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Light Scattering Studies of Poly(γ-benzyl L-glutamate) Solutions and Films

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Summary

Concentrated solutions (>20 wt%) of poly(γ-benzyl L-glutamate) (PBLG) were investigated using small angle light scattering (SALS). The gels and cholesteric liquid crystals formed in PBLG concentrated solutions, were analyzed in terms of theories previously developed for SALS from crystalline polymers. It was found that there are two types of the fibrillar aggregation of α-helices in gels and furthermore, two types of the orientation correlation of α-helices in cholesteric liquid crystals.

Introduction

The thermoreversible gels of PBLG are commonly observed in solutions of poor solvents such as N,N-dimethylformamide (DMF). Under the microscope, the cholesteric liquid crystal phase and the opaque rigid gel phase coexist at concentrations higher than 20 wt%. Such an opaque phase disappears at the temperature, at which an endothermic peak is observed in DSC thermograms, while the liquid crystal phase is not affected. In solutions of good solvents such as chloroform, on the other hand, only the cholesteric liquid crystal phase is observed.

In this paper, the SALS from PBLG solutions was examined in order to clarify the type of the fibrillar aggregation of α-helices in gels and the orientation correlation of α-helices in cholesteric liquid crystals.

Experimental

The solutions of PBLG (Mv = 150,000) were prepared from two types of α-helical solvents; good solvents such as ethylene dichloride (EDC) and chloroform, and

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poor ones such as DMF, benzyl alcohol (BA), and benzyl propionate (BP). The concentrated solutions (>20 wt%) in both types of solvents form uniform cholesteric liquid crystals. Those in poor solvents, however, form rigid gels at the temperature below ca. 60°C. The melting point of such rigid gels was determined by DSC measurements.

Light scattering measurements were made using He-Ne gas laser with the wavelength, $\lambda = 6328$ A. The samples with thickness in the range of 10μ — 80μ, were prepared by placing a drop of solution between the microscopic cover glasses, which were sealed by cementing in order to avoid the evapolation of solvent. The incident light was irradiated perpendicular to the samples, and scattered light was projected onto the screen. Photographs were taken with both parallel (Vv) and crossed (Hv) polars.

Results and Discussion

SALS from PBLG Gels

Figure 1 shows the Hv and Vv patterns of PBLG gel obtained in BA solution (45 wt%). The observed patterns are azimuthal-dependent, indicating that the scattering arises from anisotropic particles. Two different SALS patterns were observed for gels prepared by the different cooling rates from the melt. When a gel was prepared by rapid-cooling process (20 — 40°C/min), the clear + -type Hv pattern and X-type Vv pattern were observed, while the diffuse X-type Hv pattern and the Vv pattern with a shape elongated in the vertical direction, were observed for the slowly-cooled gel (a cooling rate: 0.1°C/min).

Light scattering measurements offer a convenient way to follow the process of structural changes with temperature. Alteration of Hv patterns during the slow heating of samples is shown in Figure 2. The +-type Hv pattern for the rapidly-cooled gel disappeared and the X-type Hv pattern appeared around the melting point of gel (about 60°C). At the same temperature, the diffuse X-type Hv pattern for the slowly-cooled gel changed also drastically to the X-type Hv pattern, which is observed in the smaller scattering region in comparison to patterns from gels and may be associated with the orientation of α-helices in liquid crystals as mentioned below. When the samples were cooled, both +-type and X-type Hv patterns reappeared depending on the cooling rate. Thus, it is clear that the anisotropic rods or bundles with a size comparable to the wavelength are formed on gelation.

According to RHODES and STEIN (1969), the intensity of SALS for a random assembly of anisotropic rods should

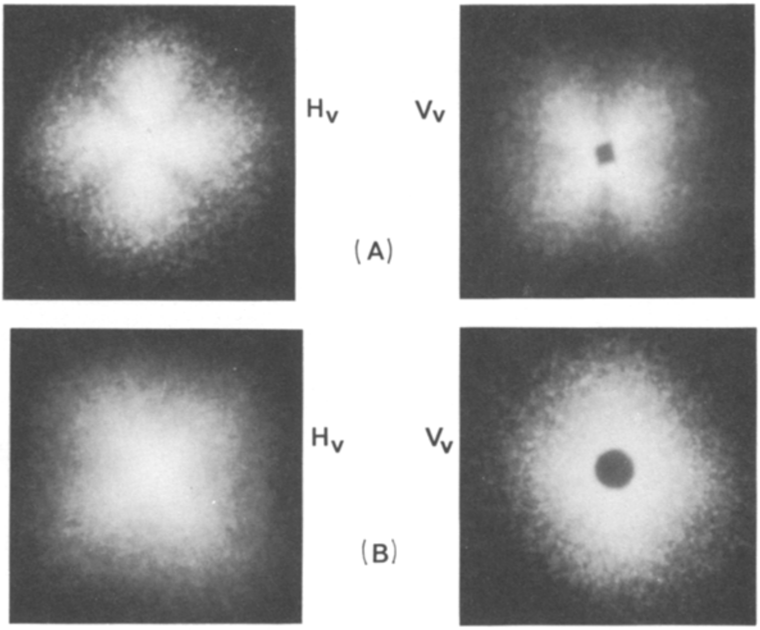

Figure 1. Hv and Vv patterns of (A) the rapidly-cooled gel and (B) the slowly-cooled gel obtained in BA solutions (45 wt%).

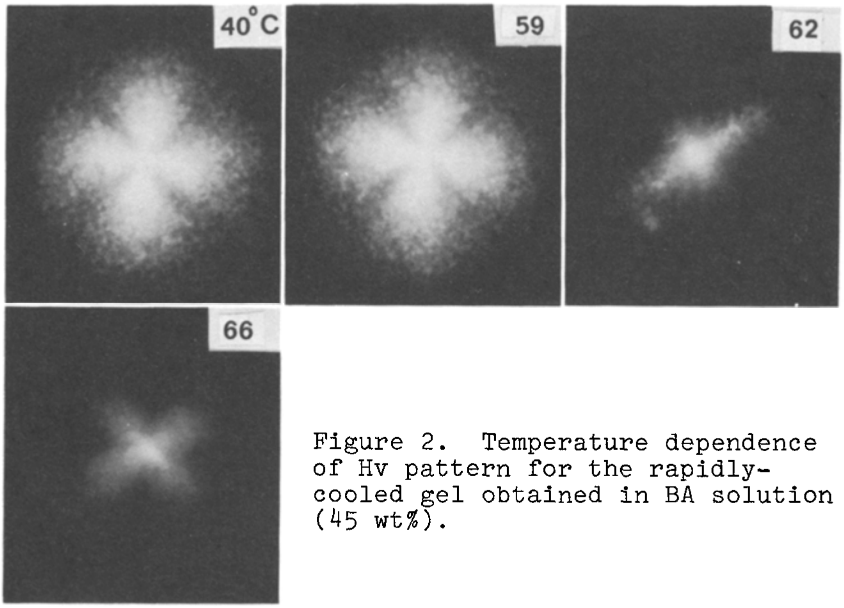

Figure 2. Temperature dependence of Hv pattern for the rapidly-cooled gel obtained in BA solution (45 wt%).

decrease monotonically with scattering angle. The azimuthal dependence of pattern is determined by the angle ω which is the direction of principal optic axes for rods as measured from the long axis of the rod. In the polypeptide, the principal optic axis corresponds to the chain axis. For ω = 45°, the Hv pattern should be of the + -type with intensity maxima at 0°, 90°, 180°, and 270° with respect to the polarizer direction. The Vv pattern, on the other hand, should be of the X-type. The Hv and Vv patterns of the rapidly-cooled gel satisfy these characteristics (Figure 1 (A)). Therefore, this gel consists of superstructure which scatters light as thin fibrils or fibers with 45° principal optic axes.

For the slowly-cooled gel which showed the X -type Hv pattern, an absolute determination of the type of rods is difficult by light scattering method alone. The speculation is made for two types of scattering elements; (1) rods with optic axes parallel or perpendicular to rod axes and (2) rods with optic axes arranged cylindrically symmetric with respect to rod axes (RHODES, STEIN 1969; HAYASHI, KAWAI 1972; MURAKAMI et al. 1973). Superhelices precipitated from DMF — propionic acid solution of PBLG are classified into the second type of rod (ISHIKAWA, KURITA 1964). From Figure 1 (B), the Vv pattern is found to be elongated in the vertical direction, but there is also a weak but well-defined intensity in the horizontal one. According to MURAKAMI et al. (1973), such a Vv pattern should be characteristic of the second type with polar angle ω = 70° — 90° with respect to rod axes. This view is supported by the fact that the similar scattering patterns were observed in the pressed films of superhelices prepared from DMF — propionic acid solution and DMF solution of PBLG (see Figures 3 and 4).

SALS from PBLG Cholesteric Liquid Crystals

When thick samples were used for this experiment, clear scattering patterns were not obtained probably because of the effect of optical rotation (PICOT, STEIN 1970) and some departure from two dimensional arrangement of scattering elements (MORITANI et al. 1971). A better scattering pattern can be obtained for the thin samples (about 10μ — 20μ) in which uniform twisted structure of cholesteric liquid crystals might be collapsed. Figure 5 shows the SALS from a cholesteric liquid crystal phase. Two distinctly different cross Hv patterns were obtained; one is observed for the solutions in a poor solvent system and has the X-type Hv pattern, while the other is the +-type Hv pattern in a good solvent system and is somewhat diffuse. Thus, the cholesteric liquid crystals

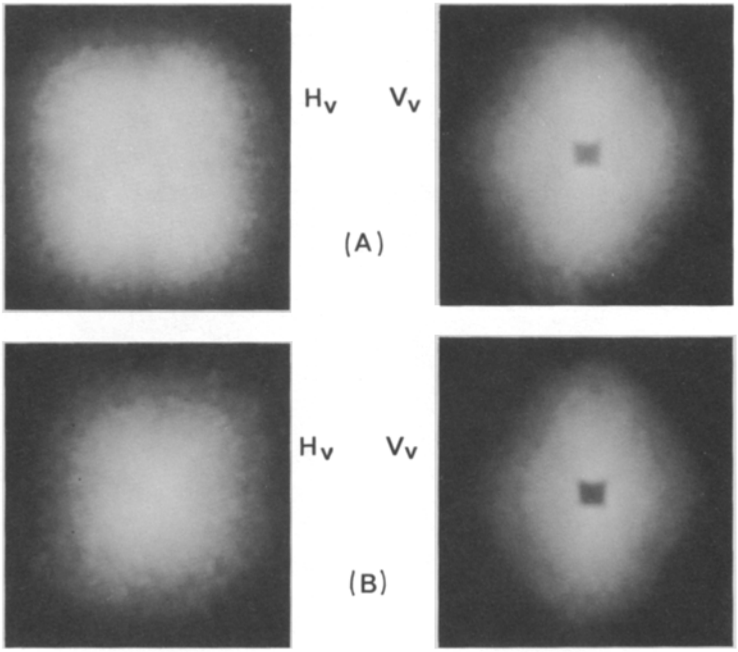

Figure 3. Hv and Vv patterns of pressed PBLG films of the precipitates from (A) DMF solution and (B) DMF — propionic acid solution.

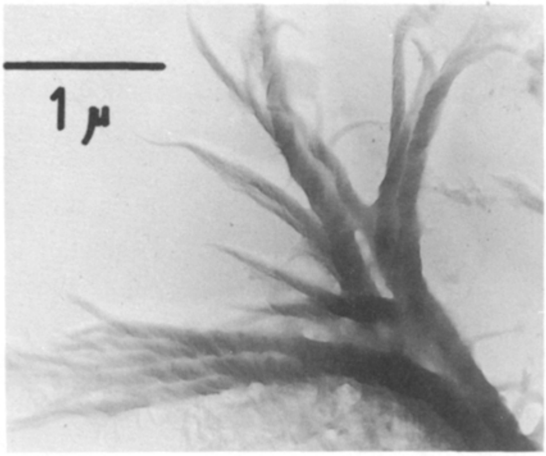

Figure 4. Electron micrograph of PBLG superhelices precipitated from DMF — propionic acid solution.

for PBLG solutions have two types of orientation correlation of the helical molecules and such an orientation correlation should exist in a domain with a statistically defined size so that scattering elements may be randomly oriented with respect to each other. In a poor solvent system, the preferred orientation direction was parallel or perpendicular to the optic axes and hence α-helical chain axes, while, in a good solvent, the orientation direction was at about 45° to the α-helical chain axes.

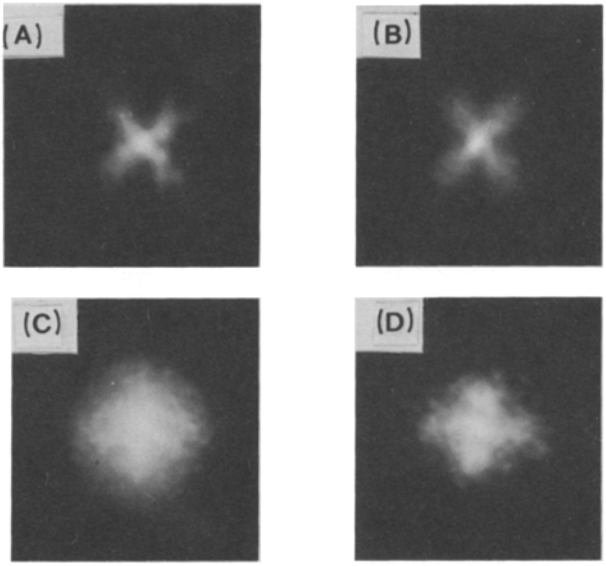

Figure 5. Hv patterns of cholesteric liquid crystals in (A) BP solution (at 70°C), (B) DMF solution (at 70°C), (C) chloroform solution (at 25°C), and (D) EDC solution (at 25°C).

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