Diffusional Behavior of Rodlike Poly(γ-benzyl L-glutamate) in Concentrated Solution As Studied by the Field-Gradient ^{1}H NMR Methods

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Introduction

It is well known that poly(glutamate)s with long n-alkyl side chains form thermotropic liquid crystalline state by melting of the side-chain crystallites and also poly(glutamate)s such as poly(γ-benzyl L-glutamate)(PBLG), poly(γ-n-alkyl L-glutamate), etc. in solvent form the isotropic, biphasic and liquid crystalline phases which contains cholesteric and columnar liquid crystalline forms depending on the polypeptide concentration. In our previous works, we have successfully measured the diffusion coefficients of rodlike polypeptides such as α-helical poly(γ-glutamate)s having long n-alkyl side chains as a function of the α-helical chain length in the thermotropic liquid crystalline state[1,2] and of α-helical poly(γ-n-octadecyl L-glutamate) and chloroform as solvent in the isotropic, biphasic and liquid crystalline phases[3] by high field-gradient ^{1}H NMR method. Most recently, we reported the diffusional behavior of Poly(β-benzyl L-aspartate) (PBLA) in the rod-like, random-coil and intermediate forms[4]. Although there is no diffusion study for PBLG in liquid crystalline state, because it is difficult to observed ^{1}H spectrum of PBLG in liquid crystalline state for its very short ^{1}H T_2. In this study, the diffusional behavior of rodlike PBLG in concentrated solution is successfully elucidated as studied by the field-gradient ^{1}H NMR methods.

Experimental

Materials. PBLG (DP (degree of polymerization) = 463)was purchased from Sigma Chemical Co. The PBLG solution was prepared by placing PBLG and 1,4-dioxane in 10mm NMR tube. The PBLG concentration was 35 %. In 1,4-dioxain solution, PBLG takes α_R-helical form. The rod length calculated by DP is 69.4 nm.

NMR measurements. The self-diffusion coefficient measurements were carried out by means of a Bruker Avance 300 NMR spectrometer using pulse field gradient stimulated echo (PFGStE) method. The echo signal intensity is measured by changing the gradient strength G from 1.5 to 11 T/m, and the gradient pulse interval Δ is 800 ms, and the gradient pulse width δ is 1.1 ms, and the recycle delay are 2 to 4 s.

If the diffusion component is able to be suppose as the single diffusion component, the relationship between the echo signal intensity as a function of G (A(G)) and the pulse field-gradient parameters in the PFGStE method is given by

$$A(G) = A(0)\exp\left(-\gamma^2\delta^2G^2D(\Delta - \delta/3)\right) \quad (1)$$

where A(0) is the signal intensity in the absence of gradient pulses, γ the magnetogyric ratio 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 $–D$. Therefore, the D value can be determined from this slope.

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

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

where D_i and f_i are the 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.

Results and discussion

To obtain the diffusion coefficients (D) of PBLG in concentrated solution at wide temperature range, ^{1}H PGStE NMR measurements were performed from 20 to 60°C. Figure 1 shows ^{1}H PGStE NMR spectra of PBLG (35%) in 1,4-dioxane by varying field-gradient strength G at 25 and 60°C. The observed signal is mainly assigned to the phenyl protons of PBLG. The signal of 1,4-dioxane disappear in this experimental condition (G >1.5 T/m), because of the larger D of 1,4-dioxane compared with PBLG. So only the signal from PBLG can be observed. From the phase diagram of PBLG solution, it assumed that there exit the isotropic and columnar phases at lower temperature and there exist the cholesteric(nematic in the magnetic field) and columnar phases at higher temperature in 35% PBLG solution. From the decay of signal attenuation, 2 kinds of D component can be determined at every temperature.
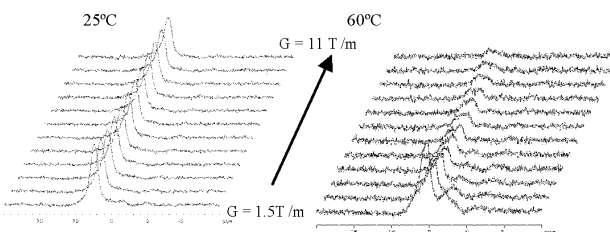

Figure 1 ^{1}**H PGStE NMR spectra of PBLG(35%)of DP 463 in 1,4-dioxane by varying field-gradient strength G at 25 and 60°C.**

Figure 2 shows the plots of the Ds of PBLG (35 %) of DP 463 in 1,4-dioxane against temperature. The isotropic and columnar phases coexist below 310 K, and the nematic and columnar phases coexist above 310K. The D of the isotropic phase is 3.98 to 7.71×10^{-12} m^2/s, that of the nematic phase is 1.84 to 4.83×10^{-12} m^2/s, and that of the columnar phase is 2.43×10^{-14} to 2.18×10^{-13} m^2/s, respectively. From the D values it is possible to elucidate the radius of gyration R_g of each phase. These R_g are larger than 8.93 nm which is calculated by the rod length of 69.4 nm shown as Figure 2.
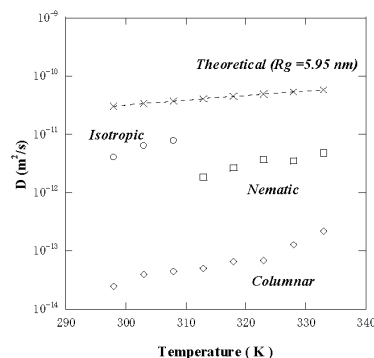

Figure 2 The plots of the determined diffusion coefficients of PBLG (35 %) of DP 463 in 1,4-dioxane against temperature.

Conclusions

The diffusion coefficient (D) of PBLG of the isotropic, nematic and columnar phases in concentrated solution is successfully determined by the field-gradient ^{1}H NMR methods.

References
[1] Yin, Y.; Zhao, C.; Kuroki, S.; Ando, I. *J. Chem. Phys.* **2000**, *113*, 7635.
[2] Yin, Y.; Zhao, C.; Kuroki, S.; Ando, I. *Macromolecules* **2002**, *35*, 2335.
[3] Yin, Y.; Zhao, C.; Kuroki, S.; Ando, I. *Macromolecules* **2002**, *35*, 5910.
[4]Kanesaka,S.; Kamiguchi,K.; Kanekiyo, M.; Kuroki, S. Ando, I. *Biomacromolecules*, **2006**,7, 1323.