Polymer Journal, Vol. 16, No. 10, pp 739—749 (1984)

Synthesis and Structural Study of the A–B–A Tri-Block Copolymer Consisting of Poly(γ-benzyl D,L-glutamate) or Poly(γ-methyl D,L-glutamate) as the A Component and Polybutadiene as the B Component

Toshio HAYASHI, Guan-Wen CHEN,* and Akio NAKAJIMA

Research Center for Medical Polymers and Biomaterials, Kyoto University, Sakyo-ku, Kyoto 606, Japan

(Received March 9, 1984)

ABSTRACT: A series of A–B–A tri-block copolymers consisting of the D,L-isomers of poly(γ-benzyl glutamate) and poly(γ-methyl glutamate) as the A component, and polybutadiene as the B component were synthesized. The helical content of the D,L-copolymers in a helicogenic solvent and in a solid state was estimated on the basis of optical rotatory dispersion and infrared spectra. The content of the right-handed α-helix, the left-handed α-helix, and random coil conformations of the polypeptide chains was estimated. From wide-angle X-ray diffraction measurements, it was shown that the hexagonal crystalline phase almost disappeared for D,L-copolymer membranes, indicating a breakdown of the α-helical conformation in the main chains. The microheterophase structure of these block copolymer membranes was studied with an electron microscope and the D,L-block copolymers membranes were found to take on spherical structures even when the volume fractions of the B portion were rather high.

KEY WORDS ABA Tri-Block Copolymer / D,L-Isomer / Interrupted α-Helix / Wide-Angle X-ray Diffraction / Electron Microscopy / Microheterophase Structure /

Synthetic polypeptides have been used in material applications for synthetic skin analogs, surface coatings, microphone piezoelectric membranes and biocompatible materials. All these have been either derivatives of homopolypeptides or random copolypeptides. Block copolypeptides have been prepared,[1-5] but very little data on their solid state has been reported. Block copolymers of the A–B di-block and A–B–A tri-block types are of special interest from the standpoint of molecular designing. These copolymers are capable of forming organized structures, *i.e.*, microheterophase structures, when cast from solutions, and the resulting membranes are expected to exhibit specific functionalities. Attempt to incorporate a polypeptide as a component of A–B and A–B–A type block copolymers have been made by several authors.[6-8] Douy and Gallot[7] first reported an organized structure produced with an A–B di-block copolymer containing a polypeptide as the A component. We have recently put forth a series of works[9-19] on the organized structure of A–B–A tri-block copolymers, using γ-benzyl L-glutamate, γ-methyl L-glutamate, γ-ethyl L-glutamate, or N^{ε}-benzyloxycarbonyl L-lysine as the A component, and butadiene or tetramethylene oxide as the B component. The result of circular dichroism (CD) measurements in a helicogenic solvent and infrared (IR) absorption measurements in a solid state showed that the polypeptide chain in the copolymer held the same α-helical conformation

* Present address: *Institute of Chemistry, Academia Sinica Zhongguancum, Haidian, Beijing, China.*

as the homopolypeptide chain. The microheterophase structure in membranes cast from different solvents was examined with an electron microscope (EM). The micelle dimension evaluated from thermodynamic considerations, taking into account the conformational parameters of the component block chains, were in good agreement with that obtained from EM.

Next, it was considered of interest to investigate the A–B–A tri-block copolymers composed of D,L-isomers of polypeptides as the A component, and polybutadiene as the B component so as to determine the relation between the molecular conformations or microheterophase structure and the physical properties of the D,L-isomers of polypeptides and make a comparison with tri-block copolymers including the corresponding L-isomer of polypeptides as the A component.

In this paper, we report on the synthesis of a series of A–B–A tri-block copolymers consisting of the D,L-isomers of poly(γ-benzyl glutamate) and poly(γ-methyl glutamate) as well as the corresponding L-isomer of polypeptides as the A component, and polybutadiene (PB) as the B component. The chain structure and conformation of the block copolymers in the solid state were studied by X-ray diffraction and EM. The microheterophase structure in solid membranes is discussed from the standpoint of conformation.

EXPERIMENTAL

Materials

Amine-Terminated Polybutadiene. A cycloaliphatic secondary amine terminated polybutadiene (ATPB) was used as the middle block for all the block copolymers reported here. The number-average molecular weight of the ATPB was 3600. The ATPB was purified before use according to the method in the previous paper.[15]

γ-Benzyl D-Glutamate. A mixture of 100 g of D-glutamic acid, 200 ml of concentrated hydrochloric acid, and 750 ml of benzyl alcohol was slightly heated in a round-bottomed flask over a steam bath, with constant shaking, until a completely clear solution was obtained (40 to 60 min). After 10 min, the reaction mixture was cooled in an ice bath, and 2 liters of ether were added thereto. After an additional 30 min of standing in the cold bath, the mixture was filtered. The precipitate was taken up in 1200 ml of cold water, the pH adjusted to 6.0 to 6.5 with lithium hydroxide, and, after cooling for 2 h in the ice bath, the mixture was filtered. The precipitate was washed with ethanol until chlorine-free (tested with silver nitrate), and then with ether. After recrystallization from about 800 ml of boiling water, a 40 to 50% yield of pure γ-benzyl D-glutamate was obtained.[21]

γ-methyl D-Glutamate. A suspension of 30 g of D-glutamic acid in 350 ml of absolute methanol containing 20 g of dry hydrogen chloride was shaken until a completely clear solution was obtained (20 min). The clear solution was diluted to 1 liter with absolute methanol, and triethylamine (TEA) was added dropwise until the solution was made just alkaline. After standing at 0 to 5°C for 16 h, the product was filtered, washed with cold absolute methanol and ether, and air-dried on a filter. Drying was completed *in vacuo*; 60% yield. The product, after recrystallization from water-methanol, melted at 181°C.[22]

γ-Benzyl L-Glutamate and γ-Methyl L-Glutamate. These monomers were purchased from the Peptide Institute, Inc., Osaka.

N-carboxyanhydride (NCA) of Amino Acids. Phosgene was bubbled into a suspension of 50 g of amino acids (γ-benzyl L-glutamate, γ-benzyl D-glutamate, γ-methyl L-glutamate, and γ-methyl D-glutamate) in 750 ml of purified tetrahydrofuran (THF) at 50°C. A clear solution was obtained within 10 to 15 min. Nitrogen gas was then passed through the solution for 2 h and the solution was condensed to crude crystallines at 40 to 50°C using a rotatory evaporator. The crystallines

were purified by repeated recrystallization from an ethyl acetate solution with the addition of petroleum ether.

Synthesis of Homopolypeptides and D,L-Copolypeptides. Samples of poly(γ-benzyl L-glutamate) (PBLG), poly(γ-benzyl D-glutamate) (PBDG), poly(γ-methyl L-glutamate) (PMLG), and poly(γ-methyl D-glutamate) (PMDG) with different molecular weight were prepared by polymerizing the NCA of the corresponding amino acids in a dioxane–methylene dichloride (1 : 1, v/v) mixture using TEA as the initiator. The equimolar D,L-copolypeptides; poly(γ-benzyl D,L-glutamate) (PBDLG) and poly(γ-methyl D,L-glutamate) (PMDLG), were prepared by polymerizing equimolar mixtures of D- and L-amino acid NCA in the same condition as that for homopolypeptides. Polymers synthesized thus were fractionated in the system of methylene dichloride and methanol.

Synthesis of Block Copolymers. The amounts of the amino acid NCA and ATPB were determined so as to obtain the desired degree of polymerization, P, of the polypeptide block from $P=[\mathrm{NCA}]/[\mathrm{ATPB}]$, in which [NCA] and [ATPB] are the molar concentrations of NCA and ATPB, respectively. The polymerization was carried out at 25°C in a dioxane–methylene dichloride (1 : 2, v/v) mixture. After 72 to 120 h, the polymerization was terminated and the copolymer was precipitated with 4 to 5 volumes of pure cold ethanol. The copolymer was then dried *in vacuo*.

Selective Extraction and Fractional Precipitation of Block Copolymers. The purification was started with the selective extraction of the homopolymers included. The PB fragment, which was isolated, and a low molecular weight of homopolypeptide were extracted with *n*-hexane. The amounts of the isolated PB and homopolypeptides fractions were rather small. To perform the fractionation, the copolymers were dissolved in a mixture of chloroform and *n*-hexane, and ethanol was used as a precipitant. The copolymer sample was separated into four to five fractions, and the central portions were used for physical measurements. The results of all the copolymerizations are listed in Table I.

Table I. Molecular characterization of polypeptide samples

Sample code	Monomer ratio, L%	$[\eta]$ / dl g^{-1} (DCA, 25°C)	M_w	M_z/M_w
PBLG-1	100	2.91	588,000	1.15
PBLG-2	100	1.94	370,400	1.12
PBLG-3	100	1.13	197,000	1.16
PBLG-4	100	0.651	98,000	1.18
PBDLG-1	50	0.491	94,000	1.17
PBDLG-2	50	0.274	48,000	1.21
PBDLG-3	50	0.162	26,000	1.15
PBDLG-4	50	0.127	19,000	1.18
PMLG-1	100	1.11	141,500	1.16
PMLG-2	100	0.865	98,600	1.12
PMLG-3	100	0.670	69,000	1.15
PMLG-4	100	0.458	37,700	1.18
PMDLG-1	50	0.614	102,500	1.14
PMDLG-2	50	0.498	81,200	1.15
PMDLG-3	50	0.427	67,000	1.18
PMDLG-4	50	0.259	34,600	1.20
PBDG-1	0	0.966	155,000	1.20
PMDG-1	0	1.44	325,000	1.21

Measurements

Molecular Weights. The molecular weights of the samples were estimated from equilibrium runs on polymer solutions using MOM Type-3170-b ultracentrifuge. As solvents, *N*,*N*′-dimethylformamide (DMF) was used for γ-benzyl ester series, and *m*-cresol for γ-methyl ester series. In general, solutions of 0.05 to 0.20 (g dl^{-1}) concentration were used for the sedimentation equilibrium runs. Viscosity measurements were performed in DCA at 25±0.01°C with an improved Ubbelohde-type viscometer having a flow time for the solvent exceeding 100 s. DCA is known as a coil solvent for PBLG, PBDG, PMLG, and PMDG, as well as for their D,L-copolymers.[23]

Composition of the Polypeptide Blocks. The

molar content of polypeptide in each copolymer was determined by elemental analysis carried out at the Organic Microanalyses Center of Kyoto University.

Conformational Characterization of D,L-*Copolypeptides.* To estimate the helical content of D,L-copolymers in a helicogenic solvent and/or in a solid state, ORD and IR spectra were measured.[24] ORD measurements were carried out with a Yanagimoto OR-100 Type spectropolarimeter using a tungsten lamp as the light source in a temperature range from 10 to 45°C, and the helix parameter b_0 was estimated according to the Moffitt–Yang equation.[25] Furthermore, the polymer composition represented by $L\%$ in D,L-copolymers was determined from the reduced residue rotation, [m′], for D,L-copolymer dissolved in DCA, a random coil solvent, by eq 1[26]

$$L(\%)=100\,\frac{[\mathrm{m}']-[\mathrm{m}']_{\mathrm{D}}}{[\mathrm{m}']_{\mathrm{L}}-[\mathrm{m}']_{\mathrm{D}}} \qquad (1)$$

where the subscripts D and L represent the corresponding homopolymers. The IR spectra of solid films cast from solution were measured with a Shimadzu Model 30-A IR spectrophotometer in a region of 4000 to 400 cm^{-1}.

X-Ray Diffraction and Electron Microscopy. X-Ray diagrams were obtained by Ni-filtered Cu-K_α radiation. For the electron microscopy measurement, thin films cast from a solution were obtained with osmium tetroxide and examined by transmission microscopy. All micrographs were taken at an instrumental magnification of 4000.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers

The molecular weights and degree of polydispersity of the polymer samples were determined from equilibrium runs. The apparent weight-average molecular weight M_w^{app} of all the samples in the cell is obtained from eq 2 as a function of polymer concentration C_0 before centrifugation[27]

$$M_w^{\mathrm{app}}=\frac{2RT(C_{\mathrm{b}}-C_{\mathrm{m}})}{\omega^2(1-\bar{v}\rho)C_0(r_{\mathrm{b}}^2-r_{\mathrm{m}}^2)} \qquad (2)$$

where R is the universal gas constant, T the absolute temperature, ω the angular velocity of the rotor, $\bar{v}$ the partial specific volume of the solute ($\bar{v}=0.77\ \mathrm{cm}^3\,\mathrm{g}^{-1}$),[28] ρ the density of the solution ($\rho=1.034\ \mathrm{g\ cm}^{-3}$ for *m*-cresol and $\rho=0.9445\ \mathrm{g\,cm}^{-3}$ for DMF) C_{b} and C_{m} are the equilibrium concentrations at the bottom of the cell r_{b} and at the meniscus r_{m}, respectively. The weight-average molecular weight M_w was obtained by extrapolating M_w^{app} values at different concentrations to infinite dilution in the range of 0.05 to 0.20 g dl^{-1}.

The Z-average molecular weight of the whole sample, M_z^{app}, is given by

$$M_z^{\mathrm{app}}=\frac{M_{w\mathrm{b}}C_{\mathrm{c}}-M_{w\mathrm{m}}C_{\mathrm{m}}}{C_{\mathrm{b}}-C_{\mathrm{m}}} \qquad (3)$$

The degree of polydispersity of the polymer fractions is indicated by the ratio M_z/M_w; a value of 1.00 would indicate a monodisperse polymer. The molecular weights and limiting viscosity number in DCA at 25°C for various homopolypeptides and D,L-copolypeptides are

Table II. Molecular characterization of block copolymers

Sample code	Butadiene mol%	$[\eta]$ dl g^{-1} (DCA, 25°C)	M_w	P_{A}
GBG-DL-1	48.1	0.152	18,000	33
GBG-DL-2	31.3	0.230	33,000	67
GBG-DL-3	18.9	0.389	61,000	131
GBG-DL-4	12.5	0.563	97,000	213
GBG-L-1	30.5	0.340	34,000	69
GBG-L-2	18.4	0.576	63,000	135
GBG-L-3	12.3	0.889	99,000	218
GBG-L-4	4.1	2.29	310,000	699
MBM-DL-1	30.0		24,000	71
MBM-DL-2	14.0		57,000	187
MBM-L-1	32.2		22,000	64
MBM-L-2	19.8		39,000	124
MBM-L-3	8.1		102,500	346

shown in Table I. A series of A–B–A tri-block copolymers consisting of PBLG-PB-PBLG (designated as GBG-L), PBDLG-PB-PBDLG (GBG-DL), PMLG-PB-PMLG (MBM-L), and PMDLG-PB-PMDLG (MBM-DL), in which PB is the polybutadiene middle block, were synthesized and fractionated. In the previous report,[12] it was concluded that the GBG-L block copolymer was of the A–B–A tri-block type, and consisted of A block chains of equal length linked to the ends of the PB chain, produced by the nucleophilic addition of the amino acid NCA from the experimental results of ORD and viscosity measurements. The compositions, weight-average molecular weight M_w, and limiting viscosity number $[\eta]$ in DCA at 25°C are shown in Table II, in which the P_A, the degree of polymerization of the A-block chain, are those estimated from the M_w values and estimated molecular weight of PB (M=3600). In Table I, the degree of polydispersity M_z/M_w in most cases is relatively small.

Chain Conformation of D,L-*Copolypeptides*

The difference in helical content of right-handed and left-handed α-helix conformations in a solution may be determined from measurements of ORD, and estimated by eq 4

$$X^{H}_{R-L}=\frac{b_0-b_{0,c}}{b_{0,h}-b_{0,c}} \tag{4}$$

where X^{H}_{R-L} denotes the difference between right- and left-handed α-helix content, and $b_{0,h}$ and $b_{0,c}$ the b_0 values for a perfect right-handed α-helix and perfect random coil conformations, respectively. $b_{0,c}$ is generally close to zero, while $b_{0,h}$ gives an average value of -600 in several helicogenic solvents.[29] We adopted $b_{0,h}=-600$ for PMLG in *m*-cresol and -615 for PBLG in DMF, respectively, and $b_{0,c}=0$ for both cases.[30]

Masuda *et al.*,[24] have pointed out that the IR method is useful for estimating the helix content of solid polypeptide samples, and proposed that the IR peak intensity of the amide V band at 630 cm^{-1} relative to the 2950 cm^{-1} band gives the total helix content, *i.e.*, the sum of the right- and left-handed α-helix content, of PMLG and PMDLG solid films. Thus, the total α-helix content, X^{H}_{R+L}, was estimated by eq 5,

$$X^{H}_{R+L}=\frac{(I^{c}_{620-630}/I^{c}_{2950})}{(I^{h}_{620-630}/I^{h}_{2950})} \tag{5}$$

where I^{c}_{ν} and I^{h}_{ν} denote the intensity of the IR absorption spectra at ν cm^{-1} for the D,L-copolymer and homopolymer, respectively. The aliphatic C–H stretching vibration gives rise to a band at 2950 cm^{-1} and the adsorption coefficient of this vibration is expected to be independent of chain conformation. The amide V band, assigned to the N–H out-of-plane bending, has been found[31,32] to be sensitive to conformations even for unoriented samples.

Table III summarises the conformational characterization of D,L-copolymers, PBDLG and PMDLG, and the corresponding homopolymers, PBLG, PBDG, PMLG, and PMDG. It should be noted that the L%'s in the equimolar-D,L-copolymers are almost the same as the L%'s in the NCA mixture used for polymerization (Table I). The intensity ratios obtained from IR measurement and eq 5 are shown in the third column of Table III. In the fourth column of Table III are shown X^{H}_{R+L} estimated from the intensity ratio, assuming

Table III. Conformational characterization of PBDLG and PMDLG samples

Sample code	Polymer comp. L%	Intensity ratio	X^{H}_{R+L}	X^{H}_{R-L}
PBLG-3	100.0	0.68	1.00	1.00
PBDLG-1	50.3	0.48	0.71	0.02
PBDLG-3	50.5	0.47	0.70	0.00
PBDG-1	0.0	0.68	1.00	−1.00
PMLG-1	100.0	0.72	1.00	1.00
PMDLG-1	50.6	0.44	0.60	0.04
PMDLG-4	50.1	0.44	0.60	0.01
PMDG-1	0.0	0.72	1.00	−0.99

tentatively that the α-helix content of the corresponding homopolypeptide is equal to unity. Though these values may not strictly be equal to the absolute values of the sum of the α-helix content, they afford a measure of the relative helix content in solid films.[26,32] The IR spectra were obtained with solid films cast from an α-helicogenic solvent: chloroform (CF) for γ-benzyl ester series (Figure 1) and trifluoroethanol (TFE) for γ-methyl ester series (Figure 2). The IR spectrum measured with PMLG-1 film cast from a trifluoroacetic acid (TFA) solution showed exactly the same characteristic absorption bands as those from TFE (Figure 2). This indicates that PMLG in a random coil conformation in TFA was converted the α-helix conformation during solvent evaporation, and that the α-helix content was not affected by the type of solvent from which the films were cast. From the values of b_0 and eq 4, the values X^{H}_{R-L} as listed in Table III are obtained for samples. Thus, we may estimate the content of the right-handed α-helix, the left-handed α-helix, and random coil conformations for these D,L-copolypeptides, provided the α-helix content for the homopolypeptide in the solid state is known. Although the helix content, X^{H}_{R+L}, estimated from IR is somewhat overestimated because of overlapping of the amide V band of the α-helix form with the diffuse band of the dispersed form, the presence of a considerable amount of helix content indicates the D-residues (or L-residues) to be appreciably incorporated into the right-handed (or left-handed) helical chains consisting of L-residues (or D-residues). Doty, *et al.*[33] suggest that the helical sense of a few D-residues added to the right-handed α-helix conformation composed of L-residues is right-

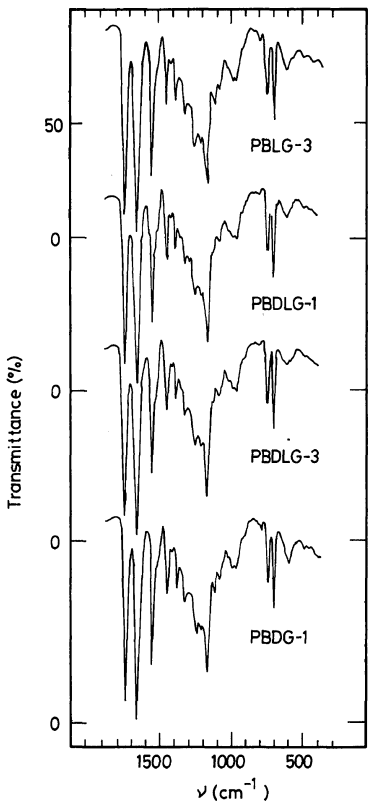

Figure 1. Infrared spectra of unoriented solid films PBLG-3, PBDLG-1, PBDLG-3, and PBDG-1 cast from CF.

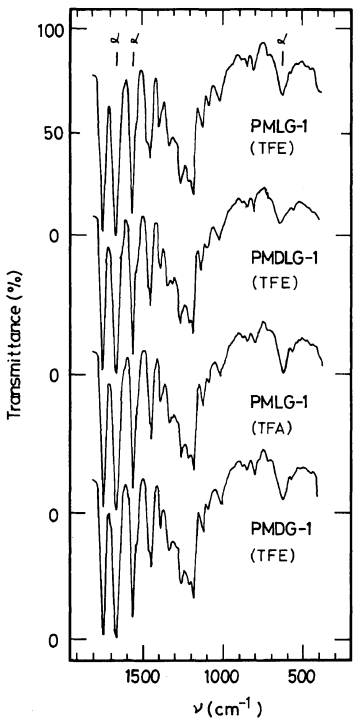

Figure 2. Infrared spectra of unoriented solid films PMLG-1 (TFE), PMDLG-1 (TFE), PMLG-1 (TFA), and PMDG-1 (TFE).

handed, but the addition of more than four D-residues may possibly change the sense of the helix. Go and Saito[34] support this opinion.

Molecular Structure of the A-Block in the Solid State

The IR spectra in the region for 1800 to 400 cm^{-1} for solid films are shown in Figures 3 and 4. The amide I, II, and V bands of GBG-L and MBM-L block copolymers appeared at 1650, 1550, and 615 cm^{-1}, respectively, as just the same wave number for the corresponding homopolymers, PBLG and PMLG. This implies that the A-block component in these block copolymers assumes the α-helix conformation, and moreover, that the helix content of the A-block component is nearly the same as that of the corresponding homopolymers. The IR-peak intensity of the amide V band for GBG-DL and MBM-DL, as well as for PBDLG and PMDLG films, somewhat decreases, compared to those of the corresponding L-isomeric polymers. This means that the D,L-copolymer chains exist mainly in the α-helix conformation, but some portions are in random coil conformations. Specific bands associated with C=C tortion and C–H out-of-plane modes[35] were observed at around 970 cm^{-1}, and the relative intensity of this band increased with increasing molar amount of PB in the block copolymers, as expected.

The wide-angle X-ray diffraction (WAXD) patterns for the GBG-L and GBG-DL block copolymers, and PBLG and PBDLG are shown in Figure 5. Figure 6 shows the WAXD patterns for MBM-L and MBM-DL block copolymers, and PMLG and PMDLG films. In Figures 5 and 6, the first main reflections correspond to an intermolecular spacing of the α-helical chains and have spacings of 12.5 and 10.34 Å for the PBLG film cast from CF (Figure 5) and the PMLG film cast from the

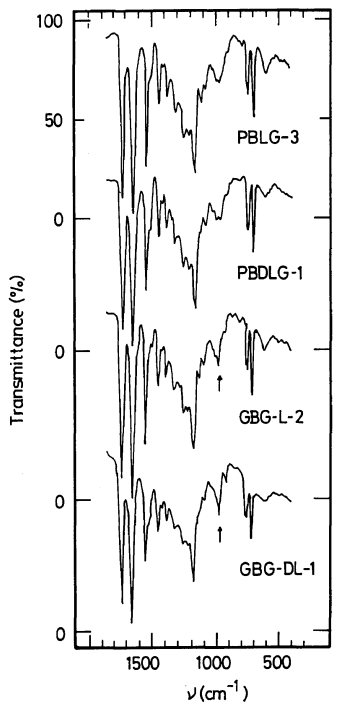

Figure 3. Infrared spectra of unoriented solid films PBLG-3, PBDLG-1, GBG-L-2, and GBG-DL-1.

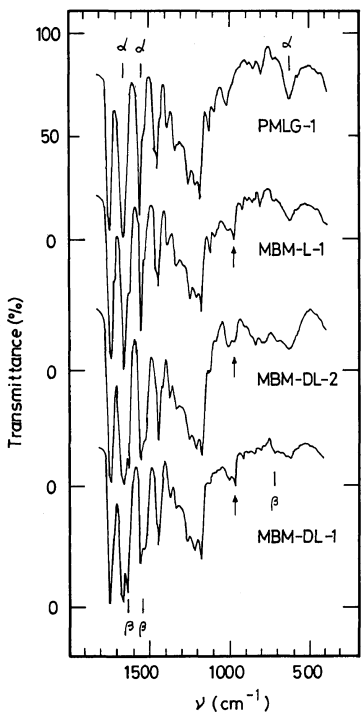

Figure 4. Infrared spectra of unoriented solid films PMLG-1, MBM-L-1, MBM-DL-2, and MBM-DL-1.

CF–TFE (4:1, v/v) mixture, respectively. Diffraction patterns for GBG-L (Figure 5) and MBM-L (Figure 6) showed basically similar reflections to those of the corresponding homopolymers, PBLG and PMLG, respectively. The breadth of the diffraction peaks for GBG-L and MBM-L block copolymers became broader than that of the homopolymers with increasing PB content in the block copolymers. This indicates that the polypeptide block por-

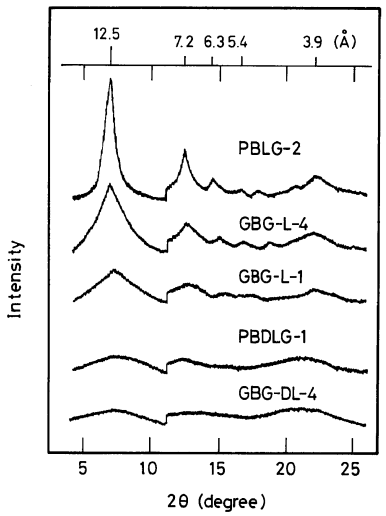

Figure 5. Wide-angle X-ray diffraction profiles of unoriented solid films PBLG-2, GBG-L-4, GBG-L-1, PBDLG-1, and GBG-DL-4.

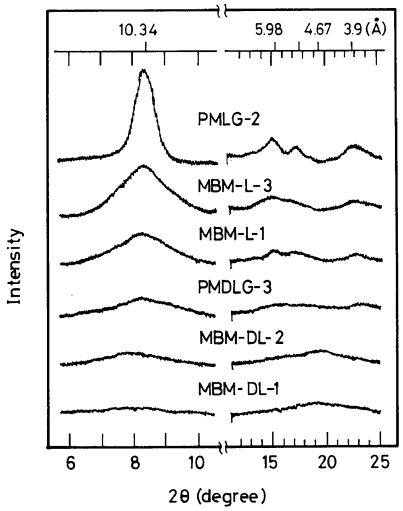

Figure 6. Wide-angle X-ray diffraction profiles of unoriented solid films PMLG-2, MBM-L-3, MBM-L-1, PMDLG-3, MBM-DL-2, and MBM-DL-1.

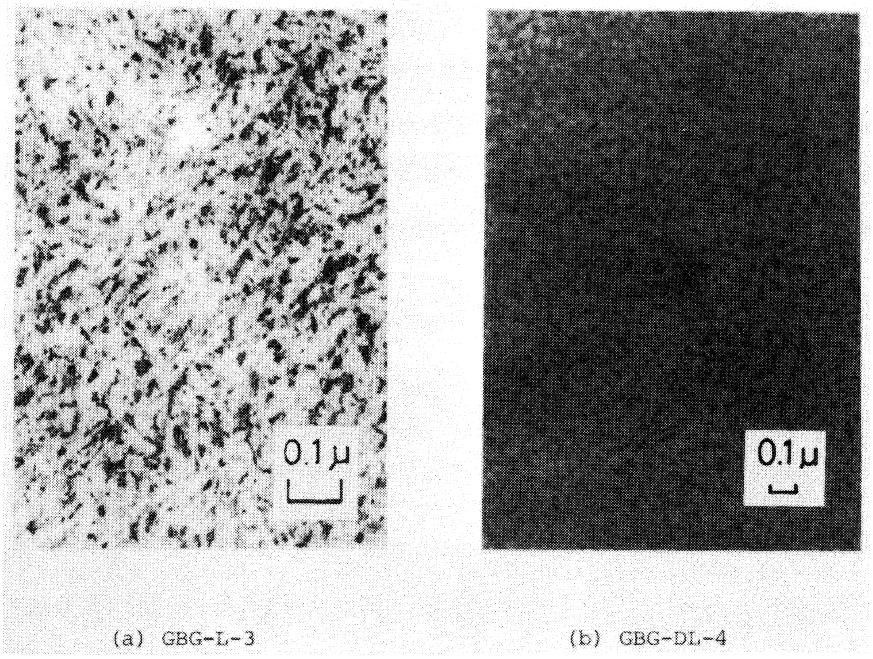

Figure 7. Electron micrographs of GBG-L and GBG-DL block copolymer films cast from CF at 25°C.

tions in GBG-L or MBM-L block copolymer films have less crystallinity and the orientation of the α-helix conformation is inferior to that in PBLG or PMLG. Further, their diffraction patterns for the D,L-isomers were very weak and became much broader than those of the L-isomers. These observations indicate that the D,L-isomers contain far fewer crystalline portions.[36]

Microheterophase Structure

To obtain information on the domain structure of GBG-DL and MBM-DL block copolymers in the solid state, the morphology of these block copolymers was investigated on the basis of EM. Figure 7 shows electron micrographs of GBG-L and GBG-DL block copolymer films cast from CF. The domains of PB, stained with osmium tetroxide (OsO_4), correspond to the dark portions. Further, electron micrographs of MBM-L and MBM-DL

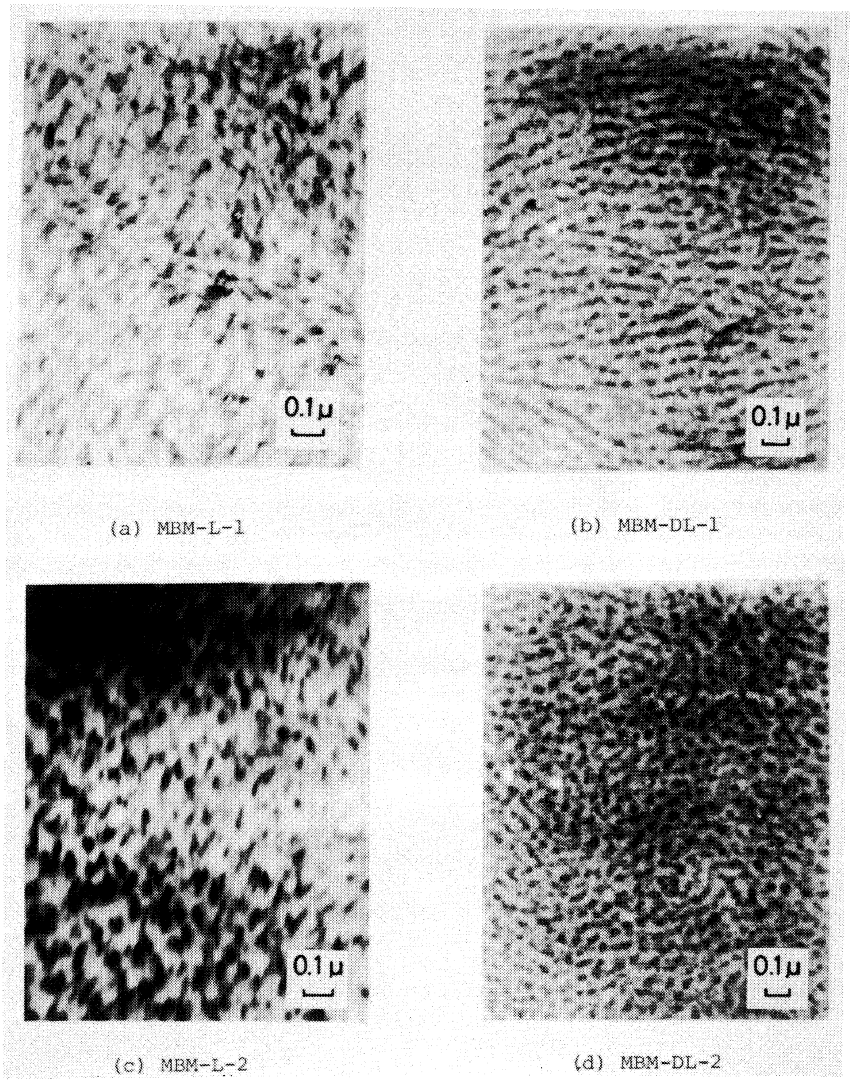

Figure 8. Electron micrographs of MBM-L and MBM-DL block copolymer films cast from CF–TFE (4:1, v/v) mixture at 25°C.

films are shown in Figure 8, whose cast solvent was a mixture of CF and TFE by 4:1 v/v. Various microheterophase structures are observed, depending on the content of PB and the A-block portion conformations. For example, MBM-L-2 (Figure 8c) takes an intermediate structure between sphere and cylinder, while MBM-L-1 has a cylindrical structure (Figure 8a). This clear difference in microheterophase structures was recognized between MBM-L and MBM-DL block copolymers, as well as between GBG-L and GBG-DL block copolymers. As shown in Figures 7 and 8, the inclusion phase of the B-portion in D,L-block copolymer films tends to take on a spherical structure more than the L-isomeric samples. For example, MBM-DL-1 (Figure 8b) has a spherical structure, even though the molar content of PB is still higher in the MBM-DL-1 block copolymer than that in MBM-L-2 block copolymer. The A-block portions of the MBM-L or GBG-L block copolymers have perfect α-helix conformations, but those of the MBM-DL or GBG-DL block copolymers have interrupted α-helices. Thus, both the shape and dispersion conditions of the inclusion phase of the B-component for MBM-DL or GBG-DL become rather uniform compared to those of the MBM-L or GBG-L block copolymers. It is, thus, concluded that the existence of molecular chains in the interrupted α-helix conformation affects the formation of the homogeneous micelle shape, as evident from the electron micrographs.

The mechanical properties and water permeability of these block copolymer films will be reported in the following paper.

Acknowledgement. The authors gratefully acknowledge Drs. K. Rieu and R. Drake, the B. F. Goodrich Chem. Co., for kindly supplying the ATPB. They also wish to thank Mr. S. Yamaguchi, Central Research Lab., Daikin Kogyo Co., for assisting with the EM.

REFERENCES

1. W. B. Gratzer and P. Doty, *J. Am. Chem. Soc.*, **85**, 1193 (1963).
2. N. Lupu-Lotan A. Berger, E. Katchalski, R. T. Ingwall, and H. A. Scheraga, *Biopolymers*, **4**, 239 (1966).
3. H-J. Sage and G. D. Fasman, *Biochemistry*, **5**, 286 (1966).
4. H. E. Auer and P. Doty, *Biochemistry*, **5**, 1708 (1966).
5. A. Cosani, E. Peggion, M. Terbojeuich, and A. Prtolan, *Chem. Commun.*, 930 (1967).
6. Y. Yamashita, Y. Iwata, and K. Ito, *Makromol. Chem.*, **176**, 1207 (1975).
7. B. Perly, A. Douy, and B. Gallot, *Makromol. Chem.*, **177**, 2569 (1976).
8. A. Douy and B. Gallot, *Polym. Eng. Sci.*, **17**, 523 (1977).
9. A. Nakajima, T. Hayashi, K. Kugo, and K. Shinoda, *Macromolecules*, **12**, 840 (1979).
10. A. Nakajima, K. Kugo, and T. Hayashi, *Macromolecules*, **12**, 844 (1979).
11. A. Nakajima, K. Kugo, and T. Hayashi, *Polym. J.*, **11**, 995 (1979).
12. T. Kotani, T. Hayashi, and A. Nakajima, *Bull. Inst. Chem. Res., Kyoto Univ.*, **58**, 449 (1980).
13. T. Hayashi, G. W. Chen, and A. Nakajima, *Rep. Prog. Polym. Phys. Jpn.*, **23**, 701 (1980).
14. T. Hayashi, G. W. Chen, and A. Nakajima, *Rep. Prog. Polym. Phys. Jpn.*, **24**, 575 (1981).
15. G. W. Chen, T. Hayashi, and A. Nakajima, *Polym. J.*, **13**, 433 (1981).
16. K. Kugo, T. Hayashi, and A. Nakajima, *Polym. J.*, **14**, 391 (1982).
17. K. Kugo, Y. Hata, T. Hayashi, and A. Nakajima, *Polym. J.*, **14**, 401 (1982).
18. K. Kugo, M. Murashima, T. Hayashi, and A. Nakajima, *Polym. J.*, **15**, 267 (1983).
19. T. Hayashi, K. Kugo, and A. Nakajima, *Rep. Prog. Polym. Phys., Jpn.*, **25**, 687 (1982).
20. M. Takayanagi, *Mem. Fac. Eng., Kyushu Univ.*, **23**, 41 (1963).
21. J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 2, John Wiley & Sons, Inc., New York, N. Y., 1961, p 930.
22. E. Sandriv, *Helv. Chim. Acta*, **46**, 1637 (1963).
23. P. Doty, *J. Am. Chem. Soc.*, **79**, 3961 (1957).
24. Y. Masuda, T. Miyazawa, and M. Goodman, *Biopolymers*, **8**, 515 (1969).
25. W. Moffitt and J. T. Yang, *Proc. Natl. Acad. Sci., U.S.A.*, **42**, 596 (1956).
26. T. Hayashi, Ph.D. Thesis, Kyoto University, 1973, Chapter 9.
27. P. H. vonDreele, N. Lotan, V. S. Ananthanarayanan, R. H. Andreatta, D. Poland, and H. A. Scheraga, *Macromolecules*, **4**, 408 (1971).

28. T. Hayashi, private communication.
29. J. Y. Cassim and E. W. Taylor, *Biophys. J.*, **5**, 553 (1965).
30. A. Nakajima and T. Hayashi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **46**, 62 (1968).
31. T. Miyazawa, Y. Masuda, and K. Fukushima, *J. Polym. Sci.*, **62**, 62 (1962).
32. Y. Masuda, *Kobunshi Kagaku*, **20**, 161, 166, 171, 206, 210 (1963).
33. P. Doty and R. D. Lundberg, *J. Am. Chem. Soc.*, **79**, 2338 (1957).
34. M. Go and N. Saito, *J. Phys. Soc., Jpn.*, **20**, 1691 (1965).
35. S. L. Hsu, W. H. Moore, and S. Krimm, *J. Appl. Phys.*, **46**, 4185 (1975).
36. M. Tsuboi, Y. Matsui, A. Wada, T. Miyazawa, and N. Nagashima, *Biopolymers*, **1**, 297 (1963).