

Transition of Mixture of Poly(γ -benzyl L-glutamate) and Poly(γ -benzyl D-glutamate)

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ABSTRACT: Mixture of poly(γ -benzyl L-glutamate) and poly(γ -benzyl D-glutamate) have a special interaction between the benzyl groups at the end of the side chain and have different properties from the pure enantiomeric form of poly(γ -benzyl glutamate). A reversible first-order transition has been observed and ascribed to the formation and breakdown of stackings of the benzyl groups at the end of the side chain. The isothermal transition was investigated by dilatometry and studied in light of present concepts of crystallization in crystalline polymers. Plots of extent of isothermal transition vs. time were sigmoidal in shape and fitted the Avrami equation. The exponent in the Avrami equation was 4. The reciprocal half-time of the transition was taken as a measure of the overall rate of transition. Plots of logarithm of transition rate against $T_m[T(T_m-T)]^{-1}$ and $T_m^2[T(T_m-T)^2]^{-1}$, where T_m is the temperature for the breakdown of stacking of the benzyl groups, taken as 100.2°C, and T is the stack formation temperature, gave reasonably good straight lines. Thus, as is usually found with polymers, no discrimination could be made between two possible mechanisms of the transition; two-dimensional or three-dimensional nucleations.

KEY WORDS Transition / Stacking / Mixture / Poly(γ -benzyl glutamate) / Avrami Equation / Kinetics /

The structure of the racemic form of poly(γ -benzyl glutamate) (PBG) is different from that of pure poly(γ -benzyl L-glutamate) (PBLG) or pure poly(γ -benzyl D-glutamate) (PBDG).^{1,2,3} The structural studies on the racemic form of PBG have revealed that regular side-chain conformations are formed between the benzyl groups; stackings of the benzyl groups at the end of the side chain are formed between neighbouring PBLG and PBDG molecules.

Some studies of the transition due to the breakdown of stacking in the racemic mixture of PBG have been reported by Fukuzawa, *et al.*⁴ From thermal analysis and dilatometric measurements, a first-order transition was observed at about 95°C. In this paper the kinetics of the formation of stacking is investigated and studied

in light of present concepts of crystallization in crystalline polymers.

EXPERIMENTAL

Synthesis and Specimen

γ -benzyl glutamate *N*-carboxyanhydride (NCA) was prepared by the method proposed by Leuch.⁵ The polymerization was initiated with triethylamine and was completed in about one day at room temperature. The molecular weights of PBLG and PBDG, which were computed from the relation of intrinsic viscosity and molecular weight, were 170,000 and 150,000, respectively.

The mixtures of PBLG and PBDG were dissolved in 1,2-dichloroethane at a concentration below 0.05 (w/v). Films 0.01-cm thick were cast at room temperature from the solution. Specimens were heated once to 140°C and then cooled

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slowly to room temperature.

Dilatometry

Specific volumes were measured by means of a dilatometer containing about 0.9 g of fully dried specimen. The specific volume-temperature relation was obtained at a heating rate of 1°C/3 min. In isothermal measurements, the racemic form of PBG, which is the equimolar mixture of PBLG and PBDG, was heated to a temperature above the transition temperature where the regular arrangement of the side chain breaks down, and then cooled to the stack formation temperature. Relative change in specific volumes was measured as a function of time by dilatometry. The thermostat was controlled to an accuracy of 0.1°C.

RESULTS AND DISCUSSION

Equatorial refractions in the X-ray diffraction pattern from the racemic form of PBG can be indexed exactly on a hexagonal lattice, as proposed by Tsuboi, *et al.*,² and Squire and Elliott.³ Squire and Elliott proposed the presence of a distorted helix with 43 residues in 12 turns; they further explained the appearance of a strong layer line near 10 Å as due to a pairing of D and L residues, with a special side-chain interaction which causes a regular arrangement of the benzyl group at the end of the side chain. From X-ray diffraction measurements at various temperatures the reflection characteristic of the regular arrangement of the benzyl group at the end of the side chain was shown to disappear on heating at 97°C and to reappear on cooling at 73°C. This reversible change was also observed in viscoelastic, thermal, and dilatometric measurements and ascribed to the breakdown and formation of stacks of the benzene ring.⁴

Information on the arrangement of the benzyl groups can be obtained from the results of infrared examination. Tsuboi, *et al.*,² have shown that the dichroic ratios observed for absorption bands attributable to the main chain vibrations for the racemic mixture are not different from those of PBLG, while three bands at 1498 cm⁻¹, 1453 cm⁻¹, and 697 cm⁻¹, assignable to vibrations in the phenyl group at the end of the side chain, show stronger dichroism in the

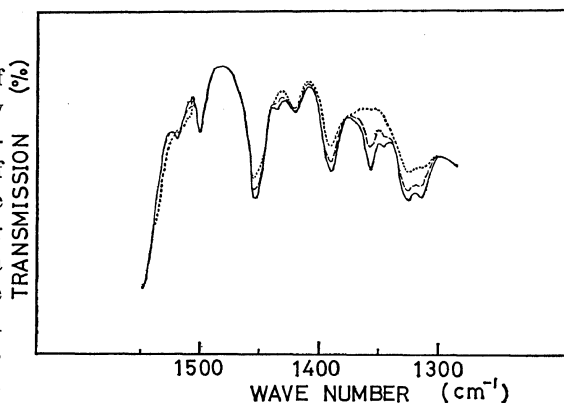


Figure 1. Infrared spectra of racemic form of PBG at various temperatures: —, 30°C; ----, 80°C; ····, 110°C.

racemic mixture than those of PBLG. These facts may be taken as indicating that the arrangement of benzyl groups in PBLG is somewhat irregular, whereas that in the racemic mixture is much more regular. To investigate the structural change of the side chain after the transition, infrared spectra in the range of wave numbers from 1300 cm⁻¹ to 1550 cm⁻¹ were studied at several temperatures. Figure 1 shows infrared spectra of the racemic form of PBG at 30°, 80°, and 110°C. A band at 1360 cm⁻¹ observed at temperatures below 100°C disappeared after the transition. The band at 1360 cm⁻¹ was not observed in the enantiomorphic form of PBG. These results suggest that the absorption band at 1360 cm⁻¹ is related to the stacks of benzene rings at the end of the side chain.

From the viewpoint of a transition in the solid state, it is interesting to study the kinetics and mechanism of transition. Fukuzawa, *et al.*,⁴ reported results of dilatometric measurements in which specific volumes of the racemic form of PBG varied reversibly against temperature with some extent of supercooling on cooling, as is usually observed in crystalline polymers.

In the study of the kinetics of nucleation and growth of crystalline polymers, the Avrami⁶ equation has proven to be of considerable importance. The Avrami equation may be expressed as

$$\log \left(\frac{V_{\infty} - V_t}{V_{\infty} - V_0} \right) = -kt^n \quad (1)$$

where t is the crystallization time, V_0 is the specific volume of the polymer at $t=0$, V_t and V_∞ are the specific volume of the polymer at crystallization time $t=t$ and $t=\infty$, respectively, k is a rate constant, and n is an integer constant. The values of k and n depend on the mechanism of crystallization.

The measurement of isotherms at various temperatures, which is often utilized in the investigation of the kinetics of crystallization in crystalline polymers, was applied in the present study of the kinetics and mechanism for the stack formation. The experimentally observed isotherms for various temperatures are shown in Figure 2. They show two features similar to

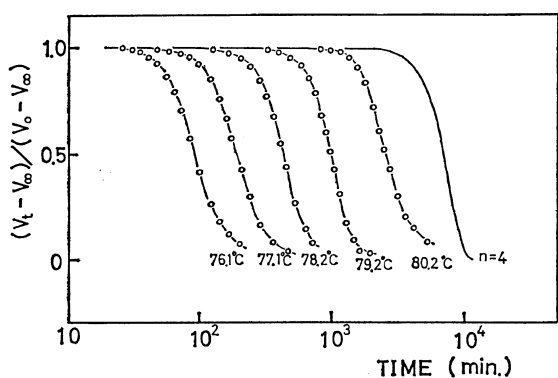


Figure 2. Relative change of specific volume with time at various temperatures. Solid line is plotted according to the Avrami equation with $n=4$.

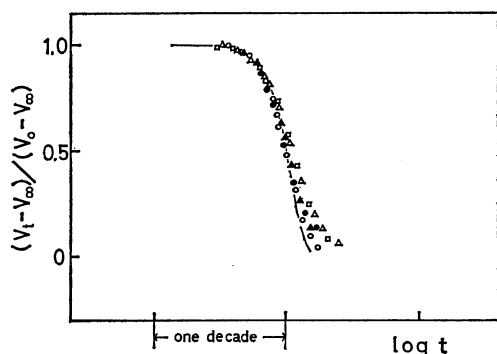


Figure 3. Demonstration of superposability of isotherms for racemic form of PBG. Solid line is plotted according to the Avrami equation with $n=4$: Δ , 76.1°C; \square , 77.1°C; \blacktriangle , 78.2°C; \circ , 79.2°C; \bullet , 80.2°C.

crystallization curves: (a) a well-defined time interval exists during which the development of stackings is not observed (so-called apparent induction time) and (b) the individual isotherms may be brought into coincidence merely by shifting each of the curves an appropriate distance along the horizontal axis. These isotherms are superimposable for at least 60% of the process, as shown in Figure 3. In Figure 2 the theoretical isotherm is shown for $n=4$ in the Avrami equation. Reasonably close agreement is obtained in the early stages of the process. Thus, the stack formation corresponds to a homogeneous nucleation followed by three-dimensional growth. The data in Figure 2 demonstrate the marked effect of temperature on the rate of stack formation. This tremendous variation of rate constant with temperature is also indicated in Figure 4 where the reciprocal of half-time, $\tau_{1/2}$, the time necessary for one-half of the transition to occur, is given as a function of temperature.

The overall crystallization rate constant k is given by⁷

$$\log k = C_1 - \frac{C_2 T_m^m}{T(T_m - T)^m} \quad (2)$$

where T_m is the melting temperature and T the crystallization temperature. C_1 involves the preexponential rate factors for growth and nucleation and a term in the activation energy for bulk flow of the polymer, and C_2 includes the interfacial energy between the crystallizing

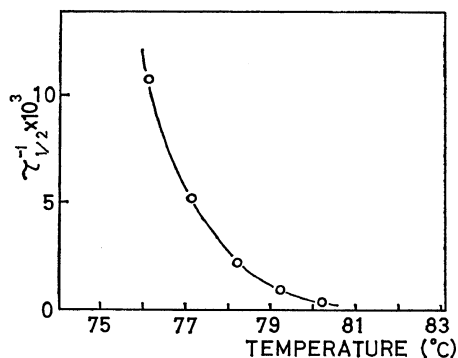


Figure 4. Rate of the stack formation of the racemic form of PBG. The rate $(\tau_{1/2})^{-1}$ plotted is the reciprocal of the time necessary for one-half of the total volume change to occur.

surface and the melt and the heat of fusion. m is 1 or 2 depending upon whether the nucleation is two-dimensional or three-dimensional. Therefore, a plot of $\log k$ against either $(T_m^2/T)(T_m-T)^{-2}$ or $(T_m/T)(T_m-T)^{-1}$ should yield a straight line, depending on which model is appropriate. However, as pointed out by Mandelkern,⁷ good straight lines are often obtained in both plots and it is thus impossible to distinguish the two models on this basis.

Changes in the rate of stack formation with

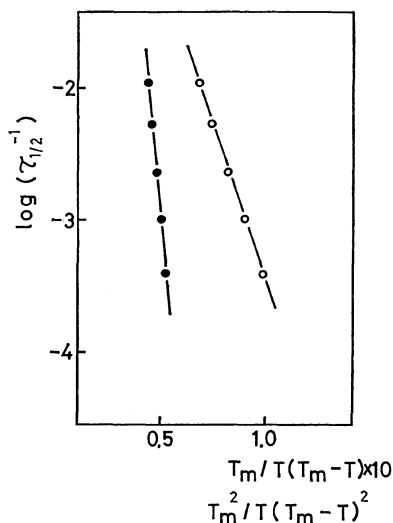


Figure 5. Plot of $\log(\tau_{1/2})^{-1}$ against $T_m^2/T(T_m-T)^2$ (○) and $T_m/T(T_m-T)$ (●) for the racemic form of PBG.

temperature were analyzed in accordance with the above treatment. In Figure 5 logarithms of the reciprocal half-times were plotted against $(T_m^2/T)(T_m-T)^{-2}$ or $(T_m/T)(T_m-T)^{-1}$, where T_m is the temperature at which the stacking of benzyl groups at the end of the side chain breaks down, and is taken as 100.2°C ; T is the stack formation temperature. Good straight lines were obtained in both plots.

From the results described above, we propose a model to account for the nucleation and growth mechanism in the stack formation of racemic mixture of PBG. These mechanisms can be schematically illustrated as shown in Figure 6. First of all, nuclei with a critical sequence length of stacks of benzyl groups are formed sporadically in the mixture as a result of thermal fluctuations. These nuclei are thought to grow through a continuous process of stacking along the α -helices, "zippering", as shown in the figure.

Specific volume—temperature relations for the mixtures with various PBDG/PBLG ratios (1/9, 3/7, 1/1) were measured and are shown in Figure 7. With decreasing PBDG/PBLG ratios,

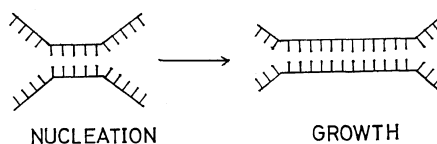


Figure 6. A model for the stack formation.

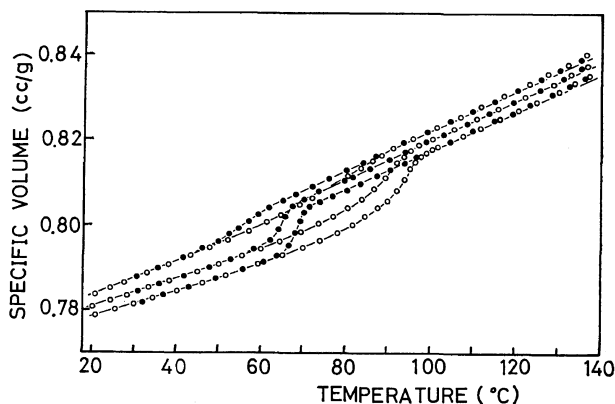


Figure 7. Specific volume—temperature relations of the mixtures with various contents of PBDG: 10% (upper curve), 30% (middle curve), 50% (lower curve); on heating (○); on cooling (●).

the change in specific volume on the transition becomes smaller and further the transition temperature tends to be lowered and the transition range becomes broader.

CONCLUSION

The kinetics of isothermal stack formation in the racemic mixture of PBG has been investigated and analyzed in light of present concepts of crystallization in crystalline polymers. From the Avrami treatment of experimental results, it has been concluded that the stack formation corresponds to a nucleation followed by three-dimensional growth. To account for these mechanisms, a model has been proposed.

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