

Molecular Aggregation and Gelation in Poly(γ -benzyl L-glutamate) Solutions

Shintaro SASAKI, Mikio HIKATA, Chihiro SHIRAKI,
and Ichitaro UEMATSU

*Department of Polymer Technology, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan.*

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ABSTRACT: Poly(γ -benzyl L-glutamate) forms a thermoreversible gel in benzyl alcohol. The network comprises fairly crystalline fibrillar aggregates. There are two types of complex structures depending on the gelation temperature, in which the interchain distances are independent of concentration and the volume fraction of polymer is roughly 0.77. The two complexes have different melting points in the range of 60—70°C, which are almost constant over a wide range of concentration. The gel rigidity depends on polymer concentration and molecular weight in the following way. There is a critical concentration, C_0 , around 0.5 wt%. For $C > C_0$, the shear modulus is proportional to $C^{1.3}$ and independent of molecular weight. For $C < C_0$, the modulus is proportional to $C^{2.6}$ and the square of molecular weight. The concentration dependence is discussed with the tendency of side-by-side aggregation.

KEY WORDS Poly(γ -benzyl L-glutamate) / Aggregation / Gelation / X-ray
Diffraction / Liquid Crystal / Complex Structure / Gel Elasticity /

Molecular aggregation of poly(γ -benzyl L-glutamate) (PBLG) in helicogenic solvents has been studied by various methods.¹⁻¹¹ The aggregation may be classified into the short-range association and the large-scale fibrillar one.

A PBLG molecule of molecular weight of 10^5 exists as an α -helical rod with a contour length of 68.5 nm. A solution of this polymer is in the semi-dilute system above a concentration of about 0.005 g/cm³. Since the side-chain groups of PBLG have a tendency to associate with each other, it is plausible that the aggregation can exist even in a fairly dilute solution. Actually, in rather good solvents such as chloroform, ethylene dichloride, and dioxane, the association was detected at extreme dilution over a wide temperature range.¹⁻⁷ The linear head-to-tail, (antiparallel) side-by-side aggregation, and their combinations are the essential features of short-range association. The side-by-side aggregation may be comprised of stacked benzene rings.

On the other hand, solutions in poor solvents such as benzene, benzyl alcohol (BA), or mixed solvents of dioxane with fatty acids, are known to

form thermoreversible gels, in which large-scale fibrillar aggregates are formed. Superhelical ropes formed by aging solutions in dimethylformamide (DMF) or dioxane with propionic acid have a striking appearance.⁸⁻¹¹ It has been suspected that these macrofibrillar aggregates might be comprised of fundamental microfibrils of *ca.* 5 nm in diameter.⁸⁻¹⁰ Rybnikar and Geil reported that there was no pronounced tendency to form fundamental fibrils.¹¹ However, such a fundamental unit may possibly be formed under certain conditions.

The morphology of the fibrillar aggregates is considered to differ greatly from the classical network structure assumed in developing the theory of rubberlike elasticity. The elasticity of gels composed of stiff-chain fibrils might be energetic unlike flexible-chain gels.

The PBLG-DMF solution has been extensively studied from various aspects. The α -helices in DMF are assumed to be molecularly dispersed in the dilute solution, but to aggregate at higher concentrations.¹⁻⁵ Thermoreversible gels are obtained by dissolving the polymer in DMF at a

temperature above 50°C, and then cooling to room temperature. The temperature of gel-sol transition is 15–40°C, depending on the concentration. For this gel, the so-called complex phase has been observed by X-ray diffraction.^{12–14} Sharp X-ray reflections appear in a concentration range from 20 to 60 wt%, the spacing being constant and independent of the total concentration. Therefore, the aggregate has a crystalline character. The apparent shape of the unit cell in the two-dimensional projection is hexagonal with a side $a=3.5$ nm. An analysis of the complex structure has been attempted on models in which three polymer chains passed through a unit cell.^{12–14} However, it was found recently that four chains pass through the cell, as will be mentioned below. The fact that four chains form a structural unit suggests the possibility of a fundamental microfibril.

Another complication in the PBLG–DMF system is the formation of cholesteric liquid crystals.^{15,16} The phase separation of solutions composed of rodlike molecules has been theoretically treated by Onsager,¹⁷ Ishihara,¹⁸ and Flory.¹⁹ There are still some controversial points on this subject.^{20,21} Miller *et al.*^{22–24} have offered a phase diagram for the PBLG–DMF system, which is consistent with the theoretical prediction. The typical fingerprint pattern was observed for solutions with concentrations exceeding *ca.* 15 wt%. Above the gel-sol transition temperature, the whole solution was occupied by the cholesteric phase. On gelation below that temperature, the cholesteric phase separated into the isotropic solvent-rich phase and the anisotropic polymer-rich (complex) phase, although it was not clear whether the complex was a thermodynamic phase or not. Miller *et al.*²⁴ proposed the spinodal decomposition mechanism^{25,26} for the kinetics of gelation. The fingerprint pattern, however, could still be seen in the gel.²⁷ It may be that the pattern suggest the existence of the cholesteric phase. The complex structure (detected by X-ray diffraction) and the fingerprint pattern (observed under microscope) may have been misunderstood as belonging to a different phase.

The situation for the PBLG–DMF system is essentially the same as the PBLG–benzyl alcohol (BA) system.¹⁴ Benzyl alcohol is not so hygroscopic as DMF, and has PBLG form gels consisting of well-developed fibrillar aggregates. The reproducibility of thermal and structural data is excellent. In

the present paper, the structure and properties of the PBLG–BA system is discussed on the basis of experimental results obtained by various techniques.

EXPERIMENTAL

Samples

About ten samples of PBLG, differing in molecular weight over the range from 4×10^4 to 6×10^5 , 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 weights were determined from intrinsic viscosities in dichloroacetic acid using the relation given by Doty *et al.*¹

Solutions with polymer concentrations less than 20 wt% were prepared by dissolving the polymer in BA with mechanical stirring at a temperature above 70°C. This direct method was limited to a concentration of about 30 wt%. More concentrated solutions were prepared by the extremely slow evaporation of solvent in a thermostat maintained at 70°C. It took a few weeks to complete this treatment. Evaporation at a faster rate gave no homogeneous solutions. Another preparation method was used for concentrated solutions. A solution of *ca.* 20 wt% was placed in a flat-bottom glass vessel and gelled to a thickness less than 5 mm. Then, a 1:1 mixture of BA and methanol was poured on top of this. After a certain period of time during which the gel shrank to some extent, the solvent layer was poured out and the gel was aged at 90°C, causing the gel to melt and the remaining methanol to be forced out. By repeating several cycles of this procedure, concentrated homogeneous solutions were obtained. Solutions prepared by these two methods gave identical data.

Melting Temperature

Melting points of PBLG–BA gels were determined by the falling-ball technique using a steel ball 2 mm in diameter. Transition temperatures and heats of transition were measured by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC Model II at a scanning rate of $10^\circ\text{C min}^{-1}$. Melting points were also detected as temperatures at which the shear modulus decreased sharply to zero.

X-ray Measurements and Electron Microscopy

X-ray measurements were carried out with Ni-filtered or graphite-monochromatized $\text{CuK}\alpha$ radiation using a flat-plate camera equipped with a temperature control unit. Specimens were prepared by sealing the solution in glass-capillary tubes of *ca.* 1 mm in diameter. Reflection spacings were calibrated against the (111) reflection of silicon which was sprinkled over the wall of capillary tubes or directly dispersed in the solutions.

Specimens for transmission electron microscopy (TEM) were prepared by depositing a droplet of 0.05 wt% solution on carbon-coated grids, and blotting most of solvent with filter paper, drying quickly *in vacuo*, and shadowing with *Pt-Pd* at an angle of 30° .

Rigidity Measurements

Shear moduli of gels with concentrations from 0.1 to 8 wt% were measured using a free-oscillating torsion pendulum with concentric cylinders. The system was heated to 70°C , and then the solution was poured into the cell. As the system was cooled to room temperature, gelation occurred at $25\text{--}30^\circ\text{C}$. The network formation still continued even after gelation, since the modulus approached a limiting value during 10–20 h. The gels were then aged for 10–20 h at room temperature prior to measurement. Measurement of temperature dependence was made by heating the system step-by-step. The oscillation periods of the torsion pendulum ranged from 0.13 to 4 s. The torsional amplitude was restricted to within 0.1° , since the larger distortion destroyed the network and was followed by a gradual recovery of the modulus.

RESULTS AND DISCUSSION

Melting Temperature

Melting behaviour of PBLG–BA gels was complex depending on the polymer concentration and the conditions for gelation. Sometimes three or four peaks appeared in the thermogram. These were due to formation of various types of aggregation, since the behaviour became simple as the conditions for gelation became better defined.

Typical thermograms of PBLG (150000) gels are shown in Figure 1 (molecular weight: 1.5×10^5). The gels were prepared by cooling sols from 80°C to some temperatures. Slow cooling in this work was

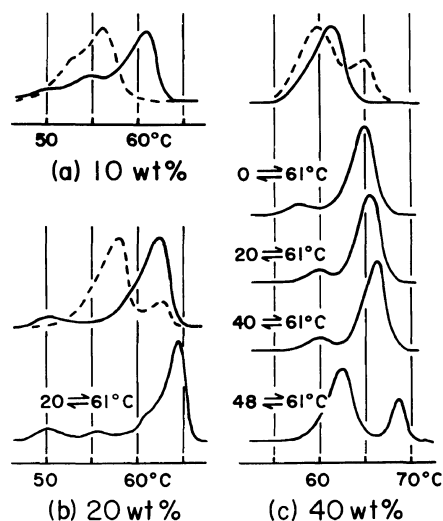


Figure 1. DSC thermograms of PBLG–BA gels with concentrations of (a) 10, (b) 20, and (c) 40 wt%. Peaks are all endothermic. Solid-line and broken-line curves are for gels formed by gelation above 50°C , and by quenching to 0°C , respectively. $T \rightleftharpoons 61^\circ\text{C}$ shows that the gel was prepared by repeating cycles of heating to 61°C and quenching to $T^\circ\text{C}$.

achieved by keeping the sol in a glass test tube in a Dewar bottle containing hot water and allowing it to gel above 50°C . Gels with concentrations less than 15 wt% showed similar behaviour as indicated in Figure 1a. The gel prepared by slow cooling exhibited a main peak around 61°C , which corresponded to the melting point measured by the falling-ball method. Sometimes a peak was observed around 51°C , but disappeared when the sol was allowed to gel at 50°C and maintained at this temperature for a few days. The gel prepared by quenching the sol at 0°C showed a peak around 56°C . The gel prepared at a higher temperature had a higher melting point and this is reasonable.

As shown in Figure 1b, the 20 wt% gel prepared by slow cooling showed a melting peak at 62.5°C . The quenching gel exhibited a peak at 58°C , and also another small peak at 63°C . The 63°C peak did not grow by aging the gel at $60\text{--}62^\circ\text{C}$, but by quenching. By repeating several cycles of quenching to 0°C and heating to 61°C , a gel was obtained showing a peak at 64°C , which was higher than that of the slowly-cooled gel.

Isothermal experiments were carried out for the

40 wt% gel (Figure 1c). When the gelation temperature was higher than 50°C, the gel melted at 62.5°C, while the gel quenched to 0°C showed peaks at 60 and 65°C. The 65°C peak suggests that another type of structure is formed in the quenched gel. Thermograms of gels prepared by the heating-quenching cycles between 61°C and T °C ($T=0, 20, 40, \text{ and } 48^\circ\text{C}$) are also shown in Figure 1c. The peak temperature increased with increasing T , and $T=48^\circ\text{C}$ is the limiting temperature for the appearance of the higher-temperature peak. The 62.5°C peak of the gel prepared by the $48 \rightleftharpoons 61^\circ\text{C}$ cycles corresponds to that of the slowly-cooled gel, and still appears even after repeating ten cycles between 48 and 65°C.

As will be mentioned below, the aggregate has a complex type structure, in which the interchain distance is independent of the total concentration of the solution and the volume fraction of polymer is *ca.* 0.77. The gel prepared above 50°C and the gel prepared by heating-quenching cycles (gelled below 48°C) have different complex structures. The former is called complex A and the latter, B.

Transition temperatures at peaks in the thermograms are plotted against concentration in Figure 2. X-ray diffraction patterns of gels with concentrations less than 20 wt% were smeared out by the scattering from the solvent. However, the continuity of the melting point curve of complex A (open circles in Figure 2) suggests that the complex A structure is formed even in dilute gels.

The gel with a concentration higher than 60 wt% showed a broad transition. Peak positions were 75°C for 70 wt% gel, 90°C for 80 wt%, 120°C for 95 wt%, and 130°C for solid film. The solid film has the structure of form A.^{28,29} The transition was irreversible above 90 wt%.

Melting phenomena of PBLG-BA gels are classified into three categories depending on the polymer concentration. The melting of dilute gels ($C < 18 \text{ wt}\%$) is a transition to the isotropic solution. As will be mentioned later, the transition of concentrated gels ($20 < C < 60\text{--}80 \text{ wt}\%$) is the mixing of the complex and the solvent-rich phase into the liquid crystal. The complex involves the stacking of side chain benzene rings.¹³ The transition of more concentrated gels ($C > 80 \text{ wt}\%$) is accompanied by the collapse of this stacking structure.²⁹

The dependence of melting points on molecular weight is remarkable below 10^5 in molecular weight,

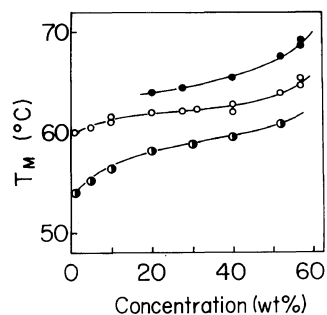


Figure 2. Concentration dependence of melting points in terms of temperatures for main peaks in thermograms for PBLG (150000)-BA gels prepared by slow cooling (○), quenching to 0°C (●), and heating-quenching cycles between 20 and 61°C (●).

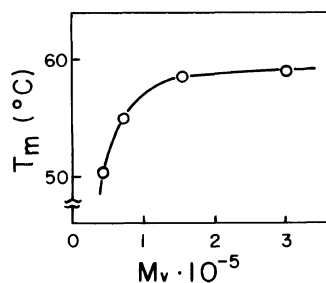


Figure 3. Molecular-weight dependence of physical melting points measured by the falling-ball method for PBLG-BA gels with $C=3 \text{ wt}\%$.

as shown in Figure 3. The data given in Figure 1 and 2 were obtained for a polymer with a molecular weight of 1.5×10^5 , which is high enough to be free from any appreciable molecular weight dependence.

The heats of transition obtained by DSC measurements were 4–5 cal g^{-1} of polymer for all concentrations, and slightly larger for slowly-cooled gels. The heats were essentially independent of molecular weight. Therefore, their origin is attributed to side-by-side aggregation, not end-to-end aggregation.

The complex B may have something to do with the liquid-crystal structure, since it appeared only at concentrations higher than 20 wt%. Judging from the X-ray patterns (Figure 6), the complex B is less crystalline than A, but has a higher melting point. During the quenching process, a structure similar to that in the liquid crystal may possibly be maintained in the complex B. Accordingly, the transition en-

trophy is expected to be smaller for B, and it may be one reason for the higher melting point.

Cholesteric Liquid Crystal

For PBLG (150000), the sol at 70°C with a concentration less than 18 wt% (A point) was isotropic, while the sol with a concentration higher than 22 wt% (B point) was totally occupied by the cholesteric phase.

The fingerprint pattern characteristic of the cholesteric structure was observed in the sol and even in the gel state. The spacing, S , between retardation lines corresponds to the half-pitch of the twisted structure. Values of $100/S$ for a 23 wt% solution are plotted against temperature in Figure 4. As was previously reported, the cholesteric sense is right-handed below 95°C, and left-handed above 100°C.³⁰ The formation of the cholesteric phase in equilibrium at another temperature usually took at least several hours. When the solution was cooled at a moderate rate from a temperature above the melting point, the pitch at that temperature was maintained in the gel. During the heating process, the different values of pitch converge to a value just above the melting point (Figure 4). This feature suggests that the macroscopically-twisted arrangement of molecules in the cholesteric phase was frozen by the local side-by-side molecular aggregation on gelation.

X-ray diffraction showed that the interchain distance above the melting point depends on the concentration according to Robinson's equation,¹⁵ assuming a uniform hexagonal molecular arrange-

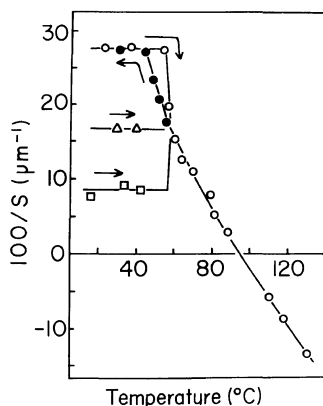


Figure 4. Plot of reciprocal half-pitch vs. temperature for a PBLG-BA solution with $C=23$ wt%.

ment. The structure may be described as a molecularly-homogeneous liquid crystal. On the other hand, the gel which continues to show the fingerprint pattern contains the complex structure with the 0.77 volume fraction of polymer. The heat of transition from the gel to the liquid crystal (4–5 cal g⁻¹ of polymer) is the same as those of the transition of dilute gels to the isotropic solution. It is unreasonable to conclude that the complex and the fingerprint pattern belong to different phases. In other words, on the scale of light wavelength the twisted molecular arrangement is maintained in the gel, but on the molecular scale the gel consists of a complex and solvent-rich phase. Thus, the structure in concentrated gels is a heterogeneous liquid crystal cross-linked by side-by-side molecular aggregations.

Morphology of Aggregates

Specimens for TEM observation were prepared from 0.05 wt% gel. Morphological changes during the preparation process were not appreciable since the characteristics appearing in TEM pictures were reproducible. Figure 5 shows TEM photographs of aggregates formed in the gels prepared by slow cooling. The features of aggregates formed by quenching were very similar to those of the slowly-cooled gel, except that the slowly-cooled gel contained large well-developed bundles. When the slowly-cooled gel was sampled at 56°C (just below the melting point), only large bundles were observed (Figure 5b). Thus, the lower melting point for quenched dilute gels can be attributed to the interfacial energy of thin fibrils.

The fibrils in these photographs appeared to be aggregates of microfibrils 10 nm or less in diameter. Fibrillar aggregation was observed for all samples of various molecular weights. Large bundles, however, developed well in the high-molecular-weight sample.

X-ray Diffraction

The complex A was found in the gel prepared above 50°C, while the complex B was formed in the gel prepared by quenching to a temperature below 48°C. Here, we note that the side-chain motion in solid-state PBLG begins just around 40–50°C.^{28,29,31} Naturally, the mechanism for interactions between the side chains may be different for complexes A and B.

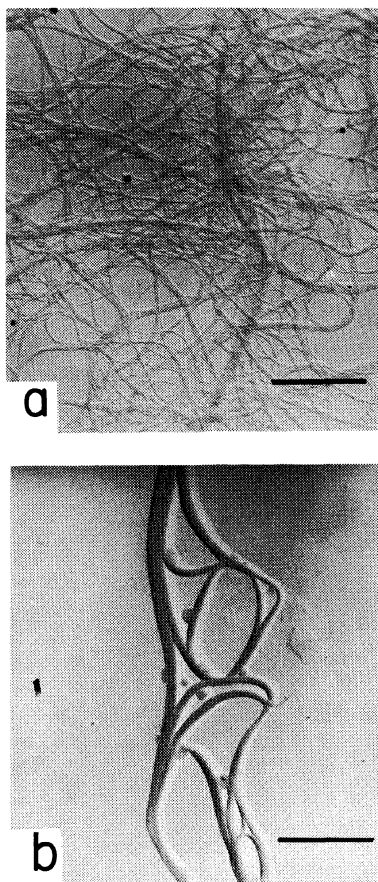


Figure 5. Electron micrographs of a PBLG (300000)-BA gel with $C=0.05$ wt% prepared by slow cooling. Sampling: (a) at room temperature, (b) at 56°C .

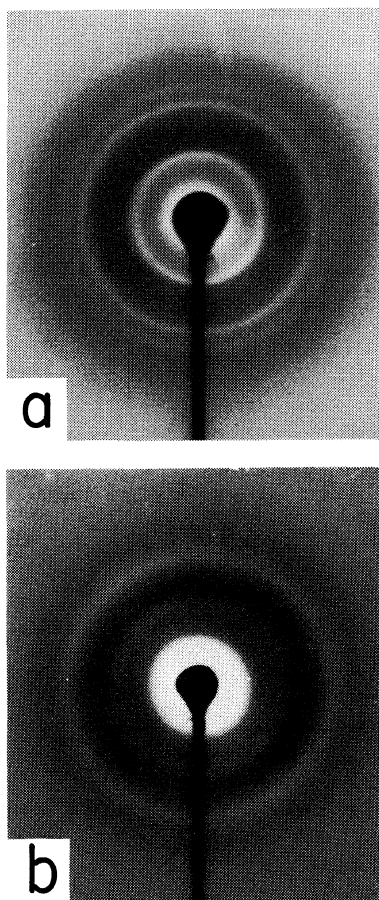


Figure 6. X-ray diffraction patterns of (a) complex A and (b) complex B formed in a PBLG-BA gel with $C=50$ wt%.

The structures of A and B were clearly distinguished by X-ray diffraction (Figure 6). Reflection spacings remained nearly constant throughout the concentration range from 20 to 57 wt% examined here. The gel prepared by quenching to 0°C showed a superposed pattern of A and B, as expected. The cholesteric phase gave a broad pattern above the melting point, in which the spacing of the intensity maximum corresponding to the interchain distance followed Robinson's equation.¹⁵

Reflection spacings of A were explained by a trigonal unit cell of side $a=3.4$ nm (Table I). The term of 'hexagonal' is avoided here, since the hexagonal symmetry can not be realized with four chains contained in this cell. The complex A was identified

from spacings and intensities to be the so-called complex structure reported for the PBLG-DMF system. Luzzati *et al.*¹² proposed a three-chain coiled-coil model, while Parry and Elliott¹³ presented a model in which three straight α -helices were arranged in the cell in such a manner that benzene rings were associated to form a quasihelical structure. The present authors also made an intensity calculation on the three-chain model.³² Recently, however, it was shown by a swelling experiment that four chains must be contained in the trigonal unit cell in the PBLG-DMF system.³³ Hence we did a swelling experiment on a film of form A type, prepared by casting the solution in DMF with *m*-cresol at 60°C .

Continuous expansion of X-ray reflection spacings was observed when the film was swollen in mixed solvents of BA and methanol. The X-ray pattern of form A turned into that of complex A in the 1:1 mixture with minor changes in the features of the pattern. Reflection spacings from the solid film are listed in the fourth column in Table I, corresponding to 0.885 times the size of those of complex A. Since the helix does not expand along the axial direction, the volume expansion from the solid to complex A is 1.276. Therefore, the volume fraction of polymer in complex A should be *ca.* 0.78. From the specific volume of the film ($0.789 \text{ cm}^3 \text{ g}^{-1}$), a PBLG molecule may be regarded as a cylinder with a cross-sectional area of 1.91 nm^2 . By assuming that four chains pass through the trigonal unit cell of $a=3.4 \text{ nm}$, the volume fraction of the polymer was found to be 0.76 (*ca.* 80 wt%), which corresponds to the arrangement of one BA molecule per two peptide units.

Table I. X-ray data of PBLG-BA complex A

<i>h k l</i>	$d_{\text{obsd.}}$	d_{calcd}^a	\sqrt{I}^b	d_{film}^c
	nm	nm		nm
1 0 0	3.0	2.94	100	2.68
1 1 0	1.70	1.70	150	1.51
2 0 0	1.48	1.47	110	1.31
2 1 0	1.11	1.11	75	0.99

^a Calculated spacings for a trigonal unit cell of $a=3.40 \text{ nm}$.

^b Square-roots of observed relative intensities.

^c Spacings of corresponding reflections from the form A film.

On the other hand, the complex B showed three reflections at spacings of 4.3, 2.2, and 1.47 nm, which are in a simple ratio of 1:1/2:1/3. Therefore, the structure has the one-dimensional periodicity with a unit distance of 4.4 nm. The volume fraction of polymer in the complex B is not clear, but may be close to that of complex A.

Structure analyses of complex A and B will be reported in the future. Regardless of what the structures may be, it is noteworthy that four chains, not one chain, form an asymmetric unit.

Gel Elasticity

Figure 7 shows the temperature dependence of the rigidity, G , of PBLG (150000) gels. The rubberlike elasticity has been confirmed for some gels from the fact that the modulus is proportional to the absolute temperature.³⁴ However, the modulus of PBLG gels decreases in a simple way with increasing temperature. Since the cross-links in this case are dissociated by an increase in temperature, such temperature dependence cannot constitute even a slight proof of energetic elasticity. Recently, Doi and Kuzuu reported a theory for the energetic elasticity of stiff-chain gels. This theory suggests that the stress-strain curve has a characteristic S-shaped form unlike that of rubber.³⁵ The strain applicable to PBLG gels is so small that the experimental verification of energetic elasticity may be difficult. Measurement of the stress-strain curve for PBLG gels is now underway.

The dependence of the modulus upon the concentration, C , has been reported for many gels, in which the modulus is roughly proportional to C^2 in a range higher than a certain concentration, C_0 , and to C^4 for $C < C_0$.^{34,36} C_0 is the concentration at which the network is completed; for $C < C_0$ there are some pendent segments which do not contribute to the elasticity.

The concentration dependence of the modulus of PBLG gels at 25°C is shown in Figure 8. The critical concentration, C_0 , is observed around 0.5 wt%. The modulus is proportional to $C^{1.3}$ for $C > C_0$, and to $C^{2.6}$ for $C < C_0$. This feature is similar to that of gels showing rubberlike elasticity. Hirai³⁴ explained the concentration dependence of such gels on the basis of the theory of rubberlike elasticity.

In the rubberlike elasticity, the modulus was assumed to be proportional to the number density, n , of effective cross-links permitting micro-Brownian motion but not macro-Brownian motion of segments. Although there is no experimental evidence at present, the elasticity of PBLG gels may be energetic, since the fibrils as observed by electron microscopy (Figure 5) are not considered to take on micro-Brownian motion and thus contribute to the elasticity. Since the energetic elasticity may come from the bending energy of segments, restriction points of some sort are needed, such as cross-links. Therefore, the modulus due to energetic elasticity may be approximated also as being proportional to the number density of the cross-links.

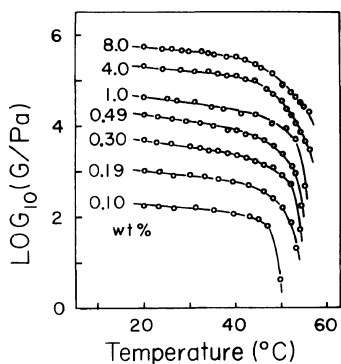


Figure 7. Temperature dependence of the shear modulus of PBLG(150000)-BA gels of various concentrations.

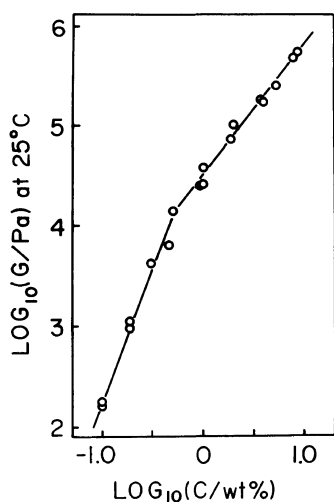


Figure 8. Concentration dependence of the shear modulus at 25°C of PBLG(150000)-BA gels.

It might be necessary for a polymer chain to contain more than three cross-links at least in order to contribute to the elasticity, since the end-to-end type of association, for instance, does not prohibit macro-Brownian motion or bending of the segment. According to Hirai,³⁴ the modulus in this case is proportional to C^2 and independent of molecular weight for $C > C_0$, while for $C < C_0$ it is proportional to C^4 and the square of molecular weight. The crossover concentration, C_0 , is inversely proportional to molecular weight in this case.

In the present case of PBLG-BA gels, the C_0 was *ca.* 0.5 wt% for a sample having a molecular weight

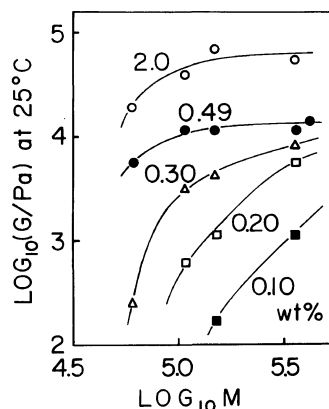


Figure 9. Molecular-weight dependence of the shear modulus at 25°C of PBLG(150000)-BA gels of various concentrations.

of 1.5×10^5 . Values for the exponents of concentration dependence are usually less than 2 and 4 by about 0.3, respectively. The reason for this is not clear.³⁴ However, these values were 1.3 and 2.6 for PBLG gels, and are significantly smaller than the normal values.

A qualitative explanation for the exponent 1.3 may be given as follows. Suppose that a network structure has been formed at a certain concentration of $C > C_0$. When a small amount of polymer is added to form new cross-links, the number of effective cross-links will increase in the following way. In the case of random crossing, $\Delta\bar{n}/\Delta C$ may be proportional to the probability of crossing, and therefore, to the concentration. This leads to the relation, $G \cong \bar{n} \cong C^2$. When the added polymer aggregates in the side-by-side manner, the number of cross-links remains unchanged. However, it may contribute to the elasticity in a way of $G \cong C$, since it reinforces the rigidity of the segment. Therefore, in the combination of these two types of cross-linking, the situation may be described by $\Delta G/\Delta C \cong C^{1-x}$; that is, $G \cong C^{2-x}$, in which x increases up to unity as the contribution of the side-by-side aggregation increases. Actually, as inferred from the fibrillar aggregation observed by electron microscopy, the side-by-side aggregation contributes considerably to the network and this may reduce the exponent to 1.3.

The dependence of the shear modulus on molecular weight is shown in Figure 9. The modulus of

gels with $C > 0.5$ wt% is almost independent of molecular weight, provided the molecular weight is higher than 10^5 . The modulus of dilute gels with $C = 0.1$ and 0.2 wt% is roughly proportional to the square of the molecular weight. This behaviour is consistent with the theoretical prediction.

Kinetics of Gelation

Miller *et al.* proposed a spinodal decomposition mechanism for the kinetics of gelation, but gave no evidence for this.²⁴ We followed the gelation process of PBLG-BA solutions by dilatometry.³⁷ In the isothermal gelation at 52°C , a change in the specific volume of gels, $\Delta\bar{v}$, corresponding to $0.0065\text{ cm}^3\text{ g}^{-1}$ of polymer, was observed. During the initial one hour on the gelation at 52°C , the process was the first-order reaction in time, t , that is, $\ln(\Delta\bar{v}_0/\Delta\bar{v}) \cong t$. According to the Avrami type of analysis,³⁸ a one-dimensional growth from instantaneous nuclei is suggested. This is plausible from the fibrillar feature of aggregation. On the other hand, the first-order reaction is also consistent with the spinodal decomposition mechanism described by the diffusion equation. An X-ray analysis on the gelation process is now in progress, and will be reported in the future.

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