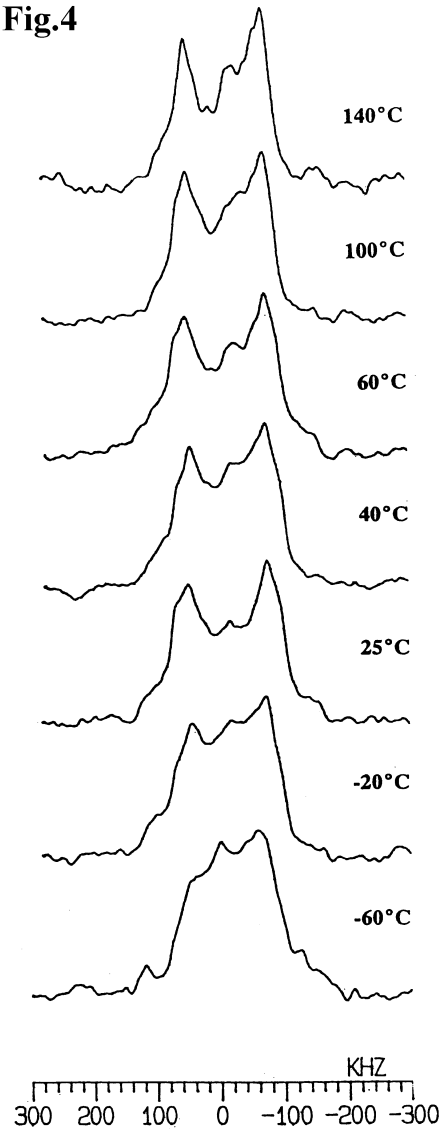
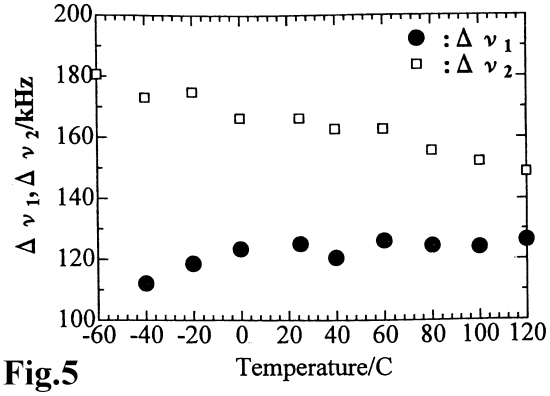
Temperature/C

Fig.3

Fig.4

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Temperature/C
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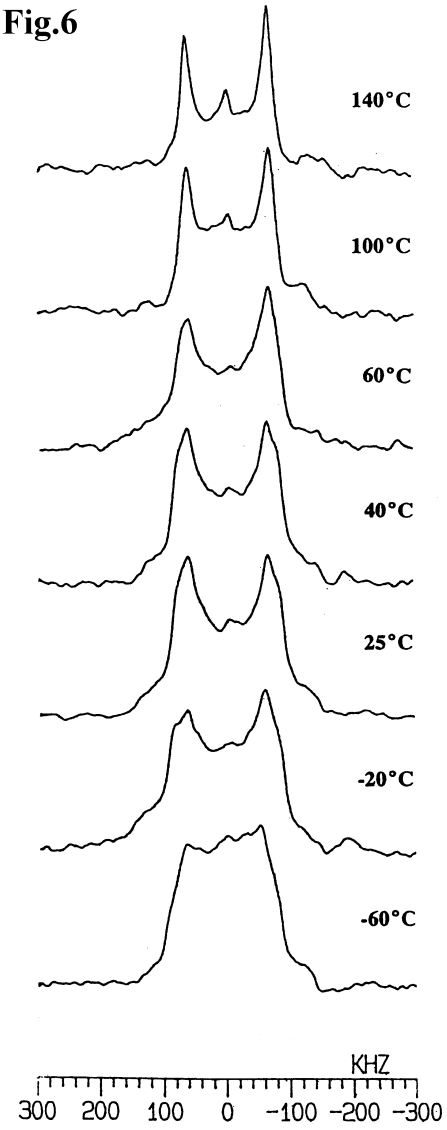
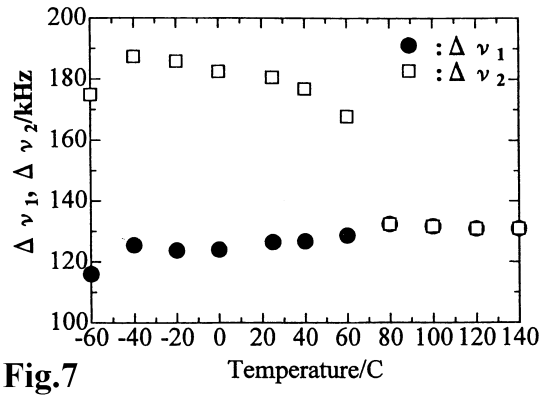
: Δ ν 2

Fig.5

Fig.6

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Δ ν 1, Δ ν 2/kHz
Temperature/C
● : Δ ν 1
□ : Δ ν 2

Fig.7