

NOTES

## Dielectric and DSC Studies on Racemic Mixtures of Poly( $\gamma$ -benzylglutamate-co- $\gamma$ -*p*-chlorobenzylglutamate)

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So far, physical properties of poly(glutamate)s in the solid state have been investigated by many workers.<sup>1-22</sup> It has been found that in the vicinity of room temperature, side chains undergo a rapid motion in keeping the backbone chain in the rigid  $\alpha$ -helical conformation. However, the temperature where such a motion onsets is widely different in various poly(glutamate)s due to the differences in interactions between side chains.

Recently, studies of the side chain motion for several copolymers have been reported. For copolymers of  $\gamma$ -benzyl L-glutamate and  $\gamma$ -methyl L-glutamate,<sup>9</sup> the side chains of both residues undergo cooperative motion and strongly interact to each other. Similar results were obtained for copolymer of  $\gamma$ -methyl L-glutamate and  $\gamma$ -*p*-chlorobenzyl L-glutamate.<sup>20</sup> For copolymers of  $\gamma$ -benzyl L-glutamate and L-leucine,<sup>22</sup> the mobility of the  $\gamma$ -benzyl L-glutamate side chain decreased with increase of the L-leucine residue which has a nonpolar side chain. The hydrophobic interaction between the benzene ring of the benzyl glutamate residue and the methyl group of the leucine

residue has been suggested as a possible cause. On the other hand, in the copolymers of  $\gamma$ -methyl L-glutamate and L-leucine,<sup>22</sup> there is no such interaction between the side chains. The side chain mobility of  $\gamma$ -methyl L-glutamate residue increased with increase of L-leucine residue.

These results indicate that the physical properties of copolymers of glutamates vary largely due to the interactions between different types of side chains. However, in the present stage, the studies on the copoly(amino acid)s in the solid state have not been made so much. This work has been performed to obtain further information on the physical properties of copolymers of glutamates.

In this work, some dielectric and differential scanning calorimetric measurements were carried out on the racemic mixtures of copolymers of  $\gamma$ -benzylglutamate BG and  $\gamma$ -*p*-chlorobenzylglutamate CBG in order to investigate the effects of chlorine atoms of CBG residues on the side chain mobility,<sup>18,20</sup> and the side chain stacking,<sup>17,19,23,24</sup> as a function of CBG content. For a comparison,

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measurements were made also on the racemic mixtures of the copolymers of BG and  $\gamma$ -*p*-methylbenzylglutamate, and the copolymers of  $\gamma$ -benzyl L-glutamate and  $\gamma$ -*p*-chlorobenzyl L-glutamate.

## EXPERIMENTAL

Poly( $\gamma$ -benzyl D-glutamate) (PBDG) and poly( $\gamma$ -benzyl L-glutamate) (PBLG) were polymerized from *N*-carboxyanhydride (NCA) in dioxane at room temperature for 5 days. A trace of triethylamine (0.01 mol) was used as an initiator. In order to obtain racemic mixture of PBG, equimolar amount of PBDG and PBLG were dissolved in chloroform in the same glass container. This racemic mixture was precipitated with ethanol and dried *in vacuo*. Copolymers of  $\gamma$ -benzyl L-glutamate and  $\gamma$ -*p*-chlorobenzyl L-glutamate (hereafter abbreviated as C(*x*)-L, *x*-being mol% of  $\gamma$ -*p*-chlorobenzyl L-glutamate) were prepared by the ester exchange reaction of PBLG with *p*-chlorobenzyl alcohol in dichloroethane at 60°C using *p*-toluenesulfonic acid as a catalyst.<sup>25</sup> Polymer concentrations were 2–4% (wt). The molar ratio of the catalyst to *p*-chlorobenzyl alcohol was 0.3. The racemic mixtures of copolymers of  $\gamma$ -benzylglutamate and  $\gamma$ -*p*-chlorobenzylglutamate (abbreviated as C(*x*)-RM), and those of  $\gamma$ -benzylglutamate and  $\gamma$ -*p*-methylbenzylglutamate (abbreviated as M(*x*)-RM), were prepared by similar procedures with those for C(*x*)-L. Compositions of the residues in the copolymers were determined by infrared spectra of the thin films cast from chloroform solutions.

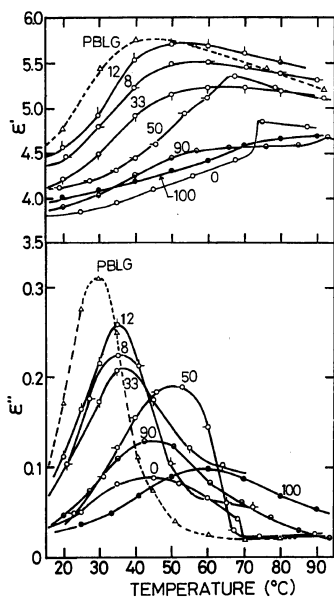
Samples in the form of film with a thickness of about 0.15 mm were cast from concentrated chloroform solutions on a glass plate at room temperature. Silver was deposited on both sides of films after evacuating for two days *in vacuo*. The dielectric constant  $\epsilon'$  and loss factor  $\epsilon''$  were measured with a TR-10C transformer bridge of Ando Denki Co. in a frequency range from 30 Hz to 1 MHz over a

temperature range from 15 to 100°C. A WBG-5 oscillator (Ando Denki Co.) and a Model LI-573 lock in amplifier (NF Circuit Design Block Co.) were used. The differential scanning calorimetric measurements were made on the same films used for the dielectric measurements with a calorimeter produced by Rigaku Denki Co. over a temperature range from 30 to 180°C in a sealed sample cell with a heating rate of 10 K min<sup>-1</sup>.

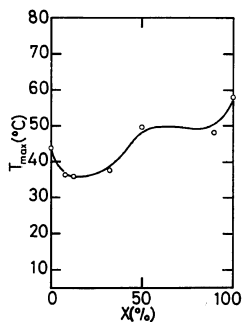
## RESULTS AND DISCUSSION

Temperature dependences of  $\epsilon'$  and  $\epsilon''$  for copolymers C(*x*)-RM measured at 1 kHz are shown in Figure 1, where figures indicate the values of *x* (mol% of  $\gamma$ -*p*-chlorobenzylglutamate residue in the copolymers). All samples show a side chain relaxation, although the temperature location strongly depends on *x*. The single peak of  $\epsilon''$  indicates that two types of side chains in the copolymers move cooperatively.<sup>9,20,22</sup> The temperature where  $\epsilon''$  shows the maximum value,  $T_{\max}$ , is plotted against *x* in Figure 2. It is found that  $T_{\max}$  is lower at  $8 \leq x \leq 33$  than that for two homopolymers, and the lowest  $T_{\max}$  occurs at *x*=12, indicating that the restriction against the side chain motion decreases at these chlorine compositions. On the higher temperature side of the relaxation for PBG (*x*=0), an abrupt change of dielectric constants is seen, which has been attributed to the disruption of the stacking structure of side chains.<sup>17</sup> This transition behavior of the dielectric constants are not, however, observed for the samples with  $8 \leq x \leq 33$ . Furthermore, it is noteworthy that for the samples with *x*=50 and 90 the transition as observed for PBG (*x*=0) appears again at around 65 and 90°C, respectively.

Figure 3 shows the DSC curves for C(*x*)-RM. An endothermic peak is observed for the polymers with *x*=0 and *x*≥50 around the temperature where the transition of dielectric constants occurs. On the contrary, no such



**Figure 1.** Temperature dependence of dielectric constant  $\epsilon'$  and loss factor  $\epsilon''$  at 1 kHz for C(x)-RM and PBLG. Figures indicate mol% of chlorine substitution.

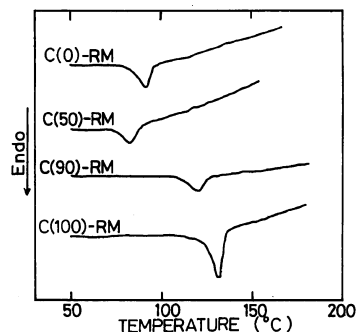


**Figure 2.** Peak temperature  $T_{\max}$  of loss factor  $\epsilon''$  at 1 kHz vs. mol% of chlorine substitution  $x$  for C(x)-RM.

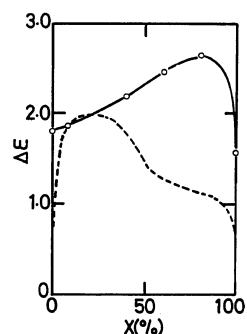
a peak was observed for  $8 \leq x \leq 33$ .

These results strongly suggest that for  $8 \leq x \leq 33$ , chlorine atom strongly hinders the formation of the stacking structure. For  $x \geq 50$ , it is considered that side chains construct again certain regular structure causing the transition phenomenon. Details about the latter structure have not been, however, clear at present stage.

For C(x)-L, all samples showed a single relaxation process and the transition phenom-



**Figure 3.** DSC curves for C(x)-RM.



**Figure 4.** Relaxation strength  $\Delta\epsilon$  vs. mol% of chlorine substitution  $x$ . —, C(x)-L; ---, C(x)-RM.

enon was not observed. The  $T_{\max}$  increases monotonically with increase of  $x$ , indicating that the side chains of two residues move cooperatively and their mobilities are weighted averages of those for two homopolymers, C(0)-L and C(100)-L, depending on the copolymer composition.

In Figure 4, is compared the dependence of the relaxation strength  $\Delta\epsilon$  on  $x$  for C(x)-RM and C(x)-L, which was obtained from the Cole-Cole circular arc law at  $T_{\max}$  (1 kHz). It is found that the value of  $\Delta\epsilon$  for C(x)-RM is similar to that for C(x)-L at  $8 \leq x \leq 33$  where there is no side chain stacking. On the other hand, at other  $x$ , where the stacking or regular structure exists,  $\Delta\epsilon$  shows pronouncedly smaller values for C(x)-RM compared with C(x)-L. The latter phenomenon is interpreted by the consideration that side chains which take regular structure are immobilized and

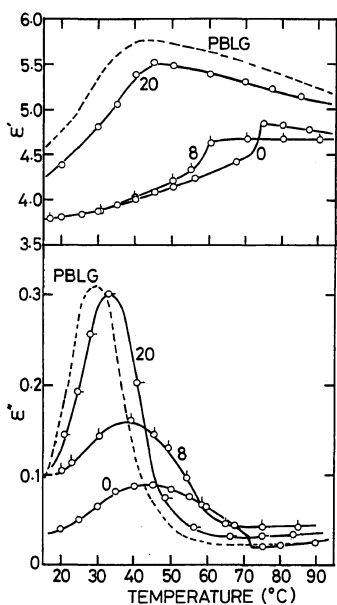


Figure 5. Temperature dependence of dielectric constant  $\epsilon'$  and loss factor  $\epsilon''$  at 1 kHz for M(x)-RM and PBLG. Figures indicate mol% of methyl group substitution.

hence cannot participate in the relaxation.<sup>17,19</sup>

It is considered that the substitution effects of chlorine atom on stacking structure consist of steric and electrostatic interactions, since chlorine atom has a relatively large van der Waals radius compared with proton and has a strong electronegativity, which makes a large dipole moment C-Cl on the *para* position of the phenyl group.<sup>18,20</sup> In order to obtain the information about these effects, methyl group, instead of a chlorine atom, is substituted on the *para* position of the phenyl group, since the van der Waals radius of the methyl group is nearly similar to that of chlorine atom and the effect on electrostatic interactions is negligibly small.

Figure 5 shows the temperature dependence of  $\epsilon'$  and  $\epsilon''$  at 1 kHz for M(x)-RM. An abrupt increase of the dielectric constant  $\epsilon'$  is observed similarly to C(0)-RM at the higher temperature region of the side chain relaxation for M(8)-RM, although the amount of  $\epsilon'$  increase is smaller and the transition tem-

perature is lower compared with those for C(0)-RM.  $\Delta\epsilon$  for M(8)-RM obtained with the Cole-Cole circular arc law was middle of those for C(0)-L and C(0)-RM, indicating the presence of the stacking unlike C(8)-RM. For M(20)-RM, this transition is not observed and the value of  $\Delta\epsilon$  is quite similar to that for PBLG, indicating that the stacking structure is completely disrupted at  $x=20$ . The DSC curves for M(8)-RM show an endothermic peak at 60°C where  $\epsilon'$  increases abruptly. For M(20)-RM, no endothermic peak was observed. Thus, DSC results correspond fairly well to those of the dielectric measurements. These results indicate that in C(x)-RM, the disappearance of the side chain stacking at the smaller value of  $x$  occurred by the overlapped effects of the steric and electrostatic interactions of chlorine atom. It is suggested that such strong interactions by the chlorine atoms, on the other hand, facilitate the formation of some regular structure in C(x)-RM at the higher value of  $x$ .

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