

Dielectric Properties of Poly(γ -benzyl L-glutamate-co-L-leucine) and Poly(γ -methyl L-glutamate-co-L-leucine) in the Solid State

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ABSTRACT: Dielectric measurements were performed on poly(γ -benzyl L-glutamate-co-L-leucine) (copoly(BLG,Leu)) and poly(γ -methyl L-glutamate-co-L-leucine) (copoly(MLG,Leu)) in the solid state. The composition dependence of the dielectric behavior of these copolymers was examined. It was found that the introduction of a Leu residue decreased the mobility of the benzyl L-glutamate side chain of copoly(BLG,Leu), while it increased the mobility of the methyl L-glutamate side chain of copoly(MLG,Leu). The results were interpreted in terms of the side chain interaction. The hydrophobic interaction between the benzene ring of the benzyl glutamate residue and the methyl group of the leucine residue is a possible cause for the decreases in mobility of copoly(BLG,Leu).

KEY WORDS Dielectric Relaxation / Poly(γ -benzyl L-glutamate-co-L-leucine) / Poly(γ -methyl L-glutamate-co-L-leucine) / Side-Chain Motion / Copolymer /

Various poly(α -amino acid)s differ only in their side chains, and interactions between side chains play major roles in determining properties. For α -helical poly(α -amino acid)s the side chain interaction is particularly important because the surface of such rod-like molecules is covered with side chains.¹ The molecular motions in a number of poly(L-glutamate)s have been investigated in detail by various methods including dynamic mechanical, dielectric, and wide-line nuclear magnetic resonance measurements.²⁻¹⁸ It has been reported that glutamate side chains have motion near room temperature, accompanied by some mechanical and dielectric relaxations, while the backbone chain remains in the rigid α -helical conformation.

In recent years, much interest has been

directed to copolymers of amino acids. For copolymers of γ -benzyl L-glutamate and γ -methyl L-glutamate, the side chains of both residues have been found to take on cooperative motion.¹¹ Similar cooperativity was observed in copolymers of γ -methyl L-glutamate and γ -*p*-chlorobenzyl L-glutamate.¹⁸

In the present work, we carried out dielectric measurements on two kinds of random copolymers: copolymer of γ -benzyl L-glutamate and L-leucine (copoly(BLG,Leu)), and copolymer of γ -methyl L-glutamate and L-leucine (copoly(MLG,Leu)). Since the Leu side chain has no polar groups, we can monitor only glutamate side chains through dielectric measurements. The purpose of this work was to investigate the effects of the Leu side chain on the motion of the glutamate side chain. The

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motion of glutamate side chains in the two copolymers was interpreted in terms of side chain interactions.

EXPERIMENTAL

All samples used in this work except poly(γ -methyl L-glutamate) (PMLG) were obtained by polymerizing *N*-carboxyanhydrides (NCA) in dioxane or in a mixture of dioxane and benzene at room temperature for 1–7 days. A trace of triethylamine was used as the initiator. PMLG was kindly supplied by Ajinomoto Co. The composition of the comonomers was determined by proton NMR spectroscopy and almost the same as the initial mixing ratio of NCA's. Amide I, II, and V bands in the IR spectra suggest that these polymers are in the α -helical conformations.

Films about 0.2 mm thick were made for dielectric measurements by casting a concentrated chloroform solution on a glass plate at room temperature. After annealing the films at 130°C for 48 h *in vacuo*, silver was deposited on both sides of films in order to ensure good contact with the electrodes.

The dielectric constant ϵ' and the loss factor ϵ'' were measured in a frequency range from 30 Hz to 100 kHz and over a temperature range from -100 to 100°C using a TR-1C transformer bridge manufactured by Ando Denki Co. A WBG-5 oscillator (Ando Denki Co.) and a Model LI-573 lock-in amplifier (NF Circuit Design Block Co.) were used.

RESULTS AND DISCUSSION

Figures 1(a) and (b) show the temperature dependence of the dielectric loss factor ϵ'' at a frequency of 1 kHz for copoly(BLG,Leu)s and copoly(MLG,Leu)s, respectively. A loss peak could be seen near room temperature for all copolymers studied. With increasing Leu content, the loss peak decreased in intensity for both copolymer series. Moreover, the maximum of loss peak shifted to higher tempera-

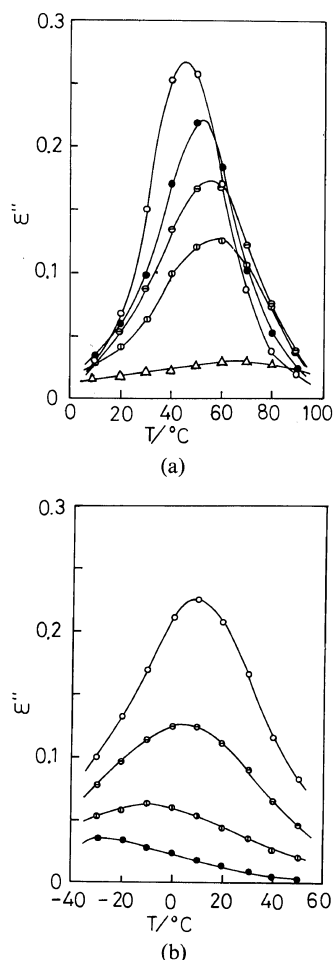


Figure 1. Temperature dependences of the dielectric loss factor ϵ'' at 1 kHz for (a) poly(γ -benzyl L-glutamate-co-L-leucine)s and poly(γ -methyl L-glutamate-co-L-leucine)s. Leucine monomer mole percents are for (a) \circ , 0; \bullet , 21; \ominus , 39; \oplus , 50; \triangle , 80, and for (b) \circ , 0; \ominus , 29; \oplus , 51; \bullet , 74.

tures for copoly(BLG,Leu)s but lower temperatures for copoly(MLG,Leu)s.

The relaxation strength $\Delta\epsilon$ was estimated from the Cole-Cole plot at a peak maximum temperature measured at 1 kHz, T_{\max} , for each copolymer. The results are shown as functions of Leu content in Figure 2. $\Delta\epsilon$ decreased linearly with increasing Leu content, and tended to zero at 100% Leu content. Hiltner and coworkers¹⁰ studied the dynamic mechanical behavior of copoly(BLG,Leu)s, and

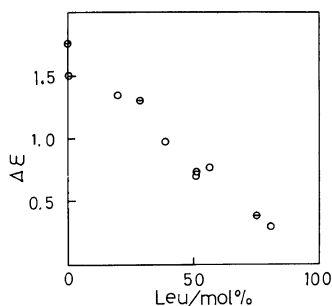


Figure 2. Leucine content dependences of the relaxation strength $\Delta\epsilon$ at a peak maximum temperature measured at 1 kHz for poly(γ -benzyl L-glutamate-co-L-leucine) (○) and poly(γ -methyl L-glutamate-co-L-leucine) (⊙).

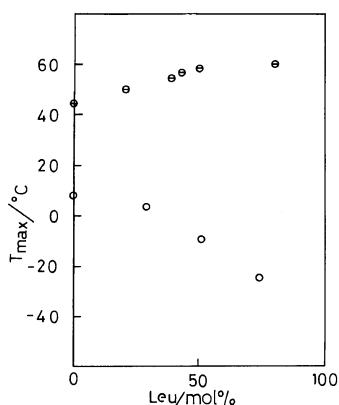


Figure 3. Leucine content dependences of the peak maximum temperature T_{\max} at 1 kHz for poly(γ -benzyl L-glutamate-co-L-leucine) (⊙) and poly(γ -methyl L-glutamate-co-L-leucine) (○).

found the intensity of the mechanical relaxation near room temperature to be proportional to BLG content. The results obtained here are in agreement with their results.

Dielectric relaxations observed near room temperature for homopolymers of BLG and MLG have been ascribed to side-chain motion.¹¹ One can, therefore, conclude that dielectric relaxation maxima observed for the copolymers are attributed to the motion of the glutamate side chain because the Leu side chain has no polar groups.

The temperature of the peak maximum measured at 1 kHz, T_{\max} , is plotted against Leu

content in Figure 3. With increasing Leu content, T_{\max} increased for copoly(BLG,Leu)s, but decreased considerably for copoly(MLG,Leu)s. Hiltner and coworkers¹⁰ reported that the introduction of Leu residues did not change the temperature of the motion of BLG side chains. However, careful inspection of their results shows a slight increase in the relaxation temperature. The results obtained here suggest that the motion of BLG and MLG side chains is affected by the introduction of Leu residues into the BLG sequence and the MLG sequence. It is of interest to note that Leu residues have opposite effects on the side-chain motion of the two copolymer series.

The values of T_{\max} were extrapolated to 100% Leu content for the two copolymer series and were 60°C for copoly(BLG,Leu) and -40°C for copoly(MLG,Leu). In such a limiting state where the BLG residue and the MLG residue are infinitely diluted by Leu residues, BLG and MLG residues interact only with Leu residues; there are no BLG-BLG or MLG-MLG interactions.

Previous NMR studies on poly(L-leucine)⁶ showed that all methyl groups rotate at -110°C and that all isobutyl groups rotate at 130°C. Poly(L-leucine) has been reported to show two mechanical relaxation peaks, a large peak due to the motion of its side chain at -150°C and another less intense one at -58°C.¹⁰ No relaxation peaks have been observed above room temperature. The limiting value of T_{\max} for copoly(BLG,Leu), 60°C, suggests that the motion of BLG at infinite dilution by Leu residues does not reflect the motion of the side chain of poly(L-leucine) but reflects that of BLG itself which is affected by neighboring Leu side chains.

Thus, the results obtained here suggest that there is a strong interaction between BLG and Leu residues, and that the interaction hinders the motion of BLG side chains. In the previous paper,¹¹ we studied the dielectric behavior of copolymers of BLG and MLG, and found that

the BLG and MLG side chains in copolymers take on cooperative motion. When MLG residues are introduced into the BLG sequence to some extent, side-chain motion occurs at rather high temperatures compared to the homopolymers of BLG and MLG. We suggested the existence of a strong interaction between BLG and MLG residues for copoly(BLG,MLG). Moreover, Hiltner and coworkers¹⁰ reported that the random introduction of a small number of BLG residues into poly(L-leucine) shifts the mechanical relaxation due to local motion of the Leu side chain observed at -150°C at 1 Hz to lower temperatures, and decreases its intensity remarkably. They concluded that the neighboring side chain interaction is an important factor in determining side-chain mobility. It is likely that BLG-Leu and BLG-MLG interactions are hydrophobic ones between benzene rings and methyl groups.

On the other hand, the limiting value of T_{max} for copoly(MLG,Leu), -40°C , seems to approach the temperature of the less intense mechanical relaxation peak of poly(L-leucine), -58°C at 1 Hz. Although the origin is not clear, this mechanical relaxation peak is possibly due to some kind of motion of the Leu side chain. Thus, the motion monitored through MLG side chains reflects the motion of Leu side chains. There is no such strong interaction between MLG and Leu residues as observed for poly(BLG, Leu).

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