

Dielectric Properties of Poly(β -benzyl-L-aspartate)

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ABSTRACT: Dielectric measurements of samples of poly(β -benzyl-L-aspartate) in the α and ω forms were performed over the frequency range from 30 Hz to 1 MHz and at temperatures from -40 to 140°C . A dispersion peak arising from the molecular motion of the side chain was found and is discussed in detail. The activation energies estimated from the Arrhenius plot were very similar for the α form and the ω form. The Cole–Cole plot showed that ($\epsilon_0 - \epsilon_\infty$) of the α form is almost equal to that of the ω form or is a little larger. But the dispersion temperature of the α form is higher than that of the ω form. On the basis of our experimental results, the motion of the carbonyl group in the side chain was discussed in relation to the interaction between the main chain and the side chain.

KEY WORDS Dielectric Properties / Arrhenius Plot / Cole–Cole Plot / Poly(β -benzyl-L-aspartate) / Side Chain Motion

The molecular motion of poly(β -benzyl-L-aspartate) (PBLAsp) has been investigated using analyses of the dynamic mechanical properties, the dielectric properties, and the method of NMR.^{1–4} The dispersion associated with the motion of the side chain of PBLAsp has not been discussed in such detail as has been devoted to the motions of the side chain of poly(γ -methyl-L-glutamate) and poly(γ -benzyl-L-glutamate).^{2,4–9} The motion of the carbonyl group on the side chain of PBLAsp, which is located closer to the main chain than that of the polyglutamate series, is interesting from the stand-point of the interaction between the main chain and the carbonyl group on the side chain.

It has been reported that two kinds of structure of PBLAsp are formed, *i.e.*, the α and ω forms.^{10,11} It is considered that these structures are produced because of different interactions between the main chain and the side chain. In this paper the dielectric behavior was studied with respect to the difference of the structures of the side chain, *i.e.*, the α and ω forms.

EXPERIMENTAL

Materials

The procedure of preparing poly(β -benzyl-L-aspartate) was as follows. *N*-carboxy- β -benzyl-L-aspartate anhydride (NCA) was synthesized by

use of Leuch's method from β -benzyl-L-aspartate produced from aspartic acid.¹² The purified NCA was polymerized in ethylene dichloride solution. The polymer thus obtained has an intrinsic viscosity of $[\eta]=0.43$ in dichloroacetic acid solution, which gives a weight-average molecular weight of 6×10^4 as calculated from the viscosity–molecular weight relation of Doty, *et al.* for poly(γ -benzyl-L-glutamate).¹³ A film consisting of the α form was prepared by casting from chloroform solution at room temperature. The film was dried under vacuum at room temperature after immersion in methanol in a day. A film in the ω form was obtained by annealing a film in the α form at 140°C for several hours. The formation of the ω form by annealing was checked by X-ray diffraction analysis and by infrared spectra.

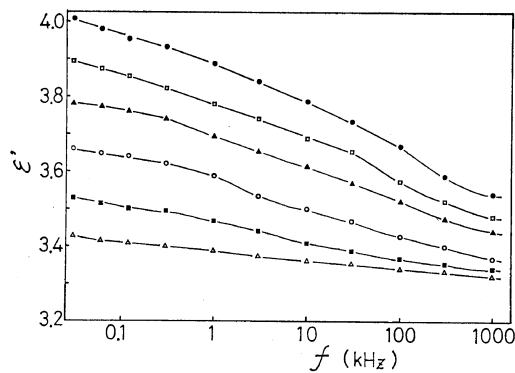
Procedures

Dielectric measurements (dielectric constant, ϵ' , and dielectric loss, ϵ'') were carried out with a mutual inductance bridge (TR-1C), a detector (BDA-1B), and an oscillator (WBG-3G) manufactured by Ando Electric Co., Ltd. and pursued from -40 to 140°C over a frequency range from 30 to 10^6 Hz.

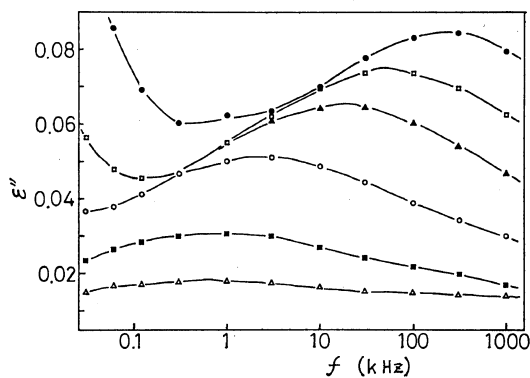
RESULTS AND DISCUSSION

The frequency dependence of ϵ' and ϵ'' for

Dielectric Properties of Poly(β -benzyl-L-aspartate)



(a)



(b)

Figure 1. Dielectric constant ϵ' (a) and dielectric loss ϵ'' (b) as a function of frequency for the α form of poly(β -benzyl-L-aspartate): ●, 91.0°C; □, 81.0°C; ▲, 72.0°C; ○, 56.0°C; ■, 41.0°C; △, 25.5°C.

the α form PBLAsp at various temperatures is shown in Figures 1a and 1b. An absorption peak against frequency was found, although the maximum of ϵ'' of the α form of PBLAsp is smaller than that of poly(γ -benzyl-L-glutamate) and poly(γ -methyl-L-glutamate) as reported by Sugai, *et al.*⁶ and Tsuchiya, *et al.*⁹ The frequency dependence of ϵ' exhibits a behavior corresponding to the result of ϵ'' . This seems to be attributable to the motion of the side chain, especially the carbonyl group, using the results of the NMR study^{1,4} and the comparison with the motion of the side chain in other polypeptides, *e.g.*, poly(γ -benzyl-L-glutamate) and poly(γ -methyl-L-glutamate). The frequency dependence of ϵ'' of the ω form is also shown

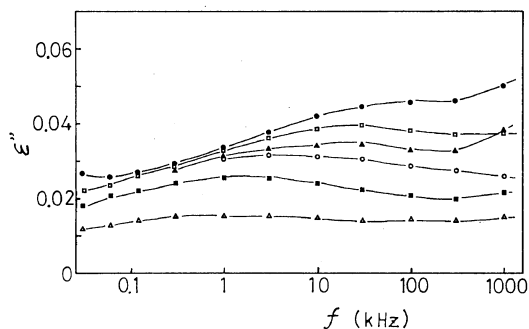


Figure 2. Dielectric loss ϵ'' as a function of frequency for the ω form of poly(β -benzyl-L-aspartate): ●, 64.0°C; □, 59.5°C; ▲, 51.0°C; ○, 43.0°C; ■, 36.0°C; △, 20.0°C.

in Figure 2. A dispersion due to the same mechanism as in the α form also appeared in the ω form. The dispersion due to the motion of the side chain of PBLAsp has never been discussed in detail from the view-point of dielectric and dynamic mechanical properties.

The slope of the Arrhenius plot, which represents the relation between the frequency at maximum loss (f_m) and the reciprocal absolute temperature T^{-1} , yields the activation energy ΔH_{act} associated with the motion of the side chain, the carbonyl group. As evaluated from Figure 3, the activation energies of the α and ω forms of PBLAsp are almost the same: 13.8

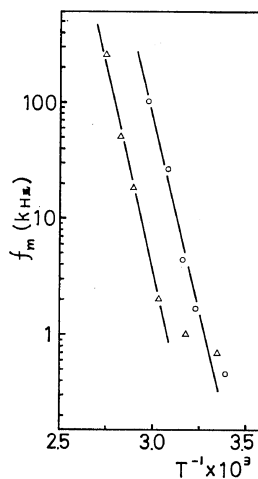


Figure 3. Relation between the frequency at maximum loss (f_m) and reciprocal absolute temperature (T^{-1}): △, α form; ○, ω form.

kcal/mol and 13.1 kcal/mol, respectively. The ω form is a helix with a four-fold symmetry and a special interaction (stacking) between the neighboring side chains (n th and $(n+4)$ th benzene ring), as pointed out by Elliott, *et al.*,^{10,11} while the α form has no such interaction of the side chain. The dispersion obtained from dielectric measurements is attributed not to the motion of all parts of the side chain but to the motion of the carbonyl group alone. Therefore the fact that the activation energy obtained from dielectric measurements of both the α and ω forms is almost the same even for different structures of the side chain suggests that the special interaction of the benzyl group does not greatly influence the motion of the carbonyl group.

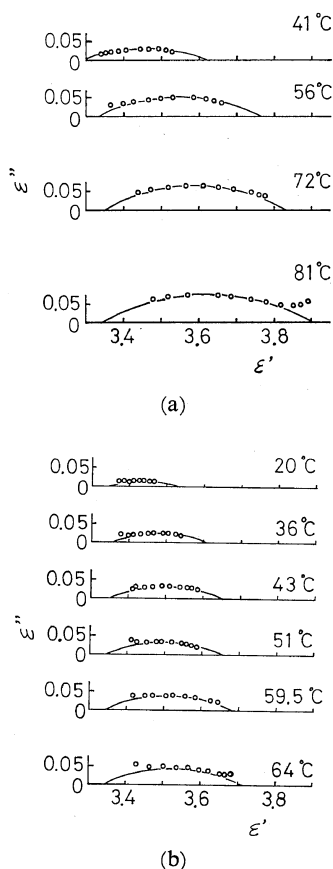


Figure 4. Cole—Cole plot of the α form (a) and the ω form (b) poly(β -benzyl-L-aspartate) (temperature is indicated in the figure).

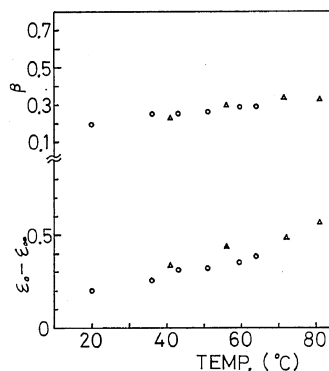


Figure 5. The temperature dependence of Cole—Cole parameter ($\epsilon_0 - \epsilon_\infty$) and β : Δ , α form; \circ , ω form.

Similarly, the magnitude of the dispersion ($\epsilon_0 - \epsilon_\infty$) of the α and ω forms provides a qualitative explanation. From the Cole—Cole plot¹⁴ (Figure 4), the magnitude of the dispersion ($\epsilon_0 - \epsilon_\infty$) was obtained against temperature, as shown in Figure 5. The magnitude of PBLAsp (α and ω forms) is small and a half or one third of that of poly(γ -benzyl glutamate). Therefore it is difficult to observe the dispersion. This may be the reason why no report and discussion has so far been made about the dielectric dispersion of PBLAsp. The magnitude of the α form is almost equal to that of the ω form or a little larger at the same temperature, as shown in Figure 5. Thus, there seems to be almost the same motional freedom of the carbonyl group in the α and ω forms or even a smaller motional freedom of the carbonyl group in the ω form, in which the neighboring benzyl groups were stacked with four-fold symmetry, than in the α form. Compared with the motion in poly(γ -benzyl glutamate) and poly(γ -methyl glutamate),^{6,9} however, the motion of the side chain of both the α and ω forms of PBLAsp seems to be greatly hindered by the peptide group of the main chain, because the carbonyl group in the side chain of PBLAsp is nearer to the main chain than that of the polyglutamate series. The temperature dependence of ($\epsilon_0 - \epsilon_\infty$) of the α and ω forms indicates similar behavior and suggests a similar motional freedom of the α and ω forms.

As shown in Figure 5, the Cole—Cole

parameter β indicating the width of the distribution of relaxation times does not change with temperature very much as the temperature increases. The width of the distribution of relaxation times remains rather broad. No important difference in β between the α and ω forms was observed.

The temperature dependence of ϵ'' at 1 kHz of the α and ω forms of PBLAsp is plotted in Figure 6. The absorption peak of the α form appeared at a higher temperature (76°C) than

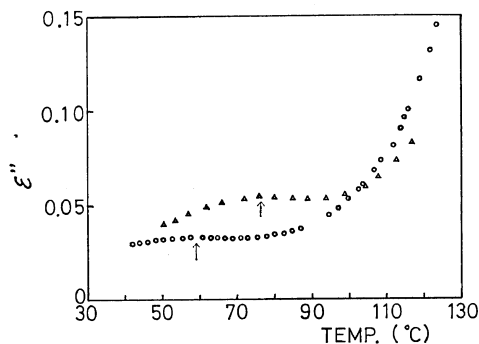


Figure 6. Dielectric loss ϵ'' as a function of temperature at a frequency of 1 kHz for the α form (Δ) and the ω form (\circ) of poly(β -benzyl-L-aspartate): \uparrow , dispersion temperature.

Table I.

	α Form	ω Form
ΔH_{act} (kcal/mol)	13.8	13.1
$(\epsilon_0 - \epsilon_\infty)$ at 50°C	0.39	0.32
Dispersion temp., °C at 1 kHz	76	59

that of the ω form (59°C), as shown in Table I and Figure 6. Thus, the dispersion temperature of the α form was about 17°C higher than that of the ω form. Happey's NMR result indicates that the decrease in line width (which may be associated with benzene-ring rotation) occurs some 20°C lower in the ω form than in the α form.⁴ On the assumption of a successive molecular motion of the carbonyl group after benzene-ring rotation, the dispersion temperature is considered to be some degrees lower in the ω form than in the α form. Our results noted above agree with Happey's results. In the ω

form, the benzene rings form four-fold stacks, in which the n th and $(n+4)$ th rings are separated by 5.3 Å along the helix axis. If the benzene ring is assumed to have a van der Waals thickness of 3.4 Å, it can rotate. In the α form, with 3.6 residues per turn, the rotation of the benzene ring is hindered by the presence of δ O and ϵ CH₂ atoms of the residue above and below the benzene ring. The benzene ring of the ω form can rotate much more freely than those of the α form. Therefore, the carbonyl group of the ω form is considered to be more mobile than that of the α form. It is thus reasonable that the dispersion temperature of the α form is higher than that of the ω form.

It is concluded that the activation energy is not greatly influenced by the different structure of the side chain, but remains almost the same. The dispersion temperature of the α form is, however, higher than that of the ω form, that is, the carbonyl group in the α form is more difficult to move than that in the ω form. From the results of $(\epsilon_0 - \epsilon_\infty)$, it is concluded that the motional freedom of the carbonyl group in the α form is almost equal to that of the ω form or is a little larger.

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