Diffusion of Rod-Like Polypeptides in the Liquid Crystalline and Isotropic Phases as Studied by High Field-Gradient NMR Spectroscopy

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Summary: In this lecture the measurements and analyses of the isotropic and anisotropic diffusion coefficients(D) of rod-like polypeptide such as poly(γ-L-glutamate)(PLG) with *n*-alkyl side chains, of which the main chain takes the α-helical conformation, as a function of the main chain length in the thermotropic and lyotropic liquid crystalline phases over a wide range of temperatures from 30 to 80°C by means of pulse high field-gradient spin echo ^{1}H NMR method have been introduced. In the anisotropic diffusion, the $D_{\parallel}$ value in direction parallel to the α-helical chain axis is found to be much larger than the $D_{\perp}$ value in direction perpendicular to the α-helical chain axis. The diffusion process is followed by the Kirkwood theory. Further, it is described that the diffusion in the nematic liquid crystalline phase is much slower than that in the isotropic phase.

Keywords: diffusion coefficient; field-gradient NMR; liquid crystals; polypeptides; rodlike polymers

[main lecture at 22nd Discussion Conference on Spectroscopy of Partially Ordered Macromolecular Systems, Prague July 21-24, 2003: Macromolecular Symposia]

Introduction

It is known that poly(γ-glutamate) with long *n*-alkyl side chains forms thermotropic liquid crystalline phase by melting of the side chain crystallites[1]. From solid-state high-resolution ^{13}C NMR experiments on poly(γ-*n*-alkyl L-glutamates)[2-6], it has been shown that the main chain of polypeptides takes a right-handed α-helical conformation and the *n*-alkyl side chains take an all-*trans* zigzag conformation in the crystallites at temperatures below the melting point, and that at temperatures above the melting point of the side chain crystallites the side chains are undergoing fast *trans-gauche* exchange, and then the main chain undergoes fast molecular motion at a frequency of about 60 kHz[5]. Poly(*n*-dodecyl L-glutamate)(PDLG) forms a typical cholesteric liquid crystalline phase at temperatures

© 2005 International Union of Pure and Applied Chemistry DOI: 10.1002/masy.200550205

above 50 °C. This shows that by melting of the side chain crystallites, the rate of reorientation of the side chains is transitionally increased. In our works[7-9], it have reported that α-helical poly(γ-glutamate)s with *n*-octadecyl side chains in the thermotropic liquid crystalline state are diffusing as demonstrated by field-gradient spin-echo(PFGSE) ^{1}H NMR method, and further the diffusion coefficients in directions parallel($D_{\parallel}$) and perpendicular($D_{\perp}$) to the α-helical chain axis were determined and the diffusion was an anisotropic.

Further, it is well known that poly(glutamate) systems such as poly(γ-benzyl L-glutamate), poly(γ-*n*-alkyl L-glutamate), *etc.* in solvent form the isotropic, biphasic and liquid crystalline phases depending on the polypeptide concentration[10-12]. However, in these phases the diffusional behavior of the polypeptides is not clarified.

Here, we have introduced the preparation of highly-oriented poly(γ-*n*-dodecyl L-glutamate) films as a function of the main-chain length and the isotropic and anisotropic diffusion coefficients of the polypeptides as a function of temperature within the temperature range from 50 to 80°C by means of pulse field-gradient spin echo(PFGSE) ^{1}H NMR method[13-23], in order to elucidate how the diffusion is affected by changes of the main-chain length[7-9]. The diffusion behavior in thermotropic liquid crystalline phase is analyzed by the translational diffusion equation on the basis of Kirkwood theory[24] of diffusion process for rod-like polymers derived by Doi and Edwards[25]. Further, we discussed the diffusional behavior of α-helical poly(γ-*n*-octadecyl L-glutamate) and chloroform as solvent in the isotropic, biphasic and liquid crystalline phases by using high field-gradient ^{1}H NMR and diffusion ^{1}H NMR imaging.

Experiments

Poly(γ-*n*-octadecyl L-glutamate)(POLG) was synthesized by ester-exchange reactions between poly(γ-benzyl L-glutamate) (PBLG) and *n*-octadecyl alcohol. The reaction was carried out in 1,2-dichloroethane with *p*-toluenesulfonic acid as a catalyst at 60°C. The complete replacement of the phenyl groups of PBLG by *n*-alkyl groups was confirmed by their ^{1}H NMR spectra recorded in solution. A series of poly(γ-*n*-dodecyl L-glutamate)s(PDLG) were synthesized by ester-exchange reactions between poly(γ-benzyl L-glutamate)(PBLG) (average molecular weight: M_w=7000, 30000 and 130000) and *n*-dodecyl alcohol. The reaction was carried out in 1,2-dichloroethane with *p*-toluenesulfonic acid as a catalyst at 60°C. The complete replacement of the phenyl

groups of PBLG by *n*-alkyl groups was confirmed by their ^{1}H NMR spectra recorded in solution. The highly-oriented PDLG films were prepared by casting the solutions in 1,2-dichloroethane at room temperature after placed in the magnetic field of an NMR magnet with 11 T for 60 h. The orientation of the polypeptide chains in the film was confirmed by optical cross-polarized microscopy. The order parameter S of the obtained film is about 0.87 as determined by the ^{13}C chemical shift value of the amide carbonyl carbon[12, 22] at room temperature.

POLG solution was prepared by placing POLG and deuterated chloroform($CDCl_3$) in an NMR tube with a diameter of 5 mm, which is used as solvent for diffusion coefficient measurements of POLG, and its NMR tube was sealed off and was kept at 50°C. Protonated chloroform($CHCl_3$) is used for diffusion coefficient measurement of chloroform in the POLG solution. The POLG concentrations employed in this work were 5, 10, 15, 17.5 and 20 w/w %. The 5 and 10 w/w % POLG solutions are in the isotropic phase, 15 and 17.5 w/w % POLG solutions are in the biphasic phase and 20 w/w % POLG solution is in the cholesteric liquid crystalline phase as seen from phase diagram[11]. When 20 w/w % POLG solution is placed in an NMR magnet with 13.5 T for 80 h, it forms highly-oriented nematic liquid crystalline phase. The degree of order parameter is 0.86 as determined by static ^{13}C NMR[12, 22].

The self-diffusion coefficient measurements of POLG in the lyotropic liquid crystalline state were carried out by means of a JEOL GSX-270 NMR spectrometer operating at 270.1 MHz for ^{1}H at 30 °C with a home-made pulse gradient generator using a standard PFGSE pulse sequence (the Hahn echo sequence : $\pi/2$ pulse-τ-π pulse)[13] with field-gradient pulse in between the $\pi/2$ and π pulses, and in between the π and spin echo[14]. In this work, a field-gradient strength of about 13.1 Tm^{-1} (1310 G/cm) was used. The spectral width was 4.0 kHz and data points were 4096. The relationship between the echo signal intensity and pulse field-gradient parameters is given by

$$A(\delta)/A(0) = \exp[- \gamma^2 G^2 D \delta^2 (\Delta - \delta/3)] \qquad (1)$$

where $A(\delta)$ and $A(0)$ are echo signal intensities at $t = 2\tau$ with and without the magnetic field-gradient pulse, respectively. The field-gradient pulse width is δ. τ is the pulse interval, γ the gyromagnetic ratio of proton, G the field-gradient strength, D the self-diffusional coefficient, and Δ the field-gradient pulse interval. The echo signal intensity was measured as a function of δ. The plot of $ln[A(\delta)/A(0)]$ against $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$ gives a straight line with a slope of –D. The τ, Δ and δ values employed in these experiments

were 4, 4 and 0.001-0.4 ms, respectively. The diffusion coefficient D of water of 2.5 x 10^{-5} cm^2/s at 303 K was used as the calibration of the field-gradient strength as well-known. The experimental error for the D value was estimated to be within 5%.

As probe molecules in the biphasic phase have two-diffusion components in diffusion on the measurement time scale, the total echo attenuation is given by a superposition of contributions from the individual components as expressed by

$$A(\delta)/A(0) = f_1 \exp[-\gamma^2 G^2 D_1 \delta^2 (\Delta - \delta/3)] + f_2 \exp[-\gamma^2 G^2 D_2 \delta^2 (\Delta - \delta/3)] \quad (2)$$

where D_i is the self-diffusion coefficient of the *i*th component, and f_i is the fraction of the *i*th component and thus $f_1 + f_2 = 1$. The fraction for the fast and slow diffusion components can be determined from the intercept of the least-squares fitted straight line.

^1H NMR imaging measurements on diffusion coefficient of chloroform solvent in POLG/$CHCl_3$ liquid crystalline solution were carried out by means of a Bruker Avance DSX300 NMR spectrometer operating at 300.13 MHz with an accessory of diffusion imaging system with field-gradient of 100 G/cm at 30°C. The diffusion imaging pulse sequence is based on the spin echo sequence including field-gradient pulses[13-23]. The slice selection is achieved with the field-gradient in the z or x direction. In an NMR magnet, POLG chains in the liquid crystalline solution are oriented to the magnetic field that is the z direction, after an NMR tube containing the liquid crystalline solution is placed for long time. Thus, by the slice selection in the z direction, the parallel diffusion coefficient of $CHCl_3$($D_{\parallel}$) in direction parallel to the α-helical POLG chain axis in POLG lyotropic liquid crystalline solution is determined and the perpendicular diffusion coefficient($D_{\perp}$) by the slice selection in the x direction perpendicular to the α-helical POLG chain axis is determined. The values of Δ and δ are 10 ms and 0.001- 0.1ms, respectively.

Results and Discussion

Thermotropic liquid crystalline phase: The self-diffusion coefficients (D) of rod-like poly(*n*-alkyl L-glutamate)s having *n*-dodecyl side chains in the thermotropic liquid crystalline state were measured as a function of the main-chain length [molecular weight (M_w) of 7000, 30000 and 130000, which are corresponding to the main chain lengths (L) of ca.30, 200 and 890Å, respectively]] within the temperature range from 50 to 80 °C by means of PFGSE ^1H NMR method as shown in Table 1, in order to elucidate the

diffusional behavior of the polypeptides in the thermotropic liquid crystalline state. From the experimental results, it was found that at temperatures above the melting point of side-chain crystallites in poly(*n*-alkyl L-glutamate) the polypeptide forms the thermotropic liquid crystalline phase, and then the isotropic diffusion coefficients (D_{iso}) of the rod-like polypeptides are decreased with an increase in the main-chain length. The diffusion process is analyzed by the Kirkwood theory[24] of diffusion process for rod-like polymers as shown in Figure 1. The diffusion coefficients of poly(L-glutamates) in the directions parallel($D_{\parallel}$) and perpendicular($D_{\perp}$) to the α-helical axis were determined, and the $D_{\parallel}$ value was found to be larger than the $D_{\perp}$ value.

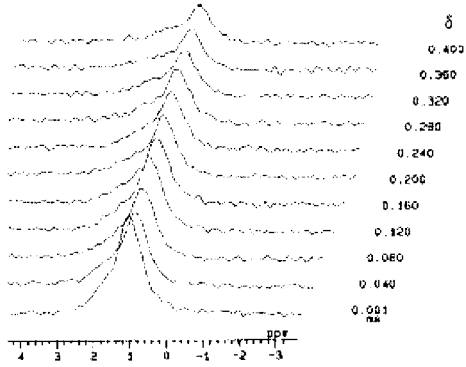

Figure 1. Typical spin echo ^{1}H NMR spectra of poly(γ-*n*-octadecyl L-glutamate)(POLG) in the thermotropic liquid crystalline phase at 80°C as a function of field-gradient pulse length d by PFGSE NMR.

The main-chain of poly(γ-glutamate) considered in this work takes the α-helical form like a long rod. At temperatures above the melting point of the side-chain crystallites the side chains take the liquid-like phase such as liquid *n*-alkane and are working as a solvent for the main chain. The rod-like polypeptide is diffusing as reported previously. The diffusion process of the polypeptide is assumed to follow the Kirkwood theory[24] for the diffusion process of rod-like polymers.

The derivation of obtaining the translational diffusion coefficient of rod-like polymers derived by Doi and Edwards[25] on the basis of Kirkwood theory[24], the isotropic diffusion coefficient D_{iso} of a rod-like polymer chain is followed by the following equation.

$$D_{iso} = (D_{\parallel} + 2D_{\perp})/3 = [ln(L/b)/L]\, kT/3\pi\eta_s \qquad (3)$$

in which

$$D_{\parallel} = [ln(L/b)/L]\, kT/2\pi\eta_s \quad (4)$$

$$D_{\perp} = [ln(L/b)/L]\, kT/4\pi\eta_s \quad (5)$$

where $D_{\parallel}$ and $D_{\perp}$ are the diffusion coefficients in parallel to and perpendicular to the rod-like polymer chain axis, respectively, L is the rod-like polymer length, *b* is the diameter of the rod-like polymer, η_s is the viscosity of the solvent corresponding to long *n*-alkyl side chains in the thermotropic liquid crystalline state, k is the Boltzmann constant and T is the absolute temperature.

By using the standard bond lengths and bond angles determined by X-ray diffraction we can straightforwardly estimate the rod-like main chain length and the diameter of α-helical polypeptides. Then, the main-chain lengths of α-helical poly(γ-*n*-alkyl L-glutamate)s with average molecular weights of 7000, 30000 and 130000 can be estimate to be L = ca. 30, 200 and 890 **Å**, respectively, and the diameter of the α-helical main-chain including the ester group of side chain to *b* = ca. 10 **Å**. The diffusion process of these rod-like polypeptides is expected to follow eq.(3). This equation shows that the plots of D_{iso} against $ln(L/b)/L$ become a straight line.

As described above, the diffusion process of the rod-like polypeptides is expected to follow eq.(2). This shows that the plots of D_{iso} against $ln(L/b)/L$ become a straight line at any given temperature. Here, it is assumed that the viscosity of the solvent corresponding to long *n*-dodecyl side chains is independent of the main-chain length, which is undergoing rapid exchange between the trans and gauche conformations like liquid *n*-alkanes. In Figure 2 the plots of the isotropic diffusion coefficients of PDLG in the thermotropic liquid crystalline state against $ln(L/b)/L$ are shown at various temperatures. It is found that its plots become a straight line. This trend does not conflict with the theoretical prediction. Therefore, it can be said that the isotropic diffusion of rod-like PDLG chains follows approximately the translational diffusion equation of rod-like polymers derived by Doi and Edwards[25] on the basis of Kirkwood theory[24]. Further, it seen from Figure 2 that the slope of the plots of D_{iso} against $ln(L/b)/L$ is increased with an increase in temperature. This agrees with the theoretical prediction as seen from eq.(3) because the slope is a function of temperature.

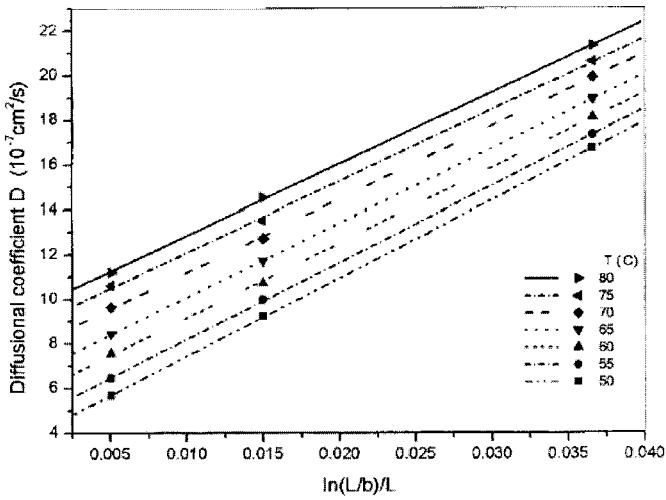

Figure 2. The plots of the isotropic diffusion coefficients of poly(γ-*n*-dodecyl L-glutamate)s(PDLG) in the thermotropic liquid crystalline state against *ln*(L/b)/L are shown at various temperatures.

The diffusion coefficients of the highly-oriented polypeptide films for directions in parallel and perpendicular to the α-helical main-chain were determined. In Table 1 the determined diffusion coefficients, $D_{\parallel}$ and $D_{\perp}$, of the polypeptides with different main-chain lengths and the ratio of $D_{\parallel}$ to $D_{\perp}$ are listed. From the table, it is seen that the $D_{\parallel}$ value is larger than the $D_{\perp}$ value. Their values are decreased with an increase in temperature. These agree with the results of *n*-alkanes in the rotator phase[26].

Lyotropic liquid crystalline solution: By using these decay signals, the diffusion coefficient D of POLG in solution can be determined from the slope of the plots of *ln*[A(δ) /A (0)] against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ as shown in Figure 3. As shown in Figures 2(a) and (b), the plots of *ln*[A(δ) /A (0)] for 5 and 10 w/w % POLG solutions against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ keep to be a straight line. This shows that the diffusion of POLG becomes a single diffusion component. Then, the diffusion coefficients D for α-helical POLG in 5 and 10 w/w % POLG solutions which are in the isotropic phase are obtained as shown in this table.

In 15 and 17.5 w/w % POLG solutions which are in the biphasic phase, the plots of *ln*[A(δ) /A (0)] against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ consist of two straight lines with different slope as shown in Figures 3(c) and (d). This shows that the diffusion becomes two kinds of diffusion components such as the slow diffusion component and fast diffusion component.

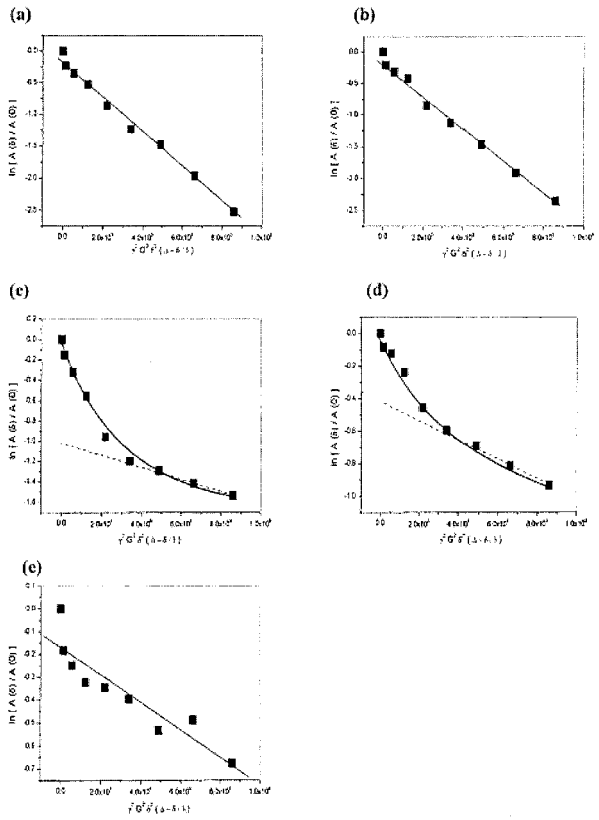

Figure 3. The plots of $ln[A(\delta)/A(0)]$ against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ for determining diffusion coefficient D of poly(γ-*n*-octadecyl L-glutamate)(POLG) in 5(a), 10(b), 15(c), 17.5(d) and 20(e) w/w % POLG/deuterated chloroform solutions at 30°C.

The diffusion coefficients D for the slow diffusion component and fast diffusion component were determined from the slopes. The fast diffusion component and slow diffusion component in the biphasic phase are corresponding to the isotropic region and the liquid crystalline region, respectively. The D value for the fast diffusion component is very close to the D values for 5 and 10 w/w % POLG solutions in the isotropic phase as shown in Table 1. On the other hand, the diffusion coefficient of the slow diffusion component is very close to that for 20 w/w % POLG solution in the liquid crystalline phase. These results means that the diffusion processes for the isotropic region and the liquid crystalline region in the biphasic phase are very similar to those in the isotropic phase and in the liquid crystalline phase, respectively.

Table 1. Determined diffusion coefficients of poly(γ-dodecyl L-glutamate) in the thermotropic liquid crystalline phase at temperatures from 50 to 80°C.

mol wt	$D/\times 10^{7}$ cm²/s	temp (°C) 50	55	60	65	70	75	80
7000	$D_{\parallel}$	17.6	18.3	19.1	19.7	20.4	21.2	21.8
	D_{iso}	16.7	17.3	18.1	18.9	19.9	20.6	21.3
	$D_{\perp}$	15.7	16.2	17.2	18.1	19.1	19.8	20.6
	$D_{\parallel}/D_{\perp}$	1.12	1.13	1.11	1.09	1.07	1.07	1.06
30 000	$D_{\parallel}$	10.4	11.1	11.9	12.8	13.6	14.3	15.4
	D_{iso}	9.21	9.96	10.7	11.7	12.7	13.5	14.5
	$D_{\perp}$	7.94	8.72	9.51	10.5	11.6	12.6	13.6
	$D_{\parallel}/D_{\perp}$	1.31	1.27	1.25	1.22	1.17	1.13	1.13
130 000	$D_{\parallel}$	6.33	7.33	8.44	9.31	10.6	11.4	12.1
	D_{iso}	5.67	6.44	7.56	8.43	9.63	10.5	11.2
	$D_{\perp}$	4.77	5.65	6.78	7.62	8.67	9.73	10.8
	$D_{\parallel}/D_{\perp}$	1.33	1.30	1.24	1.22	1.22	1.17	1.12

The fractions of the two kinds of diffusion components can be determined by analyzing the plots of $ln[A(\delta)/A(0)]$ against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ with two straight lines as shown in Figures 3(c) and (d). As for 15 w/w % POLG solution, the fractions of the diffusion components for the isotropic and liquid crystalline regions in the biphasic phase are determined to be 62 and 38 %, respectively, and as for 17.5 w/w % POLG solution to be 31 and 69 %, respectively. The fraction of the fast diffusion component corresponding to the isotropic region is largely decreased in spite of small concentration increase in going from 15 % w/w POLG concentration to 17.5 w/w POLG concentration. Figures 2(a), (b) and (e) show the first data point somewhat higher than the straight indicates. It is thought that it does not come from a faster-moving species. Probably, it may be an artifact. At this stage, it is no conclusive.

In 20 w/w % POLG solution which is in the liquid crystalline phase, as shown in Figure 3(e), the plots of $ln[A(\delta)/A(0)]$ for α-helical POLG against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ keep to be a straight line. This shows that the diffusion of POLG becomes a single diffusion component. Then, the diffusion coefficient for α-helical POLG in 20 w/w % POLG solution is obtained. This value is very close to that for the liquid crystalline region in the biphasic phase. For example, the diffusion coefficient as determined from Figure 3(a) is 2.76×10^{-6} cm²/s. This diffusion for a polypeptide chain with 200 Å is very fast. Probably such a fast diffusion comes from the fluidity of the liquid crystal.

In Figure 4 the determined D values are plotted against the POLG concentration in order to understand diffusional behavior of α-helical POLG in the isotropic, biphasic and liquid

crystalline phases. From this Figure, it is seen that the diffusion coefficient of α-helical POLG chain in the isotropic region of the isotropic and biphasic phases is decreased with an increase in the POLG concentration and is transitionally decreased in going from the isotropic region to the liquid crystalline region. The diffusion coefficient of α-helical POLG chain in the liquid crystalline region is slightly decreased with an increase in the POLG concentration.

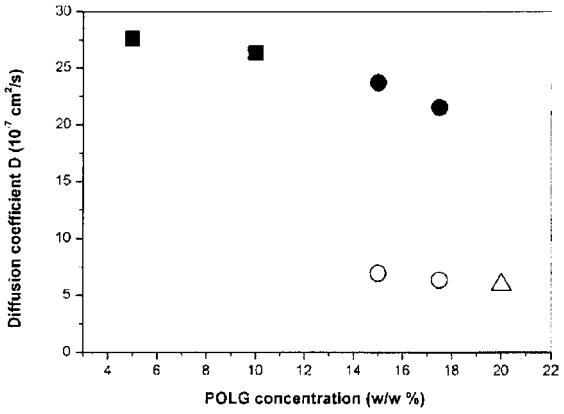

Figure 4. The plots of diffusion coefficients D of poly(γ-*n*-octadecyl L-glutamate)(POLG) in POLG/deuterated chloroform solutions against the POLG concentration at 30°C. ■: 5 and 10% w/w POLG concentration(the isotropic phase), ●: 15 and 17.5 w/w % POLG concentration(isotropic region in the biphasic phase), ○: 15 and 17.5 w/w % POLG concentration(liquid crystalline region in the biphasic phase and △: 20 w/w % POLG concentration(the liquid crystalline phase).

As shown in Table 2, the determined diffusion coefficient of chloroform in neat liquid is larger than that in 20% POLG/chloroform cholesteric liquid crystalline solution at 30°C. This means that the diffusion of chloroform in the liquid crystalline solution is restrained by intermolecular interaction with POLG chains. After an NMR tube containing 20% POLG/chloroform cholesteric liquid crystalline solution was placed in a magnet with 13.5 T for 80 h, the POLG chains are highly oriented to the magnetic field, and the solution forms the nematic liquid crystalline solution.

Table 2. Determined diffusion coefficients D of chloroform in 20 % w/w poly(γ-dodecyl L-glutamate)(POLG)/chloroform solution.

	diffusion coeff D (10^{-5} cm^2/s)				
solvent	neat liquid	D_{iso}[a]	$D_{\parallel}$	$D_{\perp}$	$(D_{\parallel} + 2D_{\perp})/3$[b]
chloroform	2.55	1.82	1.61	1.18	1.32

[a] The diffusion coefficient measurement on the cholesteric liquid crystalline solution was carried out immediately after the POLG sample tube was placed in an NMR magnet. At that time, the POLG chain is still unoriented to the magnetic field. [b] Averaged over anisotropic diffusion coefficients of $CHCl_3$ in POLG liquid crystalline phase highly oriented in the magnetic field.

By applying the field-gradient pulse from the directions parallel and perpendicular to the POLG chain axis to the highly-oriented POLG/chloroform liquid crystalline solution the diffusion coefficients $D_{\parallel}$ and $D_{\perp}$ for chloroform were determined to be 1.61 x 10^{-5} and 1.18 x 10^{-5} cm^2/s, respectively, as shown in Table 2 and its rate is ca. 1.4. This shows that the diffusion of chloroform in the direction parallel to the α-helical POLG chain axis is much faster than that perpendicular to the α-helical POLG chain axis. The diffusion process of chloroform in highly-oriented POLG field is anisotropic. This result is very similar to the previous work[12, 22] that the diffusion of dioxane solvent and probe n-alkanes in highly-oriented poly(γ-benzyl L-glutamate)(PBLG) gel in the direction parallel to the α-helical PBLG chain axis is much faster than that in the direction perpendicular to the α-helical PBLG chain axis and thus the diffusion process is anisotropic. Such a behavior is appeared in diffusion of solvent in lyotropic low-molecular weight liquid crystal systems.

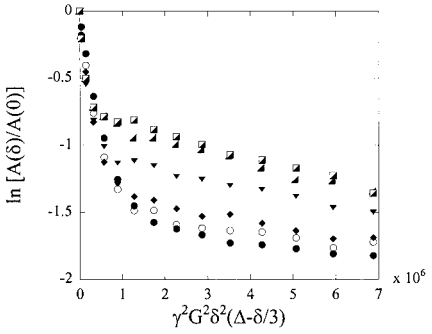

Figure 5. The plots of *ln*[A(δ) /A (0)] against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ for determining diffusion coefficient D of poly(γ-*n*-dodecyl L-glutamate)[Mw: 230,000](POLG) in 5 w/w % PDLG/deuterated chloroform solution at temperatures of –40(a), -30(b), -20(c), -10(d), 0(e), 10(f), 20(g) and 30°C(h).

In 5% w/w PDLG(Mw: 230000)/chloroform-*d* solution, the two fast and slow diffusion components were observed in the temperature range from –40 to 30 °C as shown in Figure 5, in which the fractions of the fast and slow diffusion components are decreased and increased from 0.8 to 0.5 and 0.2 to 0.5, respectively. This shows that the PDLG solution is in the biphasic phase. From these plots, the diffusion coefficient of the fast diffusion component is increased from 2.1 to 9.9 x 10^{-6} cm^2/s in the temperature range from –40 to 30 °C and that of the slow diffusion component is increased from 3.6 to 8.8 x 10^{-8} cm^2/s, as shown in Figure 6. The diffusion coefficient of the fast diffusion component is very close to that for the isotropic phase for POLG/chloroform solution, and, on the other hand, the diffusion coefficient of the slow diffusion component is much smaller by a factor of 10 that that for the liquid crystalline phase for POLG/chloroform solution. According to the above experimental results of the POLG/ chloroform-*d* solution, we can straightforwardly assigned the fast and slow diffusion components to the isotropic and liquid crystalline components in the biphasic phase. The activation energies for diffusion in the isotropic and liquid crystalline phases are obtained to be 13.5 and 8.0 kJ/mol, respectively.

Finally, it can be concluded that diffusional behavior of rod-like polypeptides in the thermotropic and lyotropic liquid crystalline phases was successfully elucidated by using high field-gradient NMR spectroscopy and then high field-gradient NMR spectroscopy is a very useful means for measuring relatively slow diffusion coefficients of rod-like polymers in the liquid crystalline phase.

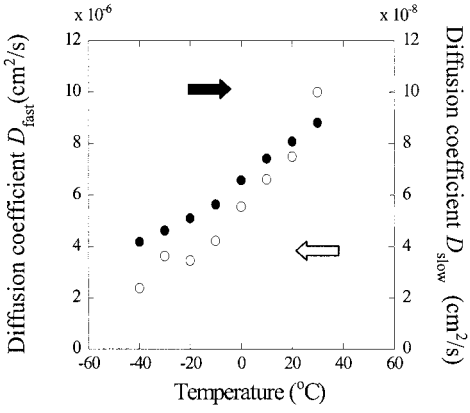

Figure 6. The plots of the isotropic diffusion coefficients of poly(γ-*n*-dodecyl L-glutamate)(PDLG) in the isotropic(a) and liquid crystalline(b) phases against temperature.

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