BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 859—861 (1970)

Conformations of Low-molecular-weight Poly-γ-Benzyl-L-Glutamate Films

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(Received October 20, 1970)

We wish to report here our infrared (IR) studies of the conformations of low-molecular-weight poly-γ-benzyl-L-glutamate (PBLG) films cast from various helix-forming solvents, such as *N,N'*-dimethylformamide (DMF), *m*-cresol, dioxane, 1,2-dichloroethane (DCE), benzene, and chloroform.[1] We adopted five kinds of low-molecular-weight PBLG samples with different degrees of polymerization (DP), the DP values being 8, 13, 21, 28, and 49, and one high-molecular-weight PBLG (DP=250). The characters of the samples are shown in Table 1.

Table 1. The characters of the polymers

Sample	Initiator	A/I[a]	DP
PBLG-5	*n*-hexylamine	5	8[b]
PBLG-10	*n*-hexylamine	10	13[b]
PBLG-20	*n*-hexylamine	20	21[b]
PBLG-30	*n*-hexylamine	30	28[b]
PBLG-50	*n*-hexylamine	50	49[b]
PBLG-100	triethylamine	100	250[c]

a) Molar ratio of the anhydride to the initiator.
b) Determined by the method (1).
c) Determined by the method (2).

The IR spectra of the PBLG films are shown in Fig. 1. The high-molecular-weight PBLG exhibits the amide I band at about 1650 cm^{-1} and the amide II band at about 1548 cm^{-1}, these bands are due to the α-helix.[2]

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[1] S. J. Singer, *Advances in Protein Chemistry*, **14**, 1 (1959).

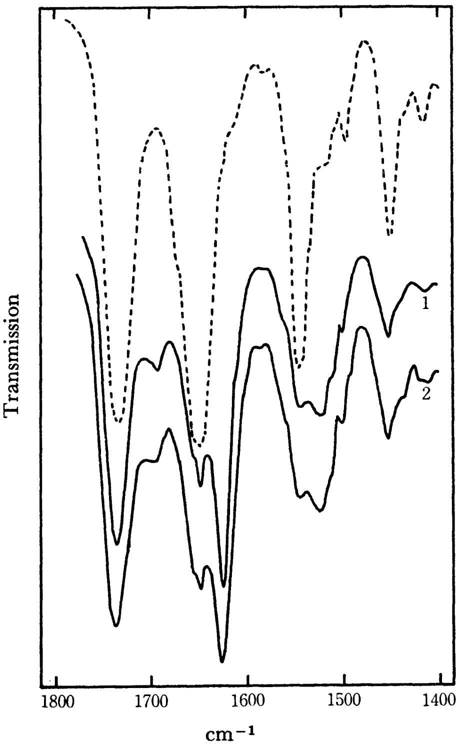

Fig. 1(a). IR spectra of PBLG-5 films cast from DMF (1) and chloroform (2) solutions. Dashed curve is that of PBLG-100 film cast from chloroform solution.

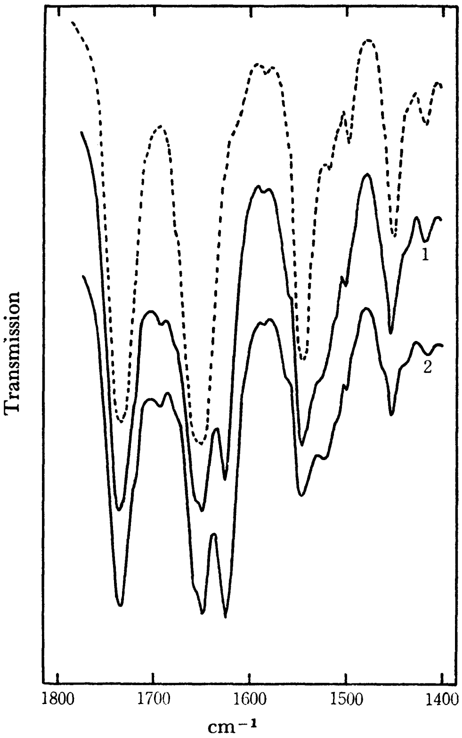

Fig. 1(b). IR spectra of PBLG-10 films.

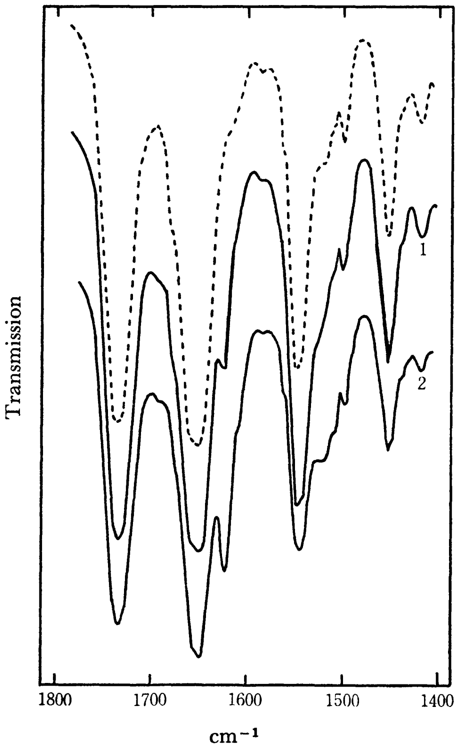

Fig. 1(c). IR spectra of PBLG-20 films.

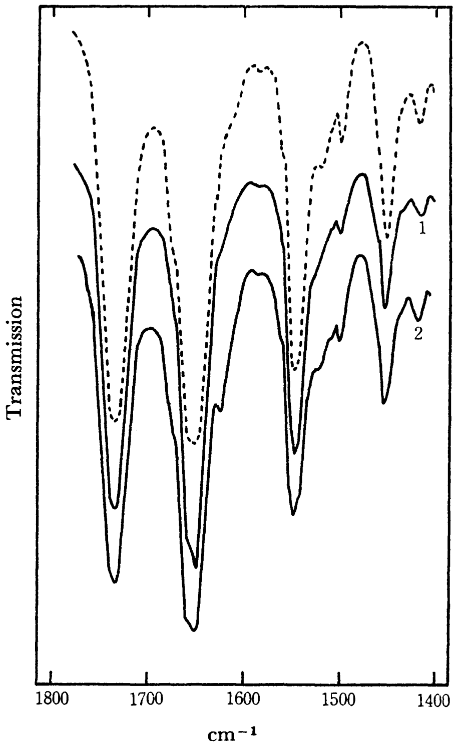

Fig. 1(d). IR spectra of PBLG-30 films.

On the other hand, the low-molecular-weight PBLG samples exhibit the amide I bands at about 1690 and 1625 cm^{-1}, positions which are attributable to the antiparallel pleated sheet or the β-form, and at about 1650 cm^{-1}, a position which is due to the α-helix.[2] It is remarkable that the intensity of the 1625-cm^{-1} component depends not only on the value of DP, but also on the solvents from which the PBLG film was cast. This solvent effect on the degree of the β-formation is a new finding in this experiment.

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[2] T. Miyazawa and E. R. Blout, *J. Amer. Chem. Soc.*, **83**, 712 (1961).

The extinction coefficient of the 1625-cm^{-1} component of the amide I in the β-form is believed to be similar to that of the 1650-cm^{-1} component of the α-helix,[3] therefore, the apparent value of the β-form content, f_β, of the PBLG film may be obtained from the IR spectrum by using this equation:

$$f_\beta = \frac{OD_{1625}}{OD_{1625} + OD_{1650}}$$

where OD is the optical density of each component, calculated from the value of the transmission by the usual method.[4] The content of the α-helix equals $(1-f_\beta)$.

The f_β values are plotted in Fig. 2 as a function of the DP value. As may be seen in Fig. 2, the content of the β-form decreases as the DP value increases up to 49. The PBLG films cast from DMF and *m*-cresol solutions have smaller f_β values than have those cast from chloroform, DCE, and benzene solutions; the films from the dioxane solution have values of f_β intermediate between these two classes. Thus, it is found in this experiment that the helix-forming solvents make the low-molecular-weight PBLG films take not only the α-helix but also the β-form, and that the content of the β-form of the film depends on the solvent as follows: chloroform-benzene-DCE > dioxane > *m*-cresol-DMF.

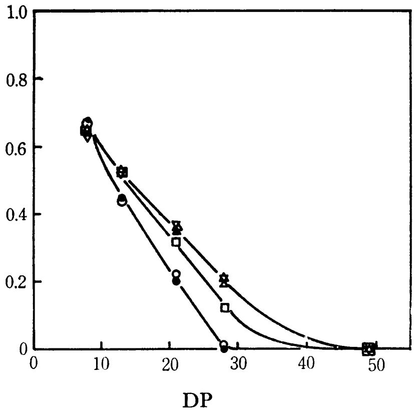

Fig. 2. Variation of the β-form content, f_β, of the PBLG films cast from the chloroform (▽), benzene (▲), DCE (△), dioxane (□), DMF (●), and *m*-cresol (○) solutions.

Experimental

Preparation of the Polymer. The low-molecular-weight PBLG samples, with different values of DP were obtained by polymerizing γ-benzyl-L-glutamate-*N*-carboxyanhydride in dioxane, using *n*-hexylamine as the initiator; the molar ratios of the anhydride to the initiator were 5, 10, 20, 30, and 50. The high-molecular-weight PBLG was obtained by using triethylamine as the initiator. The polymer was precipitated with ether from the dioxane solution, and dried under a vacuum. The DP value was determined by one of the following two methods: (1) we measured the nuclear magnetic resonance (NMR) spectra of the polymer in a chloroform and trifluoroacetic acid mixture,[5] and determined the number average DP value by calculating the ratio of the areas of the $C_\beta H_2$–$C_\gamma H_2$ proton resonances of the PBLG side-chain and the $(CH_2)_4$ proton resonances of the *n*-hexylamine bound to the C-terminal of the PBLG[6]; (2) we measured the intrinsic viscosity of the polymer in dichloroacetic acid at 25.0°C, and then applied the intrinsic viscosity *vs.* DP value relationship of Bradbury and Fenn to determine the DP value.[7] The results are summarized in Table 1.

IR Study. The dried polymer was dissolved into each helix-forming solvent, the solution was spread on a NaCl plate, and then the solvent was evaporated under a vacuum at room temperature. The IR spectrum of each unoriented film on the NaCl plate was measured with an infrared spectrophotometer, IR-G, made by the Japan Spectroscopic Co., Ltd.

The author wishes to thank Dr. Akira Minakata for his helpful advice and discussions, and Dr. Akira Warashina for his help in determining the DP values of the polymers by the NMR method.

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[3] a) C. H. Bamford, A. Elliott, and W. E. Hanby, "Synthetic Polypeptides," Academic Press, New York (1956), p. 143. b) S. M. Bloom, G. D. Fasman, C. deLoze, and E. R. Blout, *J. Amer. Chem. Soc.*, **84**, 458 (1962).

[4] A. Elliott, "Infrared Spectra and Structure of Organic Long-Chain Polymers," Edward Arnold, London (1969), p. 30.

[5] The NMR spectra were obtained on a Japan Electron Optics Laboratory Model JNM-4H-100 NMR spectrometer at a frequency of 100 MHz.

[6] J. A. Ferretti and B. W. Ninham, *Macromolecules*, **3**, 30 (1970).

[7] J. H. Bradbury and M. D. Fenn, *J. Mol. Biol.*, **36**, 231 (1968).