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Elementary Processes in Side-Chain Motions of Poly(α-amino acids)

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ABSTRACT: Dielectric measurements covering a frequency range from 10 MHz up to 10 GHz were performed on poly(γ-methyl L-glutamate), poly(γ-benzyl L-glutamate), and poly[γ-(*p*-chlorobenzyl) L-glutamate] in dioxane solution at 25 °C by means of time-domain reflectometry. Two relaxation processes with relaxation times around 440 and 20 ps were observed for each polymer. The lower frequency relaxation process can be attributed to restricted rotations of C–C bonds in the side chain, neighboring to the α-helical backbone. The higher frequency process is caused by free rotations of C–O bonds in the side chain.

I. Introduction

Physical and chemical properties of poly(α-amino acids) have been studied extensively as simple models of proteins and rodlike molecules. It has been pointed out that side chains play important roles in chain conformations of protein molecules.[1-3] There remains a great interest in understanding the side-chain motions of synthetic analogues.

A number of investigations of the side-chain motions of poly(α-amino acids) have been made in the solid state by the dielectric method. An important result of these studies is that only one relaxation process is observed, even if the side chains have several dipole components.[4-7] A reasonable interpretation is that the process results from cooperative motions of neighboring side chains. Observation of a single-relaxation process in some copolymers supports strongly existence of cooperative motions.[4,5] A detailed discussion of cooperative motions has been given elsewhere.[6]

Recently, Nakamura et al.[8] found a side-chain relaxation process of poly(γ-benzyl L-glutamate) (PBLG) in dioxane solution, the relaxation time of which is about 150 ps at 20 °C by the time-domain reflectometry (TDR) method. However, cooperative interactions between neighboring side chains are thought to be weaker in dilute solution than in the solid state. Therefore, in order to examine whether multiple relaxation processes according to various kinds of localized motions in the side chain exist or not, relaxation measurements over a wide and high frequency region have long been desired.

Recent developments in the TDR method are remarkable and make it possible to measure the complex permittivity easily even at 10 GHz.[9-11] Single-bond rotations in some oxide polymers have already been observed in the gigahertz region by the TDR method.[10] Employing the TDR method in this work, we performed dielectric measurements on poly(γ-methyl L-glutamate) (PMLG), PBLG, and poly[γ-(*p*-chlorobenzyl) L-glutamate] (PpClBLG) in dioxane solutions in order to clarify elementary processes of their side-chain motions.

Table I
Relaxation Parameters for Poly(α-amino acids) in Dioxane Solution at 25 °C[a]

	lower frequency process			higher frequency process		
sample	τ_l, ps	$\Delta\epsilon_l$	μ_{el}, D	τ_h, ps	$\Delta\epsilon_h$	μ_{eh}, D
PMLG	480	0.028	0.92	16	0.054	1.3
PBLG	430	0.049	1.1	22	0.040	1.0
PpClBLG	420	0.033	1.0	20	0.077	1.6

[a] Concentrations are 2.5 wt % for PMLG and 5 wt % for the others.

II. Experimental Section

PMLG (Ajicoat A-2000) was provided by Ajinomoto Co., Ltd. PBLG was obtained from Sigma Co., Ltd. PpClBLG was prepared by the ester-exchange reaction of PMLG and *p*-chlorobenzyl alcohol.[6,12] The mole fraction of *p*-chlorobenzyl glutamate was determined as 99% from proton NMR spectra. The concentrations of the polymers in dioxane solution used were 2.5 wt % for PMLG and 5 wt % for both PBLG and PpClBLG.

Dielectric measurements were made in the frequency range 10 MHz to 10 GHz at 25 °C by the TDR method. The apparatus and detailed procedures have already been reported.[10] We used a cell with a length of the inner conductor d = 0.402 mm for measurements at frequencies lower than 1 GHz, and a cell with d = 0.128 mm at frequencies higher than 0.5 GHz. Effective lengths γd for these cells are 1.92 and 1.11 mm, respectively.

III. Results

Figures 1–3 show frequency dependences of the complex permittivity for the PMLG, PBLG, and PpClBLG solutions, respectively. Two relaxation processes are found in each polymer solution. Nakamura et al.[8] pointed out that relaxations observed in such a high-frequency region must reflect the side-chain motions.

In order to obtain relaxation parameters for each process, the permittivity ϵ^* $(=\epsilon' - j\epsilon'')$ is assumed to be given as a superposition of two single-relaxation processes[13]

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon_l}{1 + j\omega\tau_l} + \frac{\Delta\epsilon_h}{1 + j\omega\tau_h} \qquad (1)$$

where ϵ_∞ is the high-frequency limit of the permittivity,

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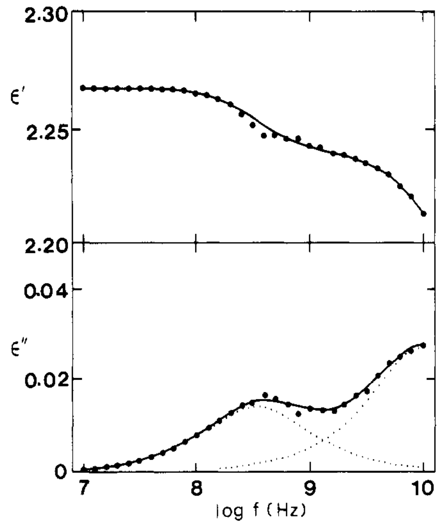

Figure 1. Frequency dependence of the complex permittivity for PMLG in 2.5% dioxane solution at 25 °C. Solid curves are calculated from eq 1. Dotted curves show the second and the third terms in eq 1.

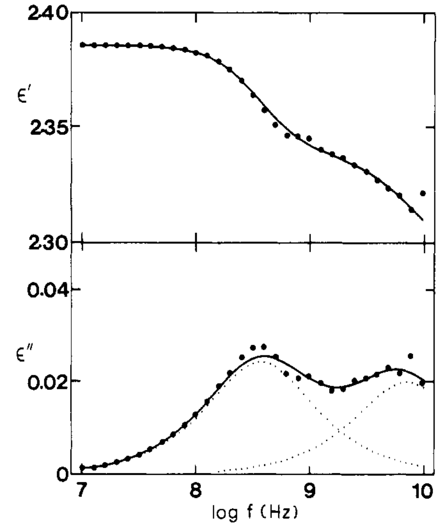

Figure 2. Frequency dependence of the complex permittivity for PBLG in 5% dioxane solution at 25 °C. Solid and dotted curves have the same meanings as in Figure 1.

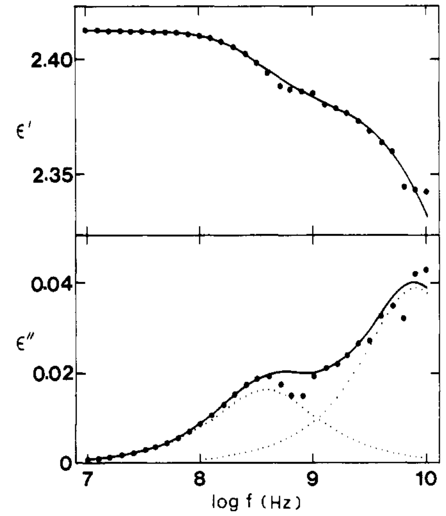

Figure 3. Frequency dependence of the complex permittivity for PpClBLG in 5% dioxane solution at 25 °C. Solid and dotted curves have the same meanings as in Figure 1.

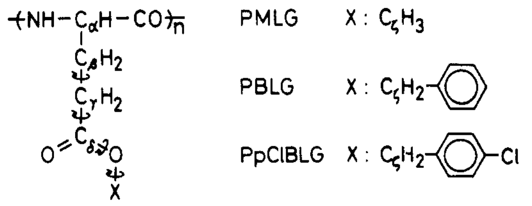

Figure 4. Chemical structures and bond rotations active in dielectric relaxation of PMLG, PBLG, and PpClBLG.

$\Delta\epsilon$ is the relaxation strength, ω is the angular frequency, τ is the relaxation time, and subscripts l and h denote the lower and higher frequency relaxations, respectively. Values of the relaxation parameters in eq 1 are chosen by the best fitting procedure to the experimental results, which are listed in Table I. Solid curves calculated from eq 1 with these values explain the experimental data quite satisfactorily as is shown in Figures 1–3. Uncertainties of 10% for the relaxation time, the relaxation strength, and the resultant dipole moment are unavoidable in the TDR method.[8-11]

An effective dipole moment μ_e for each relaxation process can be calculated from the Onsager equation[14]

$$\mu_e = \left[\frac{3kT\Delta\epsilon}{4\pi N_0} \frac{2\epsilon_0 + \epsilon_\infty}{3\epsilon_0} \right]^{1/2} \frac{3}{\epsilon_\infty + 2} \tag{2}$$

where N_0 is the number of dipoles per unit volume and ϵ_0 is the lower frequency limit of the permittivity. Values of μ_e thus obtained are listed in Table I.

IV. Discussion

As seen in Table I, values of τ_l are nearly the same (about 440 ps) for all polymers. This result implies that the lower frequency process is due to an orientation of a dipole of the same group for all polymers. Chemical structures and bond rotations active in dielectric relaxation are shown in Figure 4. The elementary process in the chain motion should be essentially a single-bond rotation[10] and not be affected by C_α–C_β bond rotation in the present case. It is clearly seen that the lower frequency process is caused by an orientation of a resultant dipole of the $C_\gamma C_\delta OO$ group and comes from rotations of the C_β–C_γ and C_γ–C_δ bonds.

The relaxation time of τ_l = 440 ps seems to be too long for the lower frequency process at first sight if compared with that of 84 ps observed in poly(ε-caprolactone).[11] Furthermore, a mean value of the effective dipole moments in Table I, 1.0 D, is considerably smaller than the dipole moments expected for free rotations of ester groups such as methyl acetate or ethyl acetate.[3,8] If a rotation of the C_δ–O bond is assumed to be free, the effective dipole moment for the C_γ–C_δ bond rotation is calculated as 1.7 D and is fairly large compared to the value observed. These results indicate that the motion of the $C_\gamma C_\delta OO$ group is considerably restricted.

Hikichi[7] pointed out from a computer simulation of side-chain motions of PBLG that if electrostatic interaction between the side chain and backbone is neglected, the rotational angle around the C_γ–C_δ bond takes all values except the cis angle. This suggests that the origin of the restricted motion of the $C_\gamma C_\delta OO$ group is not steric hindrance but the dipole–dipole interaction between a large dipole moment (3.5 D) per residue in the α-helical backbone and that of the $C_\delta OO$ group.

Since the O–C_ζ bond rotation is not active in dielectric relaxation for PMLG, it is definite that the higher frequency process is caused by the C_δ–O bond rotation. Similar ester-bond rotation is observed in poly(methyl methacrylate).[15] Using a value of 1.3 D for a dipole moment of the O–$C_\zeta H_3$ group, we obtain the effective dipole moment for free rotation of the C_δ–O bond as 1.2 D. This value is in good agreement with the experimental one for PMLG.

In the case of PBLG, the dipole moment of the benzyl group (0.4 D)[16] is smaller than that of the O–$C_\zeta H_3$ group. Therefore the higher frequency process of PBLG seems to be predominantly caused by C_δ–O bond rotation. If we take the dipole moment of the benzyl group into account, the effective moment for the C_δ–O bond rotation is calculated as 1.0 D and agrees completely with the experimental one. The fact that the value τ_h of PBLG is larger than that of PMLG indicates an increase in the moment of inertia of the motional unit.

Adachi et al.[17] pointed out from a dielectric study on dichloromethane solutions of PBLG with concentrations of 20–100 wt % that dipoles of the side chains cannot reorient freely in all directions. The present results indicate that such restriction is confined only in the motions of C–C bonds close to the backbone chain in dilute solution.

It is clear from a comparison between the dipole moments of PpClBLG and PBLG that the high-frequency process for PpClBLG is caused not only by the C_δ–O bond rotation but also by the O–C_ζ bond rotation. If the O–C_ζ bond rotation is assumed to be free and the dipole moment of *p*-chlorotoluene (1.9 D)[16] is taken as that of the *p*-chlorobenzyl group, the effective moments for the C_δ–O and O–C_ζ bond rotations are calculated as 0.3 and 1.7 D, respectively. When each rotation occurs independently, the total moment is obtained simply as 1.7 D $[=(0.3^2 + 1.7^2)^{1/2}$ D] and agrees well with the experimental value. It may be concluded that contribution of the O–C_ζ bond rotation to the higher frequency process is predominant and the O–C_ζ bond rotation occurs at nearly the same rate as the C_δ–O bond rotation.

Relaxations observed in this work clarify the elementary processes in side-chain motions of poly(α-amino acids). Motions of the C–C bonds neighboring to the backbone chain are fairly restricted but rotations of the C–O bonds in the end of the side chain are nearly free. We believe that the TDR method is one of the most effective techniques for studying physical, chemical, and biological functions due to elementary processes of molecular motions.

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Self-Diffusion Coefficient in Melts of Linear Polymers: Chain Length and Temperature Dependence for Hydrogenated Polybutadiene

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ABSTRACT: Self-diffusion coefficients in the molten state were determined for several samples of linear hydrogenated polybutadiene (HPB), a polymer which closely resembles polyethylene in structure and melt properties. Films with alternating layers of protonated and partially deuterated chains with the same chemical structure were used. Values of D were obtained from the growth of coherent neutron scattering intensity as the layers interdiffused. The temperature dependence of D was independent of molecular weight but slightly weaker than that for the melt viscosity. The magnitude of the difference was shown to be consistent with predictions based on recent theories of entangled-chain dynamics. The chain length dependence accurately obeyed the inverse square law predicted by reptation, $D = k_D M^{-2}$. The value of k_D, extrapolated to 176 °C, agrees fairly well with Klein's diffusion-couple results at that temperature for both HPB and linear polyethylene. It also agrees well with a theoretical prediction of k_D based on viscoelastic measurements.

Introduction

Recent theories[1-5] on polymer chain dynamics in concentrated solutions and melts lead to a series of predictions about the effect of chain length on dynamic properties. According to the reptation model of de Gennes,[1] the translational diffusion coefficient of long, linear polymer chains in the melt is inversely proportional to the square of molecular weight:

$$D = k_D M^{-2} \qquad (1)$$

Klein and Briscoe[6] first verified the inverse square dependence by classical diffusion-couple experiments,

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