Structure and Properties of Precipitates
of Poly(γ-benzyl glutamate)

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ABSTRACT: Precipitates of poly(γ-benzyl glutamate) (PBG) were prepared from dimethylformamide—propionic acid solutions under various conditions. Electron micrographic observations and X-ray diffraction analyses of the precipitates thus obtained were carried out. The electron micrographs of the precipitates exhibited patterns similar to those reported by Ishikawa and Kurita, and Tachibana and Kambara (super helices), though lamella-like patterns (platelets) were observed under certain conditions. The viscoelastic properties, thermal analyses, and specific volume *vs.* temperature curves of the precipitates were investigated. As for the viscoelastic properties, the precipitates showed peaks of tan δ at 50°C and 120°C (110 Hz). The moduli E' decreased remarkably near 120°C. In the thermal analyses an endothermic peak appeared in the vicinity of 130°C and a transition appeared at 132°C in the specific volume *vs.* temperature curve. The phenomena observed in the vicinity of 130°C were considered to be related to a breakdown of stacks of the benzene rings of PBG in the precipitates, from comparison with the properties of cast films reported previously. The electron micrographs of the precipitates from various helicogenic solvent—precipitant mixtures were the same as those of the precipitates from dimethylformamide—propionic acid solution.

KEY WORDS   Precipitate / Super Helix / Poly(γ-benzyl glutamate)
Viscoelastic Properties / Specific Volume / Transition / Morphology /

It is well known that poly(γ-benzyl glutamate) (PBG) takes an α-helix conformation in helicogenic solvents and also in the solid state. Studies of the solid state have been carried out by many investigators.[1-7] Solid films prepared by casting are able to take several different structural forms depending upon the casting conditions, the kind of casting solvent, and the casting temperature. McKinnon and Tobolsky[8,9] have reported that films of PBG cast from dimethyl formamide (DMF) have two solid state modifications (form A and form B) depending on the casting temperature, which are quite different from films cast from chloroform (form C). The characteristic aspects of these modifications in viscoelastic properties are: higher modulus in the temperature range from 30 to 140°C and an abrupt decrease in modulus near 120°C for form A, an abrupt decrease of modulus near 90°C for form B, and a decrease of

modulus at room temperature and no considerable decrease of modulus until 110°C for form C. In a previous paper[10] the effects of solvent on the structure and properties of cast films of PBG have been studied. Cast films were classified into two types: Film A cast from the EDC (1, 2-dichloroethane) series (*e.g.*, EDC, CH$_2$Cl$_2$, and CHCl$_3$) and film B cast from the benzene series (*e.g.*, benzene and tetrahydrofuran). As for viscoelastic properties, film A showed peaks of tan δ at 40 and 105°C (110 Hz). In the case of film B, the lower temperature peak appeared at a higher temperature and the peak was broadened. Film B further exhibited a decrease of modulus at about 135°C, which was accompanied by a small peak of tan δ at this temperature. The results of film B were similar to the behavior of form A reported by McKinnon and Tobolsky.

Ishikawa and Kurita[11] and Tachibana and Kambara[12] investigated the morphology of precipitates from DMF-propionic acid solutions

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by means of electron micrography and X-ray diffraction analysis. Ishikawa and Kurita called the rope-like fibrils which were observed by the electron micrography "super-helices". Tachibana and Kambara reported that the PBG in the precipitates had the conformation of an α-helix and the super helices had the sense opposite to that of the α-helix. Luzzati, et al.,[13] suggested the presence of coiled coils or super-helices in the so-called "complex" phase, described by them and found in the system PBG—DMF from about 15 to 70% (wt/wt) PBG. Recently, Parry and Elliott[5] in their more detailed examination of this phase have concluded that coiled coils are not present; they found that benzyl groups are stacking to produce a quasi-helical arrangement with a different periodicity from that of the α-helix of the main chain and that stacks on neighbouring molecules link up to form a continuous quasi-helical side-chain configuration.

In a previous paper[10] we presumed that a molecular association caused by the benzene-ring interaction or stack proposed by Parry and Elliott was retained in the solid state and was responsible for the enhanced modulus and the higher peak temperature due to sidechain motion in film B cast from relatively poor solvents. Further, the irreversible transition observed at 135°C in the thermal and dilatometric measurements for film B was ascribed to the dissociation of the benzene-ring stack in the side chain.

In the present paper, the properties of the precipitates prepared from DMF—propionic acid mixed solutions under various conditions are discussed in relation to the properties of cast films reported previously. In particular, the structure and properties of the precipitates are compared with those of form A, form B, and form C proposed by McKinnon and Tobolsky and also with those of film A and film B proposed by Fukuzawa, et al. Furthermore, in order to elucidate the influence of solvent on the formation of super-helices, electron micrographic observations were carried out for precipitates from various helicogenic solvent—precipitant solutions.

EXPERIMENTAL

Samples

Poly(γ-benzyl glutamate) was prepared by the NCA method reported in a previous paper.[10] The molecular weight of the PBG was estimated from viscosity measurements. PBG ($M_w = 80000$) was dissolved in DMF—propionic acid (volume ratio of 1 : 4). The 0.08-% PBG solution was heated at 140°C for several hours and precipitates were obtained by slow cooling from 140°C to room temperature (S), by quenching to 0°C (Q), and by isothermal precipitation at 48.5°C ($I_{48.5}$), 61°C (I_{61}), and 64°C (I_{64}). The solvents remaining in the precipitates thus obtained were removed by washing with methanol several times. After washing, the precipitates were pressed lightly and dried in vacuo at room temperature for one week. The precipitates thus obtained as mats were used for viscoelastic measurements. For dilatometric measurements the precipitates were compression-molded at 80°C to get films. For the electron micrographic observation, the precipitates were placed on a carbon film and Cr-shadowed.

Measurement

Viscoelastic measurements were performed at a frequency of 110 Hz and a heating rate of 0.4°C/min in the temperature range from 20 to 150°C using a VIBRON DDV–II, manufactured by TOYO Baldwin Co.

Thermal analyses were performed at a heating rate of 16°C/min in nitrogen environment, by using a differential scanning calorimeter DSC–I manufactured by Perkin-Elmer Co.

RESULTS AND DISCUSSION

The dynamic mechanical behaviors at 110 Hz for samples S, Q, and $I_{48.5}$ are shown in Figure 1. The original (non-annealed) samples showed broad peaks of tan δ at 50°C and corresponding decreases of modulus E' were also observed around this temperature. This is attributed to the onset of the side chain motions, as is well known. Further, it can be seen that the moduli of the original samples decrease abruptly in the vicinity of 120°C and another small tan δ peak appears at this temperature. The results obtained here for the precipitates are similar to the be-
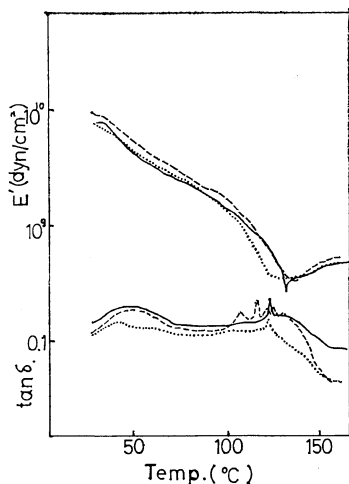
Figure 1. Tensile modulus E' and tan δ at 110 Hz as a function of temperature for the samples S, Q, and I$_{48.5}$: ——, precipitated from DMF—propionic acid solution by slow cooling (S); ------, precipitated from DMF—propionic acid solution by quenching (Q); ····, precipitated from DMF—propionic acid solution at 48.5°C (I$_{48.5}$).
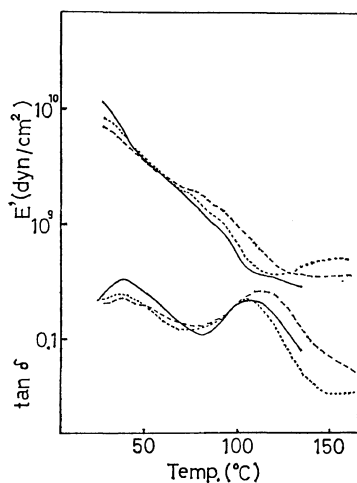

Figure 2. Tensile modulus E' and tan δ at 110 Hz as a function of temperature for the annealed samples S, Q, and I$_{48.5}$: ——, annealed sample S; ------, annealed sample Q; ····, annealed sample I$_{48.5}$.

haviors of moduli of form A reported by McKinnon and Tobolsky and to the viscoelastic properties of film B from Fukuzawa, *et al.*[10]

The dynamic mechanical behaviors of the

samples annealed at 140°C for 24 hr are shown in Figure 2. After annealing, a tan δ peak appeared near 110°C and the temperature at which an abrupt decrease of E' occurred shifted from 120 to 100°C. Simultaneously the lower temperature peak at 50°C, which was caused by the side chain motion, shifted from 50 to 40°C. The effects of annealing are the same as in film B. These results indicate that the structural change of the side chains occurs by annealing.

The results of thermal measurements for the samples Q, I$_{48.5}$, S, and I$_{64}$ are shown in Figure 3. Endothermic peaks appeared near 130°C for all the samples and the heats of the transition were 2—3 cal/g, as tabulated in Table I. The transition temperatures of the samples I$_{48.5}$, S, and I$_{64}$ were a little higher than that of the sample Q and the thermograms of the samples I$_{48.5}$, S, and I$_{64}$ exhibited sharper transitions than the sample Q. It seems that the transition temperature becomes higher and the heat of the
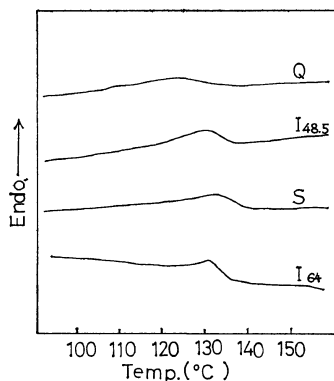

Figure 3. Differential Scanning Calorimetry for the samples Q, I$_{48.5}$, S, and I$_{64}$.

Table I. Heats of transition and transition temperatures for precipitates

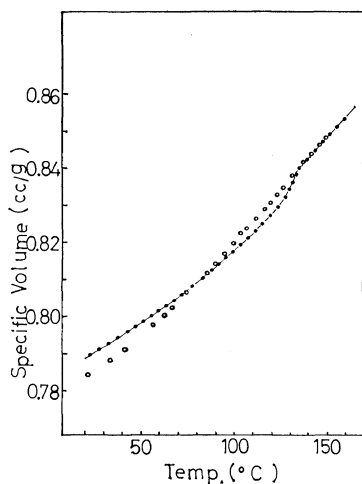| Sample	Heat of transition (cal/g)	Transition temperature (°C)	Crystallinity (%)
Q	1.5	122	7.7
I$_{48.5}$	2.4	131	8.2
I$_{64}$	2.3	131	—
S	3.4	132	6.3
Film A	—	—	35
Film B	2.9	135	8.0

Figure 4. Specific volume—temperature curve for the sample I_{61}: —·—·—·—, heating curve; —o—o—o—, cooling curve.

transition becomes larger as the samples are precipitated at higher temperatures and at a slower cooling rate. In a previous paper[10] we found that the thermogram for film B showed an endothermic peak at 135°C, while for film A such a transition was not observed. Although the transition temperature is a little lower, the thermal behaviors of the precipitates are considered to be similar to those of film B.

Figure 4 represents the specific volume vs. temperature curve of the sample I_{61}. A transition observed at about 135°C in the specific volume vs. temperature curve is considered to correspond to the endothermic peak observed in the thermal measurement. This behaviour is also similar to that of film B.

In a previous paper[10] we showed that an X-ray diagram of the superhelical aggregates of PBG was very similar to that of film B, for which a diffuse and weak diffraction ring was observed. In the present study, an X-ray diffraction analysis was carried out for the samples S, Q, and $I_{48.5}$ and the X-ray diagrams obtained were the same as in a previous paper. However, the X-ray diffraction patterns measured by a Geiger counter revealed the presence of a weak reflection at 5.1 Å in addition to a reflection at 14.7 Å, which corresponded to the spacing of the (110) plane given by McKinnon and Tobolsky. The 5.1 Å reflection is considered to

arise from the average axial translation of the benzene rings in the quasi-helices, in which the benzene rings are stacking to produce a quasi-helical arrangement with different periodicity from that of the α-helix of the main chain, as proposed by Parry and Elliott. It is possible that a molecular association caused by the benzene-ring interaction or stack in DMF—propionic acid solution is retained in the precipitates and is responsible for enhanced modulus and the higher peak temperature due to side chain motion, as in film B. The irreversible transition observed in the viscoelastic, thermal, and dilatometric measurements of the precipitates is ascribed to the dissociation of the benzene-ring stack in the side chain of PBG after being heated above 135°C. In Figure 2 it can be seen that the annealed samples show a noticeable peak near 110°C, which corresponds to a decrease in modulus at about 100°C. Although there have been no consistent interpretations for this relaxation process, we consider that this relaxation may be related to a molecular motion of the main chain in the amorphous region. Previously we found that, despite being less intense in films A and B, the peak around 110°C noticeably increased in film B after it was annealed at 140°C. As shown in Table I, the precipitates, including those after annealing, and film B all have less crystallinity than film A. In the precipitates the molecular motion of the main chain in the amorphous region is hampered by the side chain interaction. After being annealed the stacks of the benzene rings are broken down and the annealed samples are thought to show the noticeable peaks at 110°C because of the decreased crystallinity. The annealed precipitates are similar to form B in that a decrease in modulus around 100°C is observed. McKinnon and Tobolsky reported that form B is a novel well-ordered modification and the X-ray diagram contains several sharp reflections. These sharp reflections were not observed for the annealed precipitates. However, it is possible that they are form B with decreased crystallinity, which renders any judgement about the modification very difficult. Further study on the structure of the annealed precipitates is necessary.

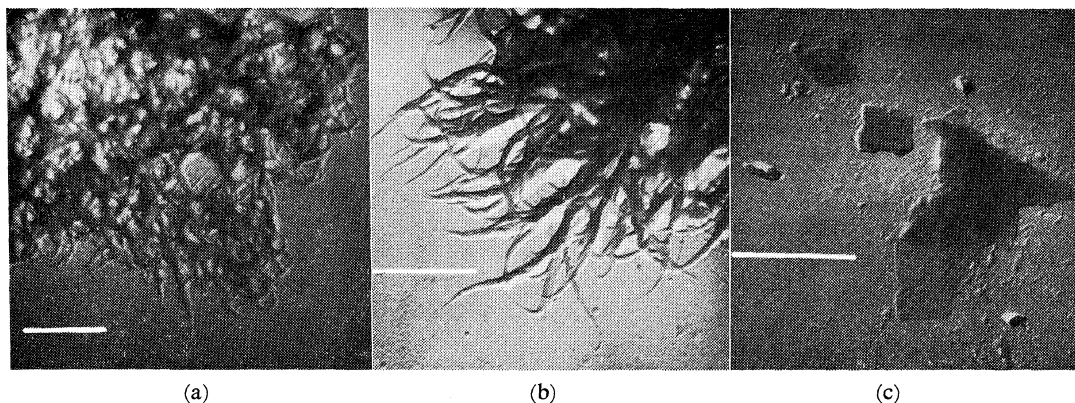Electron micrographs of the precipitates from DMF—propionic acid solution are shown in

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Photo 1. Electron micrographs of precipitates: (a), precipitated from DMF—propionic acid solution by quenching to 0°C (Q); (b), precipitated from DMF—propionic acid solution at 48.5°C ($I_{48.5}$); (c) precipitated from DMF—propionic acid solution at 64°C (I_{64}).

Photo 1. The samples Q and $I_{48.5}$ have a super-helical structure similar to that observed by Ishikawa and Kurita.[11] The diameters of the macrofibrils of the samples Q and $I_{48.5}$ were several hundred Å. It can be seen that the sample I_{64} consists of platelets. This appears to suggest that the sample I_{64} has a different higher-ordered structure from the others with typical macrofibrils of superhelices. Owing to the difficulty of the precipitates being quite unstable in the electron beam, we could not determine the molecular structure in the lamellar precipitates. However, it is presumed that the molecular aggregation which occurs in poor solvents leads to superhelical aggregates in which the morphology probably reflects the underlying molecular geometry. Further, it is considered that at a higher precipitation temperature, the precipitation occurs slowly and lamellar crystals are obtained, as is well known in synthetic crystalline polymers such as polyethylene. The experimental result that the DSC thermograms for both of the samples $I_{48.5}$ and I_{64} have the endothermic peak at about 130°C is considered to support these considerations; the molecular structure is the same for all the samples.

In order to examine the influence of solvents on the morphologies of the precipitates, the electron micrographic observation was carried out for precipitates from solutions of chloroform, EDC, methylene bromide, and benzene as helicogenic solvent, and propionic acid and acetic acid as precipitant. The morphological features of the precipitates are similar to those of the precipitates from the system of DMF—propionic acid. This points out the vital role played by polymer—solvent interactions in controlling the morphology of the precipitates.

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