only a single set of (θ,γ) should satisfy the structure. For these reasons, we can regard the virtual bond method, as applied in the analysis of bends (Figures 2 and 3), as more reliably reflecting the original experimental data than the (ϕ,ψ) expression as far as only the skeletal backbone is concerned. The conversion from the virtual bond to the (ϕ,ψ) expression is possible by use of eq 10 and 11, with the aid of the standard geometry of the peptide unit.

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Dielectric Behavior of DL Mixtures of Poly(γ-benzyl glutamates)

Tohru Takahashi, Akihiro Tsutsumi, Kunio Hikichi,* and Motozo Kaneko

Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

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ABSTRACT: Dielectric measurements were carried out for mixtures of poly(γ-benzyl L-glutamate (PBLG) and poly(γ-benzyl D-glutamate) (PBDG) over a frequency range from 110 Hz to 1 MHz and a temperature range from 20 to 130°. Mixtures of L and D molecules were found to show a dielectric dispersion (β dispersion) due to side-chain motion above room temperature as well as PBLG. It was found that the β dispersion for mixtures is reduced to a great extent and shifted to higher temperatures compared to PBLG. This fact was interpreted in terms of regular stacks of benzyl groups occurring in mixtures, which presumably restrict side-chain motion. A transition was observed for the mixtures in the vicinity of 90° in dielectric properties. The results obtained in the present work are consistent with a previous proposal that the transition is caused by the breakdown of regular stacks of benzyl groups.

Molecular motions of poly(γ-benzyl L-glutamate) (PBLG) have been investigated by means of various methods. Kail, *et al.*,[1] and one of the present authors (K. H.)[2] observed changes in the second moment of nuclear magnetic resonance spectra for PBLG with temperature, which could be accounted for wholly in terms of side-chain motion. The mechanical and dielectric relaxations due to the side-chain motion have also been studied.[3-10]

Recently, attention has been directed to the study of the racemic form of poly(γ-benzyl glutamate) (PBG), which is a mixture of equal parts by weight of poly(γ-benzyl L-glutamate) (PBLG) and poly(γ-benzyl D-glutamate) (PBDG).

X-Ray diffraction patterns of racemic PBG show the appearance of "extra" layer lines which cannot be interpreted in terms of the α helix.[11-15] Squire and Elliott[15] suggested that these layer lines are caused by regular stacks of benzyl groups from about five side chains which are formed by interaction between adjacent molecules of opposite screw sense.

On the basis of X-ray diffraction, differential thermal analysis, infrared absorption, and dilatometric measurements on the racemic form of PBG, Yoshikawa, *et al.*,[16] reported that the racemic form of PBG exhibits a reversible first-order solid–solid phase transition at a temperature of about 100°. They suggested that the phase transition is caused by the breakdown of regular stacks of benzyl groups.

Our earlier dielectric studies of PBLG showed a dispersion due to side-chain motion above room temperature.[4] Tsuchiya, *et al.*,[17] have carried out dielectric measurements for the racemic form of PBG. They reported that the dispersion due to side-chain motion is much broader and is shifted to higher temperatures compared to PBLG.

However, no detailed dielectric investigation has been made in view of the phase transition. It is of interest to examine the relationship of the dielectric properties of the racemic form of PBG and the phase transition. In this work dielectric investigations were carried out for mixtures of PBLG and PBDG. Results obtained were interpreted in terms of stacking of benzyl groups.

Experimental Section

PBLG and PBDG used in this work were prepared by polymerization of the respective *N*-carboxyanhydrides (NCA's) in dioxane. A trace of triethylamine was used as an initiator. Polymers were precipitated from the polymerization solution with ethanol and

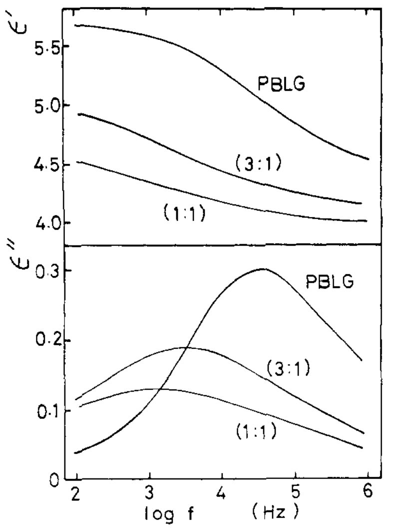

Figure 1. Dielectric constant ϵ' and loss factor ϵ'' as a function of frequency at 50° for PBLG, PBLG + PBDG (3:1), and PBLG + PBDG (1:1).

dried *in vacuo*. The molecular weights were determined from their viscosities measured in *N,N*-dimethylformamide, being 158,000 and 162,000 for PBLG and PBDG, respectively.[18]

Three samples were examined in this work. These are pure PBLG, a mixture of equal parts by weight of PBLG and PBDG (hereafter abbreviated as PBLG + PBDG (1:1)), and a mixture of the L-to-D ratio 3:1 (PBLG + PBDG (3:1)). All samples were in the form of a film 0.1–0.2 mm thick and were prepared by slow evaporation of chloroform solution on a glass plate at room temperature. Films were annealed *in vacuo* at 130° for 3 hr to remove the chloroform.

Dielectric constant and loss factor were measured on an Ando Denki TR-1C bridge in conjunction with a WBG-5 oscillator and a BDA-1B detector over the frequency range 110 to 10^6 Hz. Samples were painted with conductive silver paste in order to assure complete contact with electrodes. Temperature was changed from 20° to 130° and measured using a copper–constantan thermocouple. Measurements were performed with increasing temperature unless otherwise stated. The sample cell was evacuated to 10^{-2} Torr by a rotary pump to avoid any effect of moisture throughout measurements.

Results and Discussion

Results obtained for PBLG + PBDG (1:1), *i.e.*, the recemic form of PBG, indicate that a dielectric dispersion is clearly observed over the temperature range studied which is referred to as β dispersion. This is attributed to the onset of side-chain motion as judged from the previous results of PBLG.[4] Several definite differences are noticed between dielectric β dispersions of PBLG and PBLG + PBDG (1:1).

Figure 1 compares the β dispersion for PBLG, PBLG + PBDG (1:1), and PBLG + PBDG (3:1) at a temperature of 50°. In this figure, data points are omitted for the sake of simplicity. As the content of PBDG in the mixture is increased to 50%, values of ϵ' decrease. At the same time, the dispersion becomes smaller and broader and shifts to lower frequencies.

Figures 2a and 2b show ϵ' and ϵ'' as a function of temperature at various frequencies for PBLG + PBDG (1:1). Broken lines show data of PBLG to facilitate the comparison between them. ϵ' data of PBLG are ones at 110 Hz, 1 KHz, 10 KHz, and 100 KHz while ϵ'' data are at 10 KHz, 100 KHz, 300 KHz, and 1 MHz, going from left to the right of the figures. At each frequency ϵ' was found to increase gradually with increasing temperature until a temperature of 94° is reached, where an abrupt increase in ϵ' occurs. Above 94°, the temperature dependence of ϵ' for PBLG + PBDG (1:1) becomes almost the same as for PBLG.

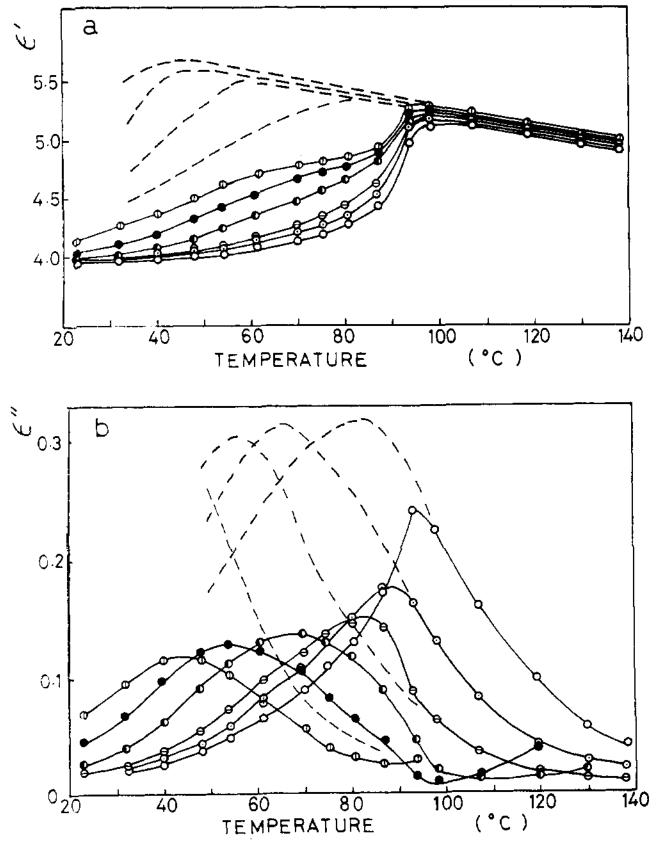

Figure 2. Dielectric constant ϵ' (a) and loss factor ϵ'' (b) as a function of temperature at various frequencies for PBLG + PBDG (1:1): ⦶, 110 Hz; ●, 1 KHz; ◐, 10 KHz; ⊖, 100 KHz; ⊙, 300 KHz; ○, 1 MHz. Broken lines show data for PBLG; data are from the left to the right of the figures (a) at 110 Hz, 1 KHz, 10 KHz, and 100 KHz and (b) at 10 KHz, 100 KHz, 300 KHz, and 1 MHz.

In the frequency range below 100 KHz, ϵ'' for PBLG + PBDG (1:1) shows a maximum at temperatures below 94°. The maximum is, however, smaller and shifted to higher temperatures compared to that of pure PBLG. Above 94°, ϵ'' for PBLG + PBDG (1:1) varies with temperature in the same way as for PBLG, as is the case of ϵ'. A peculiar behavior of ϵ'' was observed in the vicinity of 94°. At higher frequencies ϵ'' has a maximum at 94°, which is not considered as a dispersion peak but an apparent one as mentioned below.

Figure 3 shows the temperature dependence of ϵ' and ϵ'' at various frequencies for PBLG + PBDG (3:1). At all frequencies and temperatures, values of ϵ' for PBLG + PBDG (3:1) are located between those for PBLG + PBDG (1:1) and PBLG. As is the case of PBLG + PBDG (1:1), there also appears an abrupt increase in ϵ' and an apparent loss maximum at higher frequencies for PBLG + PBDG (3:1) at a temperature of 94°, though to a lesser extent.

The fact that the dispersion for mixtures of PBLG and PBDG is greatly diminished is consistent with the suggestion that regular stacks of benzyl groups occur in these systems,[15] since the regular stacks of benzyl groups presumably restrict the side-chain motion which causes the dielectric dispersion. It is clear that the sharp increase in ϵ' for the mixture observed in the vicinity of 94° is the consequence of the first-order phase transition which Yoshikawa, *et al.*, reported.[16] The results obtained in the present work are in agreement with their proposal that the phase transition is brought about by the breakdown of regular stacks of benzyl groups. Above a transition temperature of 94°, restriction to side-chain motion due to the regular stacks of benzyl groups is removed. Therefore, the differ-

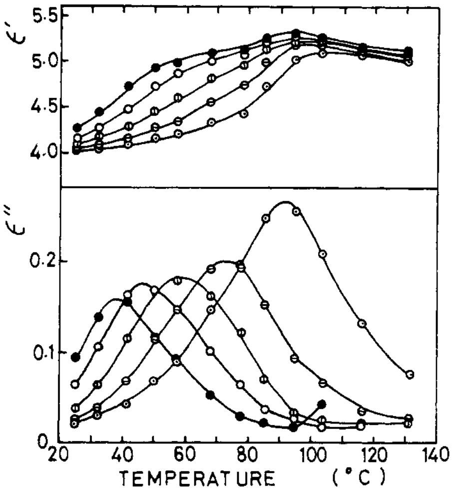

Figure 3. Dielectric constant ε' and loss factor ε'' as a function of temperature at various frequencies for PBLG + PBDG (3:1): ●, 110 Hz; ○, 1 KHz; ⊖, 10 KHz; ⦶, 100 KHz; ⊙, 1 MHz.

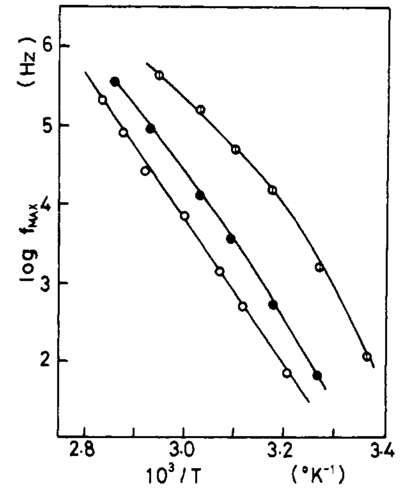

Figure 4. Logarithm of the frequency of maximum loss f_{MAX} as a function of reciprocal temperature, $1/T \times 10^3$, for PBLG, PBLG + PBDG (1:1), and PBLG + PBDG (3:1): ○, PBLG + PBDG (1:1); ●, PBLG + PBDG (3:1); ⦶, PBLG.

ence between dielectric behaviors of PBLG and mixtures of PBLG and PBDG disappears. The loss maximum observed at 94° at higher frequencies is also due to the transition from the stacked state to unstacked one as seen in Figure 2b.

In Figure 4, the logarithm of frequency of maximum loss is plotted against reciprocal temperature for three samples. In a previous paper,[10] we reported that the relationship between the relaxation time and temperature for PBLG is not a simple Arrhenius type but a WLF one. As is seen in the figure, the relation between the frequency of maximum loss and temperature for the mixtures was found to be well described by the Arrhenius equation. Apparent activation energies of the dielectric dispersion for PBLG, PBLG + PBDG (1:1), and PBLG + PBDG (3:1) estimated at 35° were found to be the same, 44 kcal/mol. This suggests that the β dispersion for mixtures is contributed from the side chain of which benzyl groups do not form stacks. Shift to higher temperatures of the dispersion for mixtures may be due to the influence of the regular stacks of benzyl groups upon side chains in the unstacked state.

In Figure 5, the relaxation strength $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ estimated from the Cole-Cole diagram is plotted against temperature for each sample. For PBLG, Δε decreases monotonically with increasing temperature. Δε for PBLG + PBDG (1:1) is smaller than that for PBLG and changes slightly with temperature until 94°, above which temperature both curves coincide. Δε for PBLG + PBDG (3:1) lies between the two and behaves in the same fashion as PBLG + PBDG (1:1).

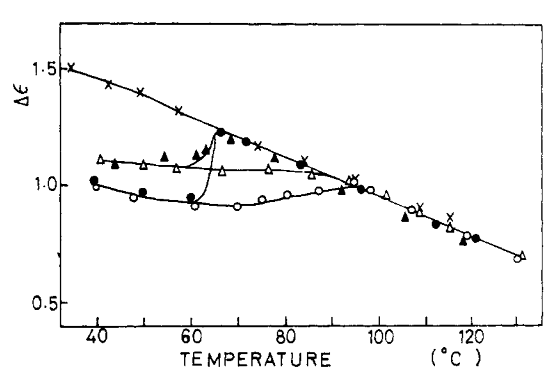

Figure 5. Relaxation strength Δε as a function of temperature for PBLG, PBLG + PBDG (1:1), and PBLG + PBDG (3:1): ○, PBLG + PBDG (1:1), heating; ●, PBLG + PBDG (1:1), cooling; △, PBLG + PBDG (3:1), heating; ▲, PBLG + PBDG (3:1), cooling; X, PBLG.

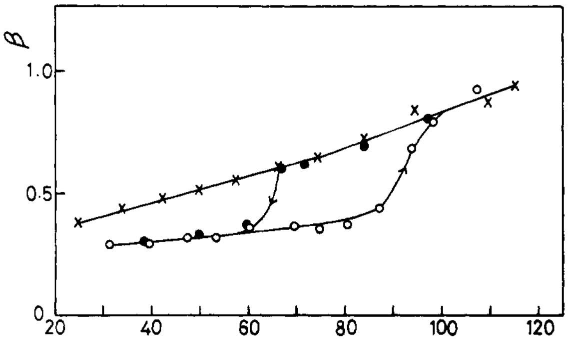

Figure 6. The Cole-Cole parameter β as a function of temperature for PBLG and PBLG + PBDG (1:1): ○, PBLG + PBDG (1:1), heating; ●, PBLG + PBDG (1:1), cooling; X, PBLG.

As the sample is cooled from 130°, Δε for PBLG + PBDG (1:1) increases in the same fashion as for PBLG until 65°, where Δε decreases abruptly to values encountered as heating. With further cooling below 65°, Δε was found to vary reversibly in the same way as heating. Such a hysteresis behavior of Δε was also observed for PBLG + PBDG (3:1).

Figure 6 shows the Cole-Cole parameter β plotted against temperature for pure PBLG and PBLG + PBDG (1:1). β for PBLG increases monotonically approaching β = 1 at higher temperatures. On the other hand, β for the racemic form PBG is less than for PBLG, indicating that the distribution of relaxation time is broader for mixtures. In the vicinity of the transition temperature, β increases abruptly and coincides with that for PBLG above 94°. A hysteresis behavior is also observed in the β-temperature curve.

Squire and Elliott[15] presented a model in which for an L molecule surrounded by six nearest neighbor D molecules 31 benzyl groups out of a total of 43 in the repeat length (the α helix of 43 residues in 12 turns) interact with those of neighboring D molecules to give stacks. This is considered as an ideal case that a maximum amount of stacks occurs. At any temperature, stacks are not fulfilled completely. We introduce the degree of stacking *S*, defined as the ratio of the number of stacked benzyl groups to the maximum number of benzyl groups possible to stack; *S* = 1 cor-

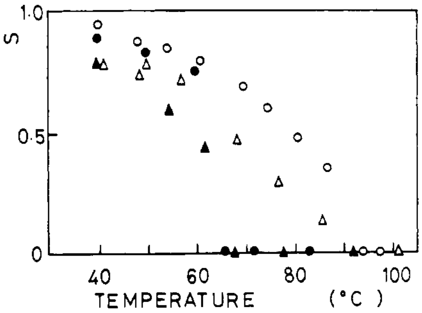

Figure 7. The degree of stacking S as a function of temperature for PBLG + PBDG (1:1) and PBLG + PBDG (3:1): ○, PBLG + PBDG (1:1), heating; ●, PBLG + PBDG (1:1), cooling; △, PBLG + PBDG (3:1), heating; ▲, PBLG + PBDG (3:1), cooling.

responds to the maximum degree of stacking and $S = 0$ to the absence of stacks.

Elliott, *et al.*,[12] have noted that a random siting of D and L molecules in the crystal seems more likely. It is, therefore, assumed that the mixing of L and D is random. Furthermore, we make assumptions that regular stacks of at most 31 benzyl groups out of 43 in the repeat length occur within an L–D pair of neighboring molecules and that only side chains of which benzyl groups do not form stacks contribute to the dielectric dispersion to the same degree as PBLG. Then, the relaxation strength $\Delta\epsilon$ for mixtures is written as

$$\Delta\epsilon = [1 - 2(31/43)Sf_{\mathrm{D}}(1 - f_{\mathrm{D}})]\Delta\epsilon_{\mathrm{PBLG}}$$

where f_{D} is the mole fraction of D molecules and $\Delta\epsilon_{\mathrm{PBLG}}$ is the relaxation strength for PBLG.

Figure 7 shows the degree of stacking S as a function of temperature for PBLG + PBDG (1:1) and PBLG + PBDG (3:1). At low temperatures, for both mixtures S tends to unity. S gradually decreases with increasing temperature until the transition temperature where S vanishes, showing a familiar behavior of the order–disorder transition. This probably indicates that the phase transition is the one from the ordered stacked state to the disordered unstacked one of the benzyl groups. It is necessary to examine theoretically the variation of S with temperature to understand the detailed mechanism of the transition.

Conclusion

All of these dielectric results are consistent with the suggestion that regular stacks of benzyl groups occur in mixtures of L and D molecules and that the phase transition is caused by the breakdown of the stacks. We believe that the mixing of L and D molecules is random. It is probably true that only the side-chains of the benzyl groups which do not form stacks contribute to the dielectric dispersion observed above room temperature. It is likely that the regular stacks of benzyl groups affect motions of side chains of the benzyl groups which do not form stacks, as evidenced by shifts to higher temperatures of the dispersion for mixtures.

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On the Osmotic Second Virial Coefficient of Athermal Polymer Solutions

A. Bellemans* and M. Janssens†

Université Libre de Bruxelles, Brussels, Belgium. *Received June 19, 1974*

ABSTRACT: The osmotic second virial coefficient $A_2(n)$ of athermal polymer solutions is discussed for a simple lattice model, each molecule (n-mer) corresponding to a self-avoiding walk of $n - 1$ steps on a simple cubic lattice. The exact evaluation of $A_2(n)$ by McKenzie and Domb (up to $n = 7$) is extended by a Monte-Carlo technique up to $n = 40$ and it is concluded that for n large $A_2(n) \simeq 0.58n^{-0.28}$.

The aim of this paper is to establish the asymptotic form of the osmotic second virial coefficient A_2 for athermal polymer solutions within the frame of the conventional lattice model. This problem was considered by McKenzie and Domb[1] who evaluated A_2 exactly for relatively short chains and made conjectures about its behavior for longer ones. By a Monte-Carlo technique we were able to extend the data on A_2 much further, so that somewhat more definite conclusions will be reached here. For the sake of clarity and definiteness, we will first rederive the expression for A_2.

Each polymer molecule is a linear chain occupying n sites (n-mer) of a regular lattice and no site may be occu-

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† Chercheur IRSIA.