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Diffusional Behavior of Poly(diethylsiloxane) in the Liquid Crystalline and Isotropic Phases As Studied by High Field-Gradient NMR

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ABSTRACT: The diffusion process of poly(diethylsiloxane) (PDES) has been studied by field-gradient NMR at temperatures from 20 to 80 °C, which is recognized to take the biphasic phase consisting of the liquid crystalline and the isotropic regions at temperatures from 20 to 40 °C and the isotropic phase at temperatures from 50 to 80 °C by solid-state ^{29}Si NMR. The diffusion coefficients (D) of PDES in the liquid crystalline region of the biphasic phase have been measured at 20 and 30 °C by pulse field-gradient stimulated-echo (PGSE) ^{13}C NMR with ^{1}H CW decoupling as designed by us, and also those in the isotropic region of the biphasic phase and in the isotropic phase have been determined by conventional PGSE ^{1}H NMR. From these experimental results, it is found that the diffusion coefficient of PDES in the liquid crystalline region is much larger than that for the PDES in the isotropic region. This shows that the smaller diffusion coefficient of PDES chains in the isotropic region ($\approx 10^{-10}-10^{-11}$ cm^2/s) compared with that in the liquid crystalline region ($\approx 10^{-8}$ cm^2/s) comes from the entanglements effect between the polymer chains.

Introduction

It is well-known that poly(diethylsiloxane) (PDES) with high molecular weight[1,2] ($M_w > 30\,000$) considered in this work forms the liquid crystalline phase in the vicinity of 30 °C by balance of intra- and intermolecular interactions between the main chain and side chains despite the absence of typical mesogenic groups. The phase diagram for PDES has been elucidated by DSC.[3] Further, the structure of the polymer in the solid phase, the liquid crystalline phase, and the isotropic phase has been characterized by static solid-state ^{29}Si NMR and ^{29}Si CP/MAS (cross-polarization−magic angle spinning) NMR.[4,5] Also, the molecular motion of PDES has been studied by the NMR method.[6−8] Nevertheless, the diffusional behavior of PDES in the liquid crystalline phase has never been clarified. It can be expected that a PDES chain in the isotropic phase behaves as a random coil because of the flexible main chain, and on the other hand, PDES chains in the liquid crystalline phase behave as a rigid rod and then are diffusing.

Most recently, we have studied diffusional behavior of rodlike polypeptides in the thermotropic and lyotropic liquid crystalline phases[9−13] and rodlike *n*-paraffins in the rotator phase[14,15] by using pulse field-gradient spin-echo ^{1}H NMR. It has been shown that the diffusion coefficients in the direction parallel ($D_{\|}$) and perpendicular ($D_{\perp}$) to the long chain axis have been determined, and then the $D_{\|}$ value has been found to be larger than the $D_{\perp}$ value, and that the isotropic diffusion coefficients of rodlike polypeptides are decreased with an increase in the main-chain length, and then the diffusion process follows the Kirkwood theory of diffusion process for rodlike polymers in solution.[16] Then, it has been shown that pulse field-gradient spin-echo ^{1}H NMR can provide very useful information for elucidating the diffusion process of rodlike polymers in the liquid crystalline phase. Nevertheless, it is difficult to determine the diffusion coefficient of polymers with short ^{1}H spin−spin relaxation time (T_2) [^{1}H $T_2 < 2$ ms] in the isotropic phase and the liquid crystalline phase by PGSE ^{1}H NMR because the echo signal is predominantly decayed by short T_2 before decayed by diffusion. For this reason, modified pulse field-gradient NMR techniques must be used for polymer systems with short ^{1}H T_2.

From such a background, we aim to measure the diffusion coefficients (D) of PDES by using the PGSE ^{13}C NMR method with ^{1}H CW decoupling as designed by us and the PGSE ^{1}H NMR method and to elucidate the diffusional behavior of PDES in the liquid crystalline phase and the isotropic phase as a function of temperature.

Experimental Section

Materials. PDES is prepared by anionic ring-opening polymerization of dried hexaethyltrisiloxane used as monomer.[17,18] Potassium hydroxide (KOH) is used as an initiator, and the polymerization reaction is made at 160 °C for 24 h. The PDES product is repeatedly fractionated using a mixture solvent of chloroform and methanol. The molecular weight of obtained PDES is $M_w = 215\,000$ as determined from the intrinsic viscosity measured by an Ubbelohde viscometer.[19]

Measurements. Static solid-state ^{29}Si NMR measurements, PGSE ^{1}H NMR measurements (Figure 1a), and PGSE ^{13}C NMR measurements under ^{1}H CW decoupling (Figure 1b) are carried out with a Bruker Avance DSX300 NMR spectrometer operating at 59.61 MHz for ^{29}Si, 75.47 MHz for ^{13}C, and 300.11 MHz for ^{1}H. For static solid-state ^{29}Si NMR measurements, a single 90° pulse under high-power ^{1}H decoupling is employed, where the 90° pulse width is 4 μs. The recycle delay and the number of scan are 180 s and 96, respectively. In PGSE ^{13}C NMR measurements under ^{1}H CW decoupling and PGSE ^{1}H NMR measurements, the echo signal intensity is measured by changing the gradient strength G from 0 to 1160 G/cm, and the gradient pulse interval Δ is 100 and 500 ms for ^{1}H and 750 and 1000 ms for ^{13}C, and the gradient pulse width δ is

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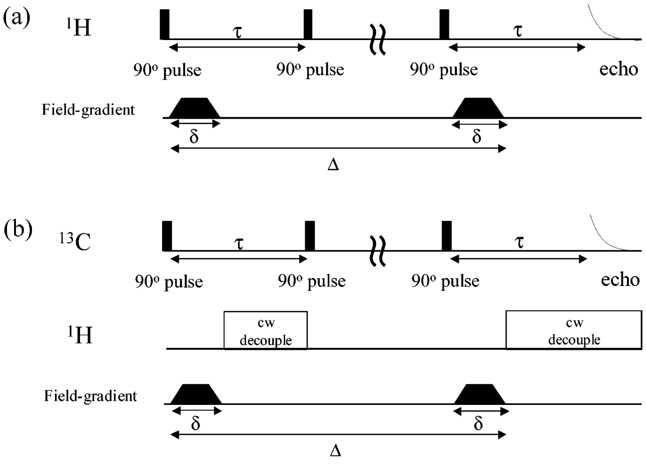

Figure 1. A diagram of PGSE ^{1}H NMR pulse sequence (a) and PGSE ^{13}C NMR pulse sequence with ^{1}H CW decoupling (b).

changed from 0.5 to 8 ms. The recycle delay and the numbers of scans are 5 s and 16 for ^{1}H and are 20 s and 128 for ^{13}C, respectively. The echo signal decay depends on T_2 and diffusion coefficient. For this, the appropriate Δ value must be chosen to determine the diffusion coefficient by considering the T_2 value. For example, if Δ is too long, the echo signal decays by T_2 and disappears within the chosen Δ, and on the other hand, if Δ is too short, the echo signal does not decay by diffusion and so it is difficult to determine the diffusion coefficient from such small decay signal.

In ^{13}C NMR measurements under ^{1}H CW decoupling, the ^{1}H decoupling is made except for the application time of the field-gradient pulse. This comes from the following reason. If the CW decoupling is made during the application of high field-gradient pulse, the ^{1}H decoupling efficiency is apparently reduced by the application of the field gradient.[20] In PGSE experiments, as δ or G is employed as variable parameter to determine the diffusion coefficient, the decoupling efficiency varies with changes of δ and G. Therefore, the echo signal decay induced by the displacement of probe molecules contains the artifact of the ^{1}H decoupling efficiency induced by changes of δ and G. However, if the ^{1}H decoupling with any specified time duration instead of steady CW decoupling is used, it provides three significant advantages. The first is that the artifact of the ^{1}H decoupling efficiency induced by changes of δ and G can be neglected, the second is that the decoupling suppresses spin−spin relaxation caused from strong ^{1}H−^{13}C dipolar interactions and the dipolar dephasing of coherence is prolonged, and the third is that the high field-gradient pulse strength can be applied by changing diffusion time.

The relationship between the echo signal intensity and the pulse field-gradient pulse parameters in the PGSE method is given by[21−23]

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

where $A(0)$ is the signal in the absence of gradient pulses, γ the magnetogyric ratio, G the field-gradient strength, and D the diffusion coefficient. The plots of $\ln[A(G)/A(0)]$ against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ give a straight line with a slope of $-D$, if the diffusion of probe molecules is in a single diffusion component. Therefore, the D value can be determined from this slope.

When the diffusion of probe molecules has two diffusion components within the measurement time, the total echo intensity is given by a superposition of contributions from the individual diffusion components as expressed by

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

where D_i and f_i are the self-diffusion coefficient and the fraction of the ith diffusion component, respectively. Then, $f_1 + f_2 = 1$. The fractions for the fast and slow diffusion components can be determined from the intercept of the least-squares fitted straight line.

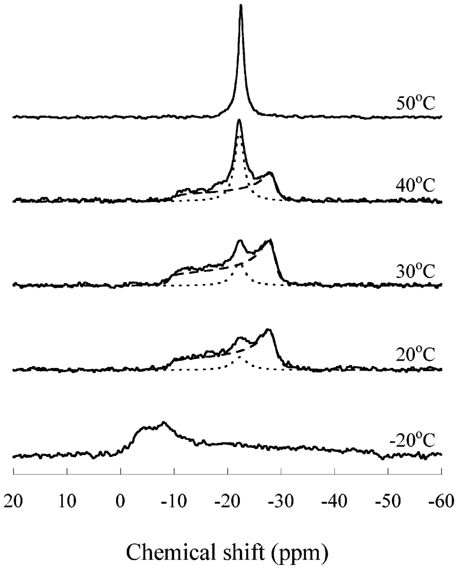

Figure 2. Observed static solid-state ^{29}Si NMR spectra of PDES at temperatures from −20 to 50 °C by single 90° pulse with high-power ^{1}H decoupling. The solid, dashed, and dotted lines indicate the observed spectra, the simulated liquid crystalline component, and the simulated isotropic component, respectively.

Results and Discussion

Static Solid-State ^{29}Si NMR and ^{1}H Solid Echo NMR Spectral Analyses. It is known that the transition from the crystalline phase to the biphasic phase consisting of the isotropic region and liquid crystalline region occurs at 17 °C.[4] The liquid crystalline region in the biphasic phase changes to the isotropic phase over ca. 50 °C. This transition temperature depends on molecular weight.[4] Such a behavior can be clarified by using static solid-state ^{29}Si NMR at temperatures from −20 to 50 °C as shown in Figure 2, where the sample is not rotated in the NMR probe. At −20 °C, the observed static ^{29}Si NMR spectrum in the crystalline phase shows a typical powder pattern, and chemical shift anisotropy is very large as reported already.[5] On the other hand, the observed static ^{29}Si NMR spectra at 20, 30, and 40 °C appear as superposition of a asymmetrical and sharp powder pattern and a sharp peak which come from the liquid crystalline and isotropic regions in the biphasic phase, respectively.[5] The chemical shift anisotropy of the asymmetrical and sharp powder pattern becomes very small because the two chemical shift components perpendicular to the long axis are averaged out by fast rotation of PDES chain around the long chain axis. The fractions of the liquid crystalline region at 20, 30, and 40 °C are approximately estimated to be 0.86, 0.83, and 0.55, respectively, by computer fitting. The fraction of the liquid crystalline region in the biphasic phase decreases with an increase in temperature. Then, the signal corresponding to the liquid crystalline region disappears completely at 50 °C. This shows that PDES is in the isotropic phase.

The ^{1}H T_2 values of the liquid crystalline and isotropic regions in the biphasic phase are determined together with their fractions by ^{1}H solid-echo (Figure 3) and

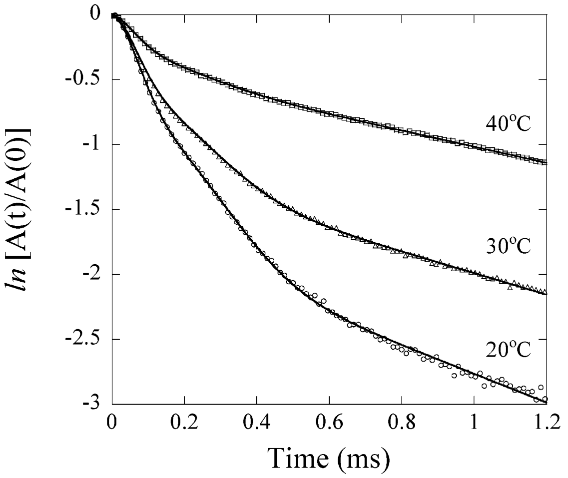

Figure 3. Temperature dependence of ^{1}H FID signal of PDES at 20 (○), 30 (△), and 40 °C (□) as measured by the solid echo method.

Hahn spin-echo[27] measurements. The ^{1}H free induction decay (FID) measured by the solid-echo method shows the presence of the three T_2 components. The appearance of the three T_2 components can be explained as follows. In this temperature range, PDES is in the biphasic phase consisting of the liquid crystalline and isotropic region as seen from static solid-state ^{29}Si NMR spectra (Figure 2). The fractions of the three components corresponding to the shorter, intermediate, and longer ^{1}H T_2 components at 20 °C are 0.50, 0.31, and 0.19, respectively, and those at 30 °C are 0.42, 0.27, and 0.31, respectively. In the liquid crystalline region, the polymer chains are strongly interacting with each other by forming the ordered structure. In such a situation it is thought that the ^{1}H T_2 values of the methyl and methylene groups are different from each other by their different dipolar−dipolar interactions. It may be supported from the experimental finding that the fraction ratio of the first ^{1}H T_2 component to the second ^{1}H T_2 component is nearly 3:2, and this corresponds to the ratio of their proton numbers. On the other hand, the fraction ratio of the third ^{1}H T_2 component to the sum of the first and second ^{1}H T_2 components agrees nearly with that of the liquid crystalline component to the isotropic component as estimated from static solid-state ^{29}Si NMR. Therefore, the three ^{1}H T_2 components can be reasonably explained as mentioned above. The fractions of the liquid crystalline component in the biphasic phase at 20, 30, and 40 °C are estimated to be 0.81, 0.69, and 0.32, respectively. It is shown that the fraction of the liquid crystalline region is decrease with an increase in temperature as agreed with the static solid-state ^{29}Si NMR results. In the diffusion experiments, the decay signal of the second ^{1}H T_2 component corresponding to the liquid crystalline region is used. The ^{1}H T_2 values for the liquid crystalline region and the isotropic region are about 0.2 and 7.4 ms, respectively. The ^{1}H T_2 value of PDES in the liquid crystalline region is much shorter than that of the isotropic region. Thus, it is thought that it is very difficult to determine the diffusion coefficient of PDES in the liquid crystalline region by PGSE ^{1}H NMR because of extremely short ^{1}H T_2. On the other hand, it is possible to the diffusion coefficient of PDES in the isotropic region by the PGSE ^{1}H method because of sufficiently long ^{1}H T_2.

Diffusion of PDES in the Isotropic Phase and in the Isotropic Region of the Biphasic Phase. Figure 4a shows the plots of ln[$A(G)/A(0)$] for PDES in the isotropic phase at 50, 60, 70, and 80 °C against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ by changing $G = 0{-}1160$ G/cm at $\Delta = 500$ ms, at $\delta = 8$ ms, and at $\tau = 11.2$ ms as obtained by using the PGSE ^{1}H NMR method. It is seen from these plots that the experimental data lie on a straight line. This shows that the diffusion of PDES in the isotropic phase is a single diffusion component. Then, diffusion coefficients D on the order of 10^{-11} cm^2/s determined from the slope are summarized in Table 1. This shows that such extremely small diffusion coefficients are successfully determined by using the present PGSE ^{1}H method. From these experimental results, it is seen that the diffusion coefficient of PDES is slowly increased from 6.2×10^{-11} to 7.4×10^{-11} cm^2/s with an increase in temperature from 50 to 80 °C. The polymer chains are completely in the isotropic phase. We must consider the cause why the polymer chains are very slowly diffusing. As suggested earlier for any specified viscosity behavior for liquid polymers and high concentrated polymer solutions,[24] it is thought that extremely slow diffusion of PDES chains in the isotropic phase may come from entanglements between the polymer chains.

Next, we are concerned with diffusion of PDES in the isotropic region of the biphasic phase. In the biphasic phase at 20, 30, and 40 °C, as mentioned above, PDES chains are in the isotropic region and liquid crystalline region and thus PDES chains in the isotropic region are surrounded by the liquid crystalline region, and those in the liquid crystalline region are surrounded by the

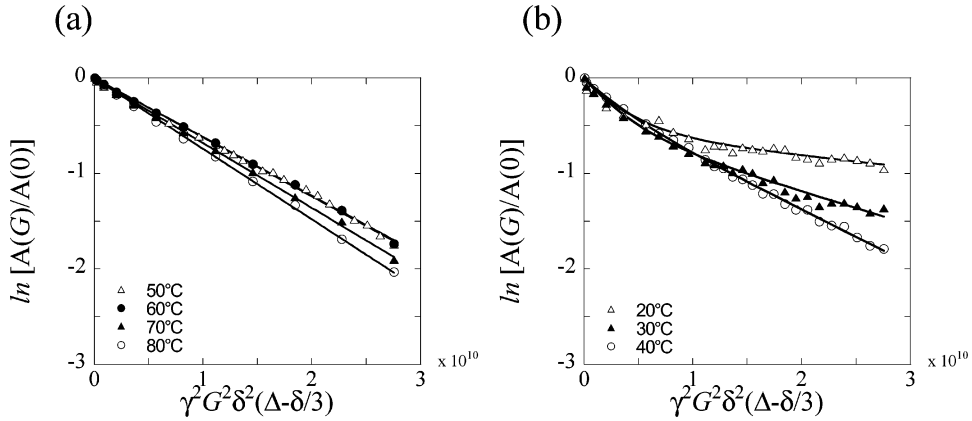

Figure 4. Plots of ln[$A(G)/A(0)$] against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ for determining diffusion coefficients D of PDES by PGSE ^{1}H NMR method: (a) for the isotropic region in the isotropic phase at 50 (△), 60 (●), 70 (▲), and 80 °C (○); (b) for the isotropic region of the biphasic phase at 20 (△), 30 (▲), and 40 °C (○).

Table 1. Determined Diffusion Coefficients *D* of PDES in the Liquid Crystalline Region in the Biphasic Region by the PGSE ^{13}C NMR Method and in the Isotropic Region of the Biphasic Phase and the Isotropic Phase by the PGSE ^{1}H NMR Method as a Function of Temperature

	diffusion coefficient D, cm^2/s			
		isotropic component[a]		
temp/°C	$D \times 10^{-9}$ (liquid crystalline component)	$D_1 \times 10^{-10}$ (fast diffusion component)	$D_2 \times 10^{-11}$ (slow diffusion component)	fraction[b] f_{D1}:f_{D2}
20	9.9[d]	2.6	1.3	0.43:0.57
30	75,[c] 50[d]	2.8	3.5	0.39:0.61
40		2.8	5.7	0.21:0.79
50			6.2	0:1
60			6.2	0:1
70			6.8	0:1
80			7.4	0:1

[a] For the isotropic region of the biphasic phase at temperatures from 20 to 40 °C and for the isotropic phase at temperatures from 50 to 80 °C. [b] D_1 and D_2 for the fast and slow diffusion components, respectively, at temperatures from 20 to 40 °C. [c] For $\Delta = 750$ ms. [d] For $\Delta = 1000$ ms.

isotropic region. The ^{1}H T_2 of PDES in the liquid crystalline region is strongly influenced by strong dipolar interactions, and then the ^{1}H T_2 becomes shorter by roughly 1/37 than that in the isotropic region at same temperature. Therefore, the echo signal of the liquid crystalline component in this PGSE ^{1}H NMR experiment conditions disappears within the time interval τ of 11.2 ms between the first $\pi/2$ pulse and the second $\pi/2$ pulse, but the signal derived from PDES in the isotropic region of the biphasic phase remains in the finally obtained echo. The plots of $\ln[A(G)/A(0)]$ against $\gamma^2 G^2 \delta^2(\Delta - \delta/3)$ consist of two straight lines with different slope as shown in Figure 4b. This shows that the diffusion has two kinds of diffusion components in the isotropic regions such as the slow diffusion component and fast diffusion component. The diffusion coefficients D's for the slow diffusion component and the fast diffusion component of the isotropic region in the biphasic phase are determined from the slopes as shown in Table 1. The diffusion coefficients D's of PDES for the fast diffusion component in the isotropic region as determined from the large slope of the plots are on the order of 10^{-10} cm^2/s, and those for the slow diffusion component as determined from the small slope of the plots are on the order of 10^{-11} cm^2/s. The magnitude of the diffusion coefficient for the slow diffusion component is close to that in the isotropic phase at 50 °C.

Next, we consider whether in the diffusional behavior at 20, 30, and 40 °C the partial-restriction effect on diffusion which comes from the obstruction at the interface between the isotropic and liquid crystalline regions is important or not. The slow diffusion component is more sensitive to the obstruction of the interface. However, the diffusion time Δ of 500 ms used in this experiment is not so long that the diffusion is hindered by the interface. For example, the slow diffusion species with $D = 3.5 \times 10^{-11}$ cm^2/s at 30 °C can diffuse only 59 nm as calculated from relation $\sqrt{2D\Delta}$ within the diffusion time of 500 ms. This is much smaller than the domain size of the isotropic region to be over several micrometers as estimated by the optical micrograph. Therefore, it is difficult to observe the partial-restriction effect on diffusion. If the observed non-Fickian behavior in the isotropic region of the biphasic phase comes from the partial-restriction effect, the slow diffusion component may be assigned to PDES in the interface region because PDES in the interface region must suffers strongly the partial-restriction effect in diffusion. Thus, the fraction of the slow diffusion component must be small because the fraction of the interface region is very small. Nevertheless, the slow diffusion component is dominantly observed. From these experimental results, it can be said that the slow and fast diffusion components should be assigned to the inside and outside regions of the isotropic region in the biphasic phase. The determined D values and the fractions of the two diffusion components are summarized in Table 1. From this table, it is seen that the D values of the slow diffusion components of the isotropic region in the biphasic phase are very largely increased with an increase in temperature, and those in the isotropic phase are very slowly increased. The plots are abruptly changed at 50 °C (not shown in figure). The activation energy E for diffusion can be obtained from the Arrhenius plots of ln D against $1/T$ to be 6.9 and 0.7 kJ/mol for the slow diffusion component of the isotropic region in the biphasic phase and in the isotropic phase, respectively. The E value for the former is much larger than that for the latter.

The fraction of the fast diffusion component of the isotropic region in the biphasic phase is decreased with an increase in temperature and that of the slow diffusion component of the isotropic region in the biphasic phase is increased. Therefore, it is expected that PDES chains are diffusing from the isotropic region to the liquid crystalline region of the biphasic phase through their interface and at the same time from the liquid crystalline region from the isotropic region. Its balance may be changed by temperature change. As mentioned above, the origin of extremely small diffusion coefficient on the order of $10^{-10}-10^{-11}$ cm^2/s may be due to the entanglements of PDES chains. To recognize the effect of the entanglements on the diffusion process, the PDES concentration dependence of the diffusion coefficient of the PDES in PDES/toluene-d_8 solution is measured at 50 °C. Figure 5 shows the plots of the D values determined by changing $G = 0-1000$ G/cm at $\Delta = 100$ ms, $\delta = 1-4$ ms, and $\tau = 11.2$ ms by using PGSE ^{1}H NMR method against the PDES concentration. It is seen that as the polymer concentration is increased, the D value of PDES chains in PDES/toluene-d_8 solution is decreased with an increase in the polymer concentration and approaches the D value of PDES chains in the melt state. This shows that the entanglements effect exists in the polymer system, which leads to reduction of the translational diffusion coefficient of the polymer chains.

To clarify the diffusional behavior of PDES in the liquid crystalline region, the PGSE ^{13}C NMR experiments under ^{1}H CW decoupling are made at 20 and 30 °C by changing $G = 0-1150$ G/cm at $\Delta = 750$ and 1000

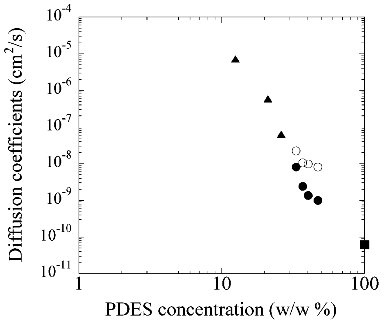

Figure 5. The log−log plots of diffusion coefficients D of PDES in PDES/toluene-d_8 solutions against the PDES concentration at 50 °C by the PGSE ^{1}H NMR method: (▲) 12.5, 21.1, and 26.2% w/w; (●) 33.2, 36.9, 40.3, and 47.3% w/w (slow diffusion component); (○) 33.2, 36.9, 40.3, and 47.3% w/w (fast diffusion component); (■) 100% w/w.

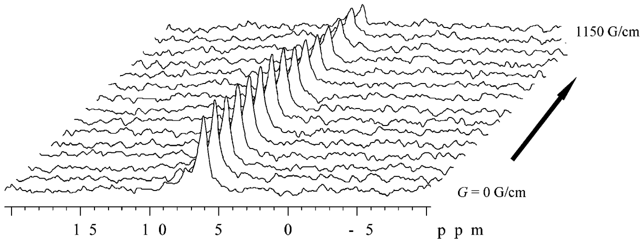

Figure 6. Observed PGSE ^{13}C NMR spectra of PDES in the biphasic phase as a function of field-gradient strength G at 30 °C.

ms, $\delta = 0.5$ ms, and $\tau = 1.7$ ms. In these temperatures, PDES chains are in the biphasic phase consisting of the liquid crystalline region and the isotropic region as characterized by static solid-state ^{29}Si NMR. The fraction of the liquid crystalline region is 0.81 at 20 °C and is 0.69 at 30 °C as determined by the ^{1}H solid-echo method. The typical observed PGSE ^{13}C NMR spectra of PDES in the liquid crystalline region at 30 °C and at $\Delta = 1000$ ms are shown in Figure 6. An asymmetric signal appears at about 6.3 ppm. This peak can be straightforwardly assigned to the methyl carbons in side chains of PDES.[25] In PGSE experiments, the magnetization is attenuated by T_2 during τ. The ^{13}C T_2 value for the methyl carbons in side chains of PDES in the liquid crystalline region is roughly 16 times longer than ^{1}H T_2 as estimated by using the magnetogyric ratios of ^{13}C($\gamma_{^{13}\mathrm{C}}$) and ^{1}H($\gamma_{^1\mathrm{H}}$) nuclei and the BPP theory (^{13}C T_2/^{1}H $T_2 \approx (g_{^1\mathrm{H}}/\gamma_{^{13}\mathrm{C}})^2 \approx 4^2 = 16$).[26] Therefore, it is better to use ^{13}C nucleus in determining the diffusion coefficient as compared with ^{1}H nucleus by the PGSE NMR method. The echo signal comes from PDES chains in the liquid crystalline region and does not disappear at the echo time interval during τ. 74% of the initial magnetization is decayed by ^{13}C T_2 during τ and ^{13}C T_1 between the second and third $\pi/2$ pulses at $\Delta = 1000$ ms and $\tau = 1.7$ ms. Then, the remaining magnetization is reduced by diffusion.

The plots of ln[$A(G)/A(0)$] for PDES as obtained from the PGSE ^{13}C NMR spectra against $\gamma^2 G^2 \delta^2(\Delta - \delta/3)$ at 20 and 30 °C and at $\Delta = 1000$ ms become a straight line as shown in Figure 7. Thus, this shows that the diffusion is a single diffusion component with $D \approx 10^{-8}$ cm^2/s. The reduction of diffusion coefficient of PDES in the liquid crystalline region with an increase in Δ from 750 to 1000 ms shows that there clearly exists the partial-restriction effect of the diffusion.

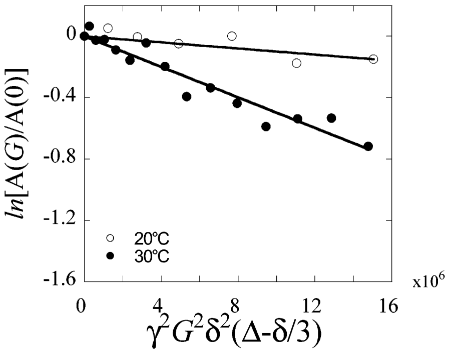

Figure 7. Plots of ln[$A(G)/A(0)$] against $\gamma^2 G^2 \delta^2(\Delta - \delta/3)$ for determining diffusion coefficients D of PDES at 20 (○) and 30 °C (●) by the PGSE ^{13}C NMR method.

In the previous works on diffusion of poly(n-octadecyl L-glutamate) (POLG)/chloroform-d solution in the lyotropic liquid crystalline phase and the isotropic phase,[28] the diffusion coefficient of POLG in the liquid crystalline phase ($\approx 10^{-7}$ cm^2/s) is much smaller D value than POLG in the isotropic phase ($\approx 10^{-6}$ cm^2/s). It is opposite the results of PDES in the liquid crystalline region and the isotropic region. In the case of POLG, the polymer takes the α-helix form in both of the liquid crystalline and isotropic phases and then diffuses as a rigid rod. As predicted from the fact, POLG chains in the liquid crystalline phase may more strongly interact with each other as compared with those in the isotropic phase. On the other hand, the PDES chain takes the extended form in the liquid crystalline region but takes the random-coil form in the isotropic region. For this reason, the random-coiled PDES chains have the entanglements in the melt state and thus diffuse more slowly compared with those in the liquid crystalline region.

Finally, we can conclude as follows. PDES chains in the isotropic region of the biphasic phase and the isotropic phase takes the random-coil form, and then their diffusion is strongly influenced by the entanglements. The strong constraint in the translational diffusion process leads to the extremely small diffusion coefficient of PDES with the order of 10^{-10}−10^{-11} cm^2/s. On the other hand, a PDES chain with the extended form in the liquid crystalline region diffuses as a rodlike polymer and then does not form the entanglements. Therefore, the diffusion coefficient of PDES in the liquid crystalline region may be much smaller than that in the isotropic region and isotropic phase. Further, it can be said that PGSE ^{13}C NMR with ^{1}H CW decoupling has more significantly advantage as compared with the conventional PFG ^{1}H NMR method for the liquid crystalline polymers with extremely short ^{1}H T_2.

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References and Notes

(1) Mölenberg, A.; Möller, M.; Sautter, E. *Prog. Polym. Sci.* **1997**, *22*, 1133.
(2) Sun, D. C.; Magill, J. H. *Polymer* **1987**, *28*, 1243.
(3) Kögler, G.; Loufakis, K.; Möller, M. *Polymer* **1990**, *31*, 1538.
(4) Mölenberg, A.; Möller, M. *Macromolecules* **1997**, *30*, 8332.
(5) Litvinov, V. M.; Whittaker, A. K.; Hagemeryer, A.; Spiess, H. W. *Colloid Polym. Sci.* **1989**, *267*, 681.
(6) Menge, H.; Hotopf, S.; Pönitzsch, S.; Richter, S.; Arndt, K.; Schneider, H.; Heuert, U. *Polymer* **1999**, *40*, 5303.
(7) Litvinov, V. M.; Macho, V.; Spiess, H. W. *Acta Polym.* **1997**, *48*, 471.

(8) Grinberg, F.; Kimmich, R.; Möller, M.; Mölenberg, A. *J. Chem. Phys.* **1996**, *105*, 9657.
(9) Matsukawa, S.; Ando, I. *Macromolecules* **1996**, *29*, 7136.
(10) Matsukawa, S.; Ando, I. *Macromolecules* **1999**, *32*, 1865.
(11) Yamane, Y.; Kobayashi, M.; Kuroki, S.; Ando, I. *Macromolecules* **2001**, *34*, 5961.
(12) Yin, Y.; Zhao, C.; Kuroki, S.; Ando, I. *J. Chem. Phys.* **2000**, *113*, 7635.
(13) Yin, Y.; Zhao, C.; Kuroki, S.; Ando, I. *Macromolecules* **2002**, *35*, 2335.
(14) Yamakawa, H.; Matsukawa, S.; Kuroki, S.; Kurosu, H.; Ando, I. *J. Chem. Phys.* **1999**, *111*, 7110.
(15) Kim, S.; Kimura. H.; Kuroki, S.; Ando, I. *Chem. Phys. Lett.* **2003**, *367*, 581.
(16) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamic*; Clarendon Press: Oxford, 1986.
(17) Brewer, J. R.; Tsuchihara, K.; Morita, R.; Jones, J. R.; Bloxsidge, J. P.; Kagao, S.; Otsuki, T.; Fujishige, S. *Polymer* **1994**, *35*, 5109.
(18) Brewer, J. R.; Tsuchihara, K.; Morita, R.; Jones, J. R.; Bloxsidge, J. P.; Fujishige, S. *Polymer* **1994**, *35*, 5118.
(19) Mark, J. E.; Chiu, D. S.; Su, T. K. *Polymer* **1978**, *19*, 407.
(20) Dvinskikh, S. V.; Sitnikov, R.; Furó, I. *J. Magn. Reson.* **2000**, *142*, 102.
(21) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.
(22) Callaghan, P. T. *Principles of Nuclear Magnetic Resonance Microscopy*; Claredon Press: Oxford, 1991.
(23) Price, W. S. *Annu. Rep. NMR Spectrosc.* **1996**, *32*, 51.
(24) Bueche, F. *Physical Properties of Polymers*; Interscience Publishers: New York, 1962.
(25) Kögler, G.; Hasenhindl, A.; Möller, M. *Macromolecules* **1989**, *22*, 4190.
(26) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679.
(27) Hahn, E. L. *Phys. Rev.* **1950**, *80*, 580.
(28) Yin, Y.; Zhao, C.; Kuroki, S.; Ando, I. *Macromolecules* **2002**, *35*, 5910.

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