Elastic Moduli of Crystal Lattices of Poly(γ -benzyl glutamate) in the Direction Perpendicular to the Chain Axis

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ABSTRACT: Elastic moduli of crystal lattices of poly(γ -benzyl glutamate) films with uniplanar orientation were measured by the X-ray diffraction method in a direction perpendicular to the film surface, *i.e.*, to the α -helical axis. Three types of specimens were prepared by casting dichloroethane solution of the polymer: forms B and C of the L-polymer, and the racemic mixture. Forms B and C showed irreversible lattice deformations around room temperature after the removal of the loads, but the racemic form did not. The lattice moduli due to reversible strain were measured at 0—60°C in the range of 1.5—0.5 GPa. The values were comparable to the macroscopic specimen moduli measured by dynamic mechanical measurement. The decrease in lattice moduli around room temperature was attributed to the side-chain dispersion.

KEY WORDS Poly(γ -benzyl glutamate) / α -Helix / Elastic Modulus / X-Ray Diffraction / Irreversible Lattice Deformation / Side-Chain Dispersion /

Lattice moduli of crystalline polymers have been studied extensively by Sakurada *et al.*¹⁻⁴ using the X-ray diffraction technique. The moduli in the direction of the chain axis were markedly different (4—240 GPa), depending on the chain conformation. In the direction perpendicular to the chain axis, the magnitude of the moduli was 3—9 GPa. The relationship between the elastic modulus and the molecular structure of many polymers has been investigated theoretically and experimentally.¹⁻⁸

In the X-ray measurement of the lattice deformation by stress, it has been assumed that the stress is homogeneous within the specimen. The homogeneous stress distribution (corresponding to the series model¹⁻⁴) has been validated. For instance, various types of polyethylene samples gave the same lattice modulus despite the difference in the macroscopic modulus.³ The macroscopic modulus depends on the crystallinity and the texture and is generally much smaller than the lattice modulus, since it contains contributions from amorphous regions.

The molecules of flexible-chain polymers in the amorphous region assume a random-coil conformation. In solid stiff-chain polymers, however, the molecules even in disordered regions are packed

nearly parallel to each other, since the films are in many cases prepared through the liquid-crystalline state. Thus, we may expect that the macroscopic moduli of stiff-polymer solids are of the same order as the lattice modulus.

A typical rodlike polymer, poly(γ -benzyl L-glutamate) (PBLG), exists as the α -helix in dilute solution and in the solid state. The PBLG molecules become aggregated in poor solvents to form a gel consisting of well-developed fibrillar aggregates.⁹ The film obtained by casting PBLG solutions in poor solvents (conventionally termed form A) showed a broad X-ray pattern.^{10,11} However, the structure comprising finely-constructed aggregates is much different from those of ordinary amorphous polymers. Other modifications of PBLG (forms B, C, D, and E), obtained by casting good-solvent solutions, are highly crystalline.¹⁰⁻¹⁵ The α -helical chains lie in the film plane with the axis parallel to the surface (planar orientation). Furthermore, the equatorial lattice plane tends to be parallel to the surface (uniplanar orientation). Therefore, the lattice modulus in a direction perpendicular to the film surface may be easily determined by X-ray diffraction with the pressure applied on the surface.

The PBLG films exhibit a mechanical relaxation around room temperature owing to the side-chain motion.^{10,11,16} It has been shown¹⁷⁻²² that the side-chain structure in PBLG films is disordered, but the structure in the racemic mixture of PBLG and the D-polymer is somewhat ordered. The side-chain dispersion may be detected in reference to the temperature dependence of the lattice modulus in the direction perpendicular to the α -helical axis (film surface). In the present paper, the results from such a study for the films of forms B, C, and the racemic mixture are reported.

EXPERIMENTAL

The L- and D-polymers of benzyl glutamate were synthesized by the N-carboxyanhydride method using triethylamine as the initiator in dioxane. The samples were recovered by precipitating with methanol and drying *in vacuo*. Molecular weight were determined from the intrinsic viscosity in dichloroacetic acid using a relation given by Doty *et al.*²³ Samples of molecular weights higher than 1.5×10^5 were used in the present work.

The form-C film was prepared by casting a PBLG solution in dichloroethane onto a glass plate and evaporating the solvent for a few days. The form-B film was made by casting the solution in DMF at about 50°C.¹⁰ However, the uniplanar orientation of the form-B film thus obtained was not very high. Hence, the form-B film with a uniplanar orientation was prepared by casting the PBLG solution in dichloroethane; however, the solvent was evaporated very slowly for a week or more. The film of the racemic mixture was prepared by casting a solution in which equimolar amounts of PBLG and the D-polymer were dissolved in dichloroethane. The structures of the films will be described later.

All films obtained were 0.01–0.02 cm in thickness. They were cut into small pieces 0.1×1.0 cm in size and then stacked up to a thickness of 0.1 cm. By moderately pressing the block between glass plates at about 100°C, the stacked films adhered homogeneously to each other with no deformation. The block was cut so as to have the dimensions $0.1 \times 0.1 \times (0.2-0.4)$ cm, and then annealed at 130°C for 20 min in order to release the lattice deformation resulting from the applied pressure. This annealing condition was previously established.¹²

Figure 1. Geometry of stress application to the specimen in the X-ray beam.

The specimen was mounted on the sample holder for X-ray exposure, as shown in Figure 1. The load up to 120 kg cm^{-2} was applied by a piston to which various weights were attached. The temperature was controlled within fluctuations of $\pm 0.5^\circ\text{C}$ by blowing either hot or cold air over the whole system. X-Ray flat-plate photographs were taken with Ni-filtered $\text{CuK}\alpha$ radiation by loading with increasing weights. One exposure required 30 min; the exposure was made in an interval of 30 min between 10 and 40 min after loading or unloading. The 10-min waiting time was considered sufficient to make strain measurements of form B and the racemic form free from creep effects, since, in most cases, the X-ray reflections remained sharp. The reflections of form C tended to become broad with loading. It is not clear whether it was due to the creep effect or to the static disorder.

The lattice deformation was determined from the change in the spacings of the reflections. The three following kinds of strains are defined as:

$$\varepsilon_1 = (d - d_0)/d_0$$

$$\varepsilon_0 = (d'_0 - d_0)/d_0$$

and

$$\varepsilon_2 = \varepsilon_1 - \varepsilon_0$$

where d_0 is the spacing for the sample annealed at 130°C prior to a series of exposures, d and d'_0 are the spacings under loading and unloading, respectively. The stress for the specimen, σ' , was calculated from the weight divided by the cross-sectional area. The correction factor f defined by $\sigma = f\sigma'$ might be necessary to calculate the effective stress σ on the lattice, but it was not considered in this work, since $f \approx 1$ as will be mentioned later. The elastic modulus E_t due to the reversible strain ε_2 was calculated by $\sigma \approx \sigma' = E_t \varepsilon_2$. The stress within the specimen was assumed to be homogeneous, since the specimens with different cross-sectional areas gave identical

data.

RESULTS AND DISCUSSION

X-Ray patterns of the original specimens are shown in Figure 2. The two-dimensional molecular arrangements corresponding to these patterns are schematically illustrated in Figure 3. The primitive unit cell containing one chain is pseudo-hexagonal in forms B and C, but is perfectly hexagonal in the racemic form. In this paper, the rectangular two-chain unit cells have been taken for convenience.

In form B, the up- and down-pointing helices are arranged alternately; the face-centered chain in Figure 3a has an opposite chain direction against the chains located at corners.^{10,12} This is the reason why the formation of form B makes necessary very slow evaporation of the solvent. The alternate siting is not considered very good in form C, obtained by quick evaporation of the solvent, since the primitive unit cell is close to the hexagonal.

Reflections with indices 020 and 220 (Figure 2a) were used for the strain measurements of form B and the racemic form. The experimental error for the diffraction angle (θ) was $\pm 0.015^\circ$, corresponding to $\pm 0.01 \text{ \AA}$ for $d(220) = 6.04 \text{ \AA}$, *i.e.*, the error of strain is $\pm 0.16\%$. Since E_t was calculated from ϵ_2 measured up to the order 1%, the error of E_t is about 15%. The 020 reflection was used in form C to give a rather broad pattern, where the error of E_t might possibly exceed $\pm 20\%$.

The correction for the stress was neglected here. The reason is as follows. Deformation of a crystallite with the b axis parallel to the stress is described by ϵ_b (in the b -axis direction) and $\epsilon_a = -\nu\epsilon_b$ (in the a -axis direction). If the crystallite is incompressible, the ratio $\nu = -\epsilon_a/\epsilon_b$ may be close to unity since the strain in the c -axis direction is small in comparison with ϵ_a and ϵ_b . The lattice strain of the crystallite in the $[hk0]$ direction (making an angle α to the direction of the stress) is given by $\epsilon_{hk0} = (\cos^2 \alpha - \nu \sin^2 \alpha)\epsilon_b$. Thus, the correction factor f to

Figure 2. X-Ray diffraction patterns of (a) form B and (b) form C of PBLG, and (c) the racemic mixture. The film surface is parallel to the X-ray beam and lies in a horizontal plane.

Figure 3. Two-dimensional molecular arrangements in (a) form B, (b) form C, and (c) the racemic mixture, corresponding to the patterns given in Figure 2.

Figure 4. (a) Stress-strain curve observed from the 220 spacing of form B at 22°C. (b) Temperature dependence of the irreversible strain at a stress of 50 kg cm^{-2} for forms B and C.

determine $E_t = \sigma/\epsilon_b$ from ϵ_{hko} is $\cos^2 \alpha - \nu \sin^2 \alpha$. The ϵ_b is obtained from spacings of the 020 reflection. In the present geometry of the stress application (Figure 1), only the crystallites with 020 planes inclined by $\theta = 6.7^\circ$ to the X-ray beam contribute to the 020 reflection. The crystallites involve, for instance, the crystallites which have the a axis tilted by θ to the beam and the c axis parallel to the film surface. Since the α -helix is like a uniform cylinder and the lattices are (closely) hexagonal, the modulus E_t may be almost uniform about the c axis. Hence, the correction factor f may be assumed to be $\cos^2 \theta - \nu \sin^2 \theta$. The crystallites which have the c axis tilted by θ to the beam contribute also to the 020 reflection, where f is approximated by $\cos \theta$. Thus, $f = 0.97$ – 0.99 for the 020 reflection. On the other hand, the 220 and 330 reflections have the intensity maxima off the vertical central line in X-ray photographs (Figure 2). However, the uniplanar orientation is rather incomplete, so that the reflections appear as arcs even on the vertical line on which the positions of reflections were measured. For crystallites contributing to these positions, the same correction factor as mentioned above for the 020 reflection may be applied; $f = 0.97$ – 0.99 for the 220 and $f = 0.93$ – 0.98 for the 330 reflection. Since the difference of these corrections from unity is comparable with the error of our experiment, the modulus E_t was calculated by assuming $f = 1$.

Figure 4a shows a typical stress-strain curve measured from the 220 reflection of form B at 22°C. The strains ϵ_1 and ϵ_0 are nonlinear, but the reversible strain ϵ_2 is linear, to the stress. The same ϵ_2 values within the experimental error were obtained from the 020 and 220 reflections in form B and the racemic form. The 330 reflection of form B was

Figure 5. Plots of the elastic moduli of forms B, C, and the racemic mixture. Curves show the macroscopic specimen moduli measured at 110 Hz.

measured for a check and found to give a comparable value for ϵ_2 . The values of the elastic modulus $E_t = \sigma'/\epsilon_2$ are plotted in Figure 5.

Lattice modulus has usually been compared with the initial modulus of the specimen. For comparison, the real parts of complex Young's moduli of film specimens may be used. The real parts (shown by the curves in Figure 5) were reproduced from Figure 6, in which the dynamic behavior measured at 110 Hz is shown. Although the stress for the Young's modulus is in the direction of the film surface, the mechanical property in the direc-

Figure 6. Real parts of the complex Young's moduli and the loss tangent of PBG films measured at 110 Hz.

tion perpendicular to the chain axis may be generally reflected. In the time scale of the present X-ray measurement (corresponding to frequencies of the order 10^{-3} Hz), the curves of macroscopic specimen moduli must be shifted by *ca.* 20° to the low-temperature direction.¹⁶ However, the feature should be essentially the same. As shown in Figure 6, there are large mechanical relaxations at $30\text{--}50^\circ\text{C}$ ($10\text{--}30^\circ\text{C}$ at 10^{-3} Hz) like a glass transition, which have been proved to be due to the side-chain motion.^{10,11,16} Figure 5 shows that the lattice moduli display the same feature, and are almost the same magnitude as the macroscopic moduli. Therefore, the macroscopic mechanical properties reflect lattice behavior. Since the side-chain region is considered to behave as an amorphous region, it is not necessary to define in particular the amorphous regions in the present films.

Form B is more crystalline than form C (Figure 2), but the elastic moduli of the two forms are of the same magnitude. The difference between B and C is clearly seen in the irreversible strain, as shown in Figure 4b at $\sigma' = 50 \text{ kg cm}^{-2}$. If the side-chain region is ordered, the lattice deformation may be reversible. Actually, it was elastic ($\epsilon_0 = 0$) in the racemic form. The side-chain structure may be more regular in form B rather than in form C, which may be responsible for the difference in the ϵ_0 .

The irreversible strain has the maximum just around the dispersion temperature (Figure 4b). This fact is interpreted as follows. In the temperature range lower than 0°C , the side-chain region is as rigid as the helix core and should be elastic. At higher temperature, it will exhibit rubberlike elasticity owing to the thermal motion of the long side chains. Therefore, the strain may be also elastic. At intermediate temperatures, the side-chain region will behave as a very viscous plastic fluid, in which the entropy elasticity may be ineffective or too weak to overcome the viscosity.

The strain ϵ_a in the direction perpendicular to the stress was determined from the 200, 400, and 600 reflections. The ratio $\nu = -\epsilon_a/\epsilon_b$ was 0.6–0.7 in form B and the racemic mixture, and 0.7–0.8 in form C. If the side-chain region behaves as a fluid, ν is expected to be close to unity. In the case of poly(alkyl glutamate) films with long side chains (alkyl = amyl and hexyl), the ν value over 0.9 has been determined.²⁴ It is reasonable for the poorly-ordered form C to have a larger value for ν than that of either form B or the racemic form.

The present results explain why the reported unit-cell dimensions of forms B and C are slightly different. First, the order of the alternate sitting of the up- and down-pointing chains may be different for samples depending on the casting condition.¹² Second, forms B and C have irreversible lattice deformation resulting from stress; the lattices may be somewhat deformed in the process of preparation. Therefore, specimen specification is very important for polymers with long side chains.

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