

Influence of Casting Conditions on the Structure of Poly(γ -benzyl-L-glutamate)

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ABSTRACT: The influence of casting conditions (solvent and temperature) on the structure of poly(γ -benzyl-L-glutamate) was investigated. From X-ray diffraction analysis and dynamic mechanical, thermal, and dilatometric measurements, it was found that from 1,2-dichloroethane—benzene solutions containing less than 60% benzene form C proposed by McKinnon and Tobolsky was cast at room temperature and from more than 80% benzene form A was prepared. The results of casting temperature studies showed that films cast at temperatures below 40°C from dimethylformamide or benzene solution had the structure of form A and films cast above 50°C had the structure of form B.

KEY WORDS Cast Film / Poly(γ -benzyl glutamate) / Complex Phase / Stack / Modification /

It is well known that poly(γ -benzyl glutamate) (PBG) retains an α -helical conformation in many organic solvents, and in weak solvents a molecular aggregation occurs: PBG molecules aggregate side by side or head-to-tail in dilute solutions, depending on the kind of solvent. In more concentrated solutions of approximately 10-vol% PBG, the α -helix molecule forms the cholesteric liquid crystal¹ in ordinary helicogenic solvents, and above the concentration of 15-(w/w) PBG, it forms a "complex phase" in dimethylformamide (DMF) solution, in which the presence of coiled coils was suggested by Luzzatti, *et al.*² Parry and Elliott^{3,4} in their more detailed examination of this phase have concluded that the coiled coils are not present and that the benzyl groups at the ends of the side chains are interacting to produce a regular side-chain arrangement (stacks of benzene rings). Since cast films are prepared through the cholesteric liquid crystalline state and or the complex phase, it is expected that cast films will have various different structures depending on the casting conditions: that is, casting solvents and casting temperatures.

McKinnon and Tobolsky⁵ investigated the structure and properties of films cast from DMF solution, and proposed form A, form B, and

form C for different modifications of films. The characteristic aspects of forms A, B, and C are as follows: decrease in modulus near room temperature for all forms, with an abrupt decrease in modulus at 135°C for form A and at 95°C for form B. Forms A and B have a higher modulus than form C in the lower temperature region (20—90°C). Fukuzawa, *et al.*,⁶ reported that cast films could be classified into two types of structures and properties: the first group was cast films from 1,2-dichloroethane (EDC), chloroform, or dichloromethane solution (film A) and the second was from benzene or tetrahydrofuran solution (film B). It was found that the viscoelastic behaviors of films A and B were respectively similar to those of forms C and A proposed by McKinnon and Tobolsky.⁵ Furthermore, from the results of thermal analysis and dilatometry, an irreversible transition was found to appear near 135°C for film B. Recently Aritake, *et al.*,⁷ have studied the viscoelastic and thermal properties of precipitates of PBG prepared from DMF—propionic acid mixed solution. They concluded that the precipitates have the same structure and the same properties as form A or film B. However, there have been few systematic investigations of the effects of the casting solvent and the casting temperature.

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In this paper, in order to investigate the influence of casting conditions on the structures and properties of cast films, X-ray, viscoelastic, thermal, and dilatometric measurements were performed for cast films prepared under various conditions. We will discuss the structures and properties of films cast from EDC—benzene mixed solution and those of films from DMF or benzene at various casting temperatures.

EXPERIMENTAL

Sample

Poly(γ -benzene L-glutamate) (PBLG) was prepared by the NCA method. The molecular weight of the PBLG was estimated to be 100,000 from viscosity measurements.⁸

5-% (w/v) PBLG solution was prepared and the solvent was evaporated slowly at a constant temperature; cast films 0.1 mm thick were obtained. The solvent remaining in the film was replaced with methanol and the cast films were dried *in vacuo* for one week at room temperature.

Method

An X-ray diffraction goniometer manufactured by Rigaku Denki Co. was used; the direction of the X-ray beam was perpendicular to the cast films.

Viscoelastic behaviors were measured at a frequency of 110 Hz and a heating rate of 0.4°C/min in the temperature range from 20°C to 150°C with a Vibron-II manufactured by Toyo Baldwin Co. Ltd.

Thermal analyses were performed in a differential scanning calorimeter (Perkin-Elmer DSC-1) at a heating rate of 16°C/min in nitrogen environment.

RESULTS AND DISCUSSION

Cast Films from EDC—Benzene Solution

Films cast from EDC have a different structure from those cast from benzene, as reported by Fukuzawa, *et al.*⁶ films cast from EDC are form C or film A and films from benzene are form A or film B. It is interesting to study the structures and properties of films cast from EDC—benzene mixed solution. Since the boiling points of EDC and benzene (84°C and 80°C

respectively) are almost the same, it is thought that not much preferential evaporation occurs during casting. That is, the volume fraction of benzene in mixed solution does not seem to change noticeably during casting. Therefore the structures in the solution are considered to be retained also in the solid state. Therefore the system of EDC—benzene mixed solution is thought to be appropriate for studying the effect of solvent on the modification of cast films. The films used in this study were designated as B-0%, B-20%, B-60%, B-80%, and B-100%, showing the volume fractions of benzene in the mixed solvents.

McKinnon and Tobolsky⁵ showed the characteristic features in the X-ray diffraction patterns for the three solid-state modifications of PBG; the magnitudes of the spacings of the first equatorial reflections are respectively 14.9 Å, 14.5 Å, and 13.2 Å for forms A, B, and C. Further, form A has less crystallinity than forms B and C; the weak reflection at 5.1 Å, which is considered to correspond to the average axial translation of the benzene rings stacking to produce a special intermolecular interaction, is another characteristic of form A. Form B is a novel well-ordered modification and the X-ray diagram contains several sharp reflections. Form C shows the diffraction patterns equivalent to a unit cell given by Bamford *et al.*⁹

The magnitudes of spacings evaluated from the first main reflections in the X-ray patterns were respectively 13.4 Å for B-0%—B-60%, and 14.9 Å for B-80% and B-100%. For the latter a weak reflection was observed at 5.1 Å. From these results it is considered that form C was obtained from the mixed solutions containing less than 60-% benzene and form A was prepared from the solutions of more than 80-% benzene.

The viscoelastic behaviors of cast films from mixed solutions at 110 Hz are shown in Figure 1. B-80% as well as B-100% shows a rather broad peak of $\tan \delta$ at 50°C and a corresponding decrease in modulus is also observed around this temperature. This is attributed to the onset of the side chain motions. Furthermore, it can be seen that B-80% and B-100% have much higher moduli in the temperature range from 20°C to 90°C. Their moduli decreased abruptly

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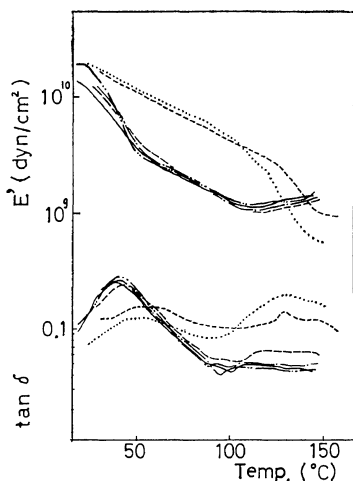


Figure 1. Tensile modulus E' and $\tan \delta$ at the frequency of 110 Hz as a function of temperature for films cast from mixed solution: —, B-0%; - - -, B-20%; - · - ·, B-40%; — · —, B-60%; - - - -, B-80%; · · · · ·, B-100%.

in the vicinity of 130°C and another $\tan \delta$ peak appeared around this temperature. The behaviors of B-80% and B-100% are the same as those of form A or film B and also those of the precipitate reported by Aritake, *et al.*⁷ The lower temperature peaks for B-0%, B-20%, B-40%, and B-60%, appeared at 40°C and no abrupt decrease in modulus was observed above 50°C. These results suggest that B-0%, B-20%, B-40%, and B-60% have the structure of form C. Further evidence for the above conclusion is found in the results of thermal analyses. B-80% and B-100% exhibited an endothermic peak at 135°C, while no peak was observed for the others. As reported previously,⁶ the endothermic peak is related to a breakdown of stacks of the benzene rings in the side chain of PBG. The stack of the benzene ring, which is formed in poor solvents and considered to be retained in cast films and precipitates, is broken at 135°C. Addition of more than 20% EDC is considered to hamper the formation of stacks of benzene rings owing to an enhanced solubility of PBG in mixed solvents.

Cast Films from DMF Solution at Various Temperatures

The films used in this study were designated as D-40, D-50, D-60, and D-70; these were cast

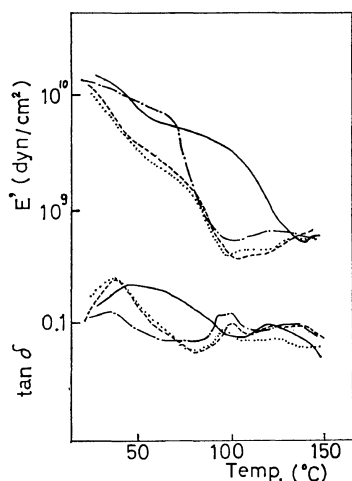


Figure 2. Tensile modulus E' and $\tan \delta$ as a function of temperature for films cast from dimethylformamide solution at various temperature: —, D-40; - - -, D-50; — · —, D-60; · · · · ·, D-70.

Table I. Spacings for films cast from dimethylformamide solution at various temperatures^a

Form A ^b	D-40	D-50	D-60	D-70	Form B ^b
14.9	15.3 (14.7)	14.4 (14.4)	14.6 (14.3)	14.6 (14.1)	14.5
12.8	13.3	12.0 (12.1)	12.0 (12.0)	12.6 (12.4)	11.9
9.7	9.8	7.71 (7.84)	7.80 (7.84)	7.81 (7.76)	7.79
8.8		7.21 (7.29)	7.38 (7.23)	7.27 (7.25)	7.27
				6.66	6.50
		(5.96)	6.02	6.01	5.59
5.15	5.15 (5.25)	5.24 (5.23)	5.18 (5.25)	5.27 (5.34)	5.32
		4.57 (4.66)	4.88 (4.64)	4.87 (4.61)	4.87
		4.26	4.27 (4.28)	4.29 (4.23)	4.29
		(4.06)	4.04		3.97
		3.91	(3.89)	3.94 (3.91)	
		(3.92)	3.93		3.96
			3.63	3.61	3.63

^a Spacings are in Å. (), spacings for annealed case.

^b Ref 5.

at temperatures of 40°C, 50°C, 60°C, and 70°C respectively.

The viscoelastic behaviors of the original (not annealed) samples are shown in Figure 2. It can be seen that the behavior of D-40 is the same as that form A. For D-50, D-60, and D-70, an abrupt decrease in modulus at about 90°C and a $\tan \delta$ peak at 100°C were observed. The lower temperature dispersion, which is ascribed to the side-chain motions, appeared at 40°C. These results are similar to the behaviors of form B proposed by McKinnon and Tobolsky.⁵ Table I gives the spacings evaluated from the X-ray patterns for the samples, which are compared with those of forms A and B reported by McKinnon and Tobolsky. The spacings of D-40 correspond to those of form A, and the spacings of D-50, D-60, and D-70 to those of form B. These results are in agreement with the presumption which was derived above from the results of viscoelastic measurements. Thermal and dilatometric measurements also support the identification of D-40 with form A: the irreversible transition at 135°C was observed.

The modulus curve for D-50, D-60, and D-70 suggests that a transition may occur around 90°C. However, volume—temperature experiments have failed to establish this definitely. From the X-ray analyses at several temperatures, McKinnon and Tobolsky have shown that an anisotropic thermal expansion of the lattice occurs and consequently the packing of the polypeptide chain changes from a pseudo-hexagonal to a pure hexagonal lattice at 95°C. However, they did not discuss the influence of the transition upon the viscoelastic properties. Since some structural change will be caused by the anisotropic expansion, we can presume that some molecular motion within the crystal may occur around 90°C, as is well known in the viscoelastic properties of crystalline polymers such as polyethylene.⁹ Although at present we can not describe definitely the mode of the molecular motion, some such motion will be responsible for the relaxation around 95°C.

In parentheses in Table I, the spacings of the samples after being annealed at 140°C are given. It can be seen that the structures are not affected by annealing. The viscoelastic behavior of the

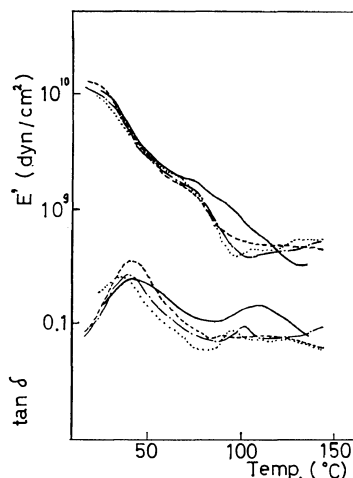


Figure 3. Tensile modulus E' and $\tan \delta$ as a function of temperature for annealed films: —, D-40; ----, D-50; - · - ·, D-60; · · · ·, D-70.

annealed samples is shown in Figure 3. The annealed sample of D-40 shows a noticeable $\tan \delta$ peak near 110°C. As discussed previously,⁷ this dispersion peak is considered to be related to some molecular motion of the chain in the amorphous region. In form A the molecular motion of the main chain is hampered by the side chain interaction. After being annealed the stack of the benzene ring is broken down and the annealed sample shows a noticeable peak at 110°C owing to less crystallinity. Although the annealed form A appears to be similar to form B in the viscoelastic properties in that it shows a decrease of modulus around 100°C, we cannot prove this similarity from the X-ray diffraction measurements shown in Table I. Regarding the structure of the annealed form A, further study may be necessary.

Cast Films from Benzene Solution at Various Temperatures

The films used in this study were designated as B-40, B-45, B-50, and B-60, which were cast from benzene solutions at temperatures of 40°C, 45°C, 50°C, and 60°C, respectively. Table II gives the spacings evaluated from the X-ray patterns. From comparison of the spacings of the cast films with those of forms A and B reported by McKinnon and Tobolsky,⁵ it is concluded that form A is prepared from benzene

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Table II. Spacings for films cast from benzene solution at various temperatures^a

Form A ^b	B-40	B-50	B-60	Form B ^b
14.9	15.4	14.2	14.3	14.5
12.8	13.3		12.5	11.9
8.8			7.96	7.79
			7.22	7.27
				6.50
				5.59
5.15	5.16	5.22	5.30	5.32
			4.69	4.87
			4.30	4.29
			3.94	3.97

^a Spacings are in Å.

^b Ref 5.

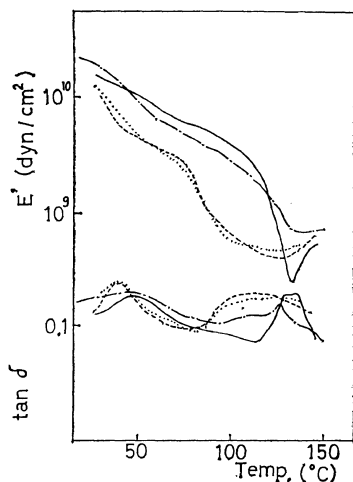


Figure 4. Tensile modulus E' and $\tan \delta$ as a function of temperature for films cast from benzene solution at various temperatures: —, B-40; ---, B-45; - - - -, B-50; ·····, B-60.

solutions at casting temperatures below 50°C and at casting temperatures above 50°C form B is prepared.

The viscoelastic results in Figure 4 also indicate that the viscoelastic behaviors of B-40 and B-45 are similar to those of form A, and B-50 and B-60 are similar to form B. Contrary to the expectation from the results of the X-ray measurements, B-50 showed the features of viscoelastic properties for form B. On the other hand the thermal analyses showed an endothermic peak at 135°C; from the standpoint of thermal properties, B-50 seems similar to form A. The heat of transition estimated from the thermogram for B-50 was 2.0 cal/g, about half of that of B-40. Therefore we presume that the stack of the benzene ring in B-50 is imperfect and that forms A and B may coexist in B-50. However further detailed study is necessary.

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