Macromolecules **1990,** *23,* 3779-3784 **3779**

(6) Garton, A.; Carlsson, D. J.; Wiles, D. M. *Dev. Polym. Photochem.* **1980,** *1,* 93.
(7) Carlsson, D. J.; Wiles, D. M. *Encycl. Polym. Sci. Eng.* **1986,** *4,* 630.
(8) Holden, D. A. *Encycl. Polym. Sci. Eng.* **1988,** *11,* 126.
(9) Egerton, P. L.; Pitts, E.; Reiser, A. *Macromolecules* **1981,** *14,* 95.
(10) Fredrickson, G. H.; Frank, C. W. *Macromolecules* **1983,** *16,* 1198.
(11) Fredrickson, G. H.; Andersen, H. C.; Frank, C. W. *Macromolecules* **1984,** *17,* 54.
(12) Ediger, M. D.; Fayer, M. D. *Macromolecules* **1983,** *16,* 1839.
(13) Zimmt, M. B.; Petersen, K. A.; Fayer, M. D. *Macromolecules* **1988,** *21,* 1145.
(14) Petersen, K. A.; Zimmt, M. B.; Fayer, M. D.; Jeng, Y. H.; Frank, C. W. *Macromolecules* **1989,** *22,* 874.
(15) Förster, T. *Ann. Phys.* **1948,** *2,* 55.
(16) Förster, T. *Z. Naturforsch., Ser. A* **1949,** *4A,* 321.
(17) Loring, R. F.; Andersen, H. C.; Fayer, M. D. *J. Chem. Phys.* **1982,** *76,* 2015.
(18) Bellus, D.; Schaffner, K.; Hoigné, J. *Helv. Chim. Acta* **1968,** *51,* 1980.
(19) Bellus, D. *Adv. Photochem.* **1971,** *8,* 109.
(20) Ohto, Y.; Shizuka, H.; Sekiguchi, S.; Matsui, K. *Bull. Chem. Soc. Jpn.* **1974,** *47,* 1209.
(21) Merle-Aubry, L.; Holden, D. A.; Merle, Y.; Guillet, J. E. *Macromolecules* **1980,** *13,* 1138.
(22) Holden, D. A.; Jordan, K.; Safarzadeh-Amiri, A. *Macromolecules* **1986,** *19,* 895.
(23) Holden, D. A.; Strauss, J. *Pôlym. Eng. Sci.* **1988,** *28,* 1373.
(24) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: London, 1984.
(25) (a) Scaiano, J. C.; Johnston, L. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1989; Vol. 10, 309. (b) Chatgilialoglu, C. In *CRC Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 2, p 3.
(26) (a) Koy, K. L. *J. Paint Technol.* **1970,** *42,* 76. (b) Burrel, H. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975.
(27) Egan, L. S.; Winnik, M. A.; Croucher, M. D. *Polym. Sci. Eng.* **1986,** *26,* 15.
(28) (a) Winnik, M. A. *ACS Symp. Ser.* **1987,** *No. 358,* 8. (b) Berens, A. R.; Hopfenberg, H. B. *J. Membr. Sci.* **1982,** *20,* 183.
(29) (a) Wang, Z.; Holden, D. A.; McCourt, F. R. 25th Canadian High Polymer *Forum*, Mississauga, ON, Aug 23-25, 1989. (b) Wang, Z.; Holden, D. A.; McCourt, F. R. (GWC)^2 annual poster session, University of Waterloo, Nov 18, 1989.

Liquid-Crystalline Polymer Gels. 1. Cross-Linking of Poly(γ-benzyl L-glutamate) in the Cholesteric Liquid-Crystalline State

Ryoichi Kishi, Masahiko Sisido,* and Shigeo Tazuke†

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Received November 3, 1989; Revised Manuscript Received February 9, 1990

ABSTRACT: Cross-linking of poly(γ-benzyl L-glutamate) in the cholesteric liquid-crystalline (CLC) state was carried out by using several diamines of different chain types as the cross-linkers in three different solvents. A PBLG/triethylenetetramine/dioxane mixture was found to be the best system, which upon heating at 70 °C for about 10 days gives a polymer gel, keeping the original cholesteric order. The cholesteric order disappeared when the gel was immersed in dichloroacetic acid, but the original CLC order was reproduced by immersing the gel again in dioxane. Therefore, the CLC structure was found to be memorized in the cross-linking networks. The reversible transition was induced also by the temperature change.

Cross-linked gels of synthetic polymers are usually isotropic and show no microscopic and macroscopic order. Gels with mechanical and optical anisotropy will be new materials that may find applications in a variety of fields. One of the promising approaches to the anisotropic gel is the cross-linking of lyotropic liquid-crystalline (LLC) polymers. If one can cross-link the LLC polymers without disturbing the original LC order and if the cross-linked polymer has the typical properties of a gel, a highly anisotropic polymer gel, which may be called a "liquid-crystalline (LC) gel", will be obtained.

Poly(γ-benzyl L-glutamate) (PBLG) forms a cholesteric LC (CLC) in a concentrated solution in chloroform, methylene dichloride, dioxane, and so on.[1,2] Aviram[3] reported the cross-linking of PBLG with 1,6-diaminohexane in chloroform and obtained an anisotropic material. However, he did not report the gel property of the cross-linked PBLG. Moreover, it was found in our experiment that the reaction mixture became heterogeneous under his condition and no gelation occurred even after 20 days at 70 °C. In this paper, the cross-linking was examined by using diamines with different chain types in three different solvents. Under the optimum condition found in this study, PBLG was cross-linked smoothly and the resulting gel showed the original cholesteric order.

The immobilization of the CLC structure of PBLG has been attempted by γ-ray irradiation of a dry film of PBLG or a film of PBLG/plasticizer mixture.[4] A mixture of poly(glutamic acid) and poly(ethylene glycol) in dimethylformamide was cast to form a film possessing the CLC order.[5] In this case the CLC order has been stabilized not by covalent bonds but by hydrogen bond networks. The CLC structure of a concentrated polypeptide solution in a vinyl monomer as a solvent was fixed by polymerizing the vinyl monomer in the presence of a small amount of divinyl monomer as a cross-linker.[6,7] However, these studies are not aimed to prepare a gel with the cholesteric order.

---

† Deceased July 11, 1989.

0024-9297/90/2223-3779$02.50/0

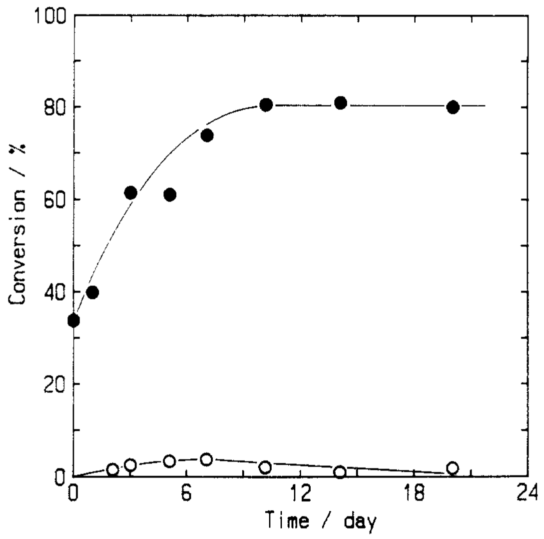

Figure 1. Amount of DAA-2 covalently attached to PBLG (●) and amount of free amino groups remaining in the gel (○), plotted against heating time at 70 °C. Molar ratio of the reaction mixture: PBLG/DAA-2/DOX = 1/0.11/8.01.

Experimental Section

PBLG (molecular weight = 1.7 × 10^5 from viscosity) was supplied from the Ajinomoto Co. (Tokyo, Japan). Dioxane (DOX) and dimethylformamide (DMF) were distilled before use. Spectrograde chloroform was used as supplied. α,ω-Diaminoalkanes $H_2N(CH_2)_nNH_2$ (DAA-*n*), α,ω-diaminooligoethylenimines, $H_2N(CH_2CH_2NH)_nCH_2CH_2NH_2$ (DAEI-*n*), and α,ω-diaminooligoethylene glycols, $H_2N(CH_2)_3O(CH_2CH_2O)_n(CH_2)_3NH_2$ (DAEG-*n*), were used as received. A solution consisting of 11.5–25% (by weight) of PBLG and the cross-linker was placed in a glass cell of 1 cm × 1 cm × 200 μm or in a glass tube of an inner diameter of 3 mm. The concentration of the cross-linker was 1–10 mol % with respect to the monomer unit concentration of PBLG. The cell was allowed to stand at room temperature (25 °C) for 7–10 days to develop cholesteric structure completely and then was heated at 70 °C to accelerate the reaction. The heating was continued for 10–20 days. The change of the CLC texture was followed by an Olympus BH-2 microscope equipped with cross-polarizers.

The content of diamines covalently attached to the cross-linked PBLG was evaluated by the elemental analysis after washing the sample with DOX thoroughly. The amount of the remaining amino groups of the cross-linkers that are bonded only at one end was determined by the amino group analysis using 2,4,6-trinitrobenzenesulfonic acid (TNBS).[8] A gel sample was washed with DOX and reacted with an excess amount of TNBS in DOX for 7 days. The sample was then immersed in DMF for 1 day, in dichloroacetic acid (DCA) for 2 h, and again in DMF for 1 day to remove unreacted TNBS. The solvent was then replaced with DOX, and the film was subjected to spectroscopic analysis. The amount of amino groups was calculated from the molar absorption coefficient of the reaction product of *n*-hexylamine with TNBS (ϵ = 6.11 × 10^3 L/cm·mol at 416 nm).

Results and Discussion

Cross-Linking Reaction. Solutions of PBLG (25% by weight) in DOX containing 10 mol % of diamino compound were stored at 25 °C for 10 days to develop the CLC order completely. Then the mixture was heated at 70 °C to accelerate the reaction. Figures 1–3 show the time dependence of the amount of cross-linkers covalently attached to PBLG. About 30% of DAA-2 was already bonded to PBLG before heating (Figure 1). The gelation occurred after 1 day of heating in this case. The amount of DAA-2 incorporated in PBLG leveled off at about 80% conversion. Presumably, some part of DAA-2 may be evaporated off during the heating. In the case of DAEI-2 (Figure 2), the gelation occurred during storage at 25 °C. The elemental analysis showed about 30% of DAEI-2 is already bonded before heating. The cross-linking was facilitated by the heating, and it was completed after about 10 days. In the case of DAEG-2, no reaction occurred before heating (Figure 3). By heating at 70 °C, the reaction started, but it was slower than those with DAA-2 and DAEI-2. It took about 20 days to complete the reaction with DAEG-2.

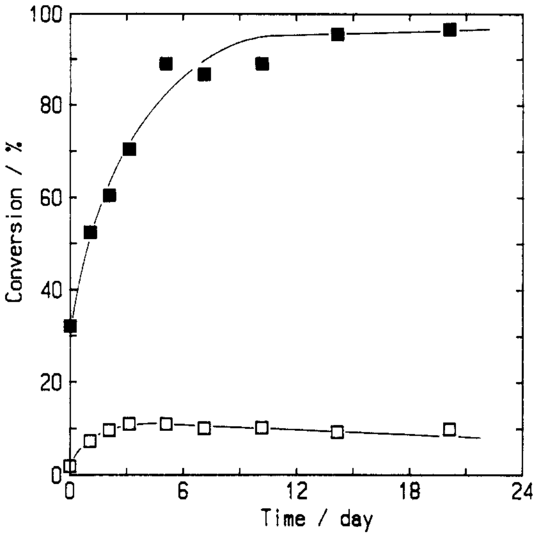

Figure 2. Amount of DAEI-2 covalently attached to PBLG (■) and amount of free amino groups remaining in the gel (□), plotted against heating time at 70 °C. Molar ratio of the reaction mixture: PBLG/DAEI-2/DOX = 1/0.10/7.37.

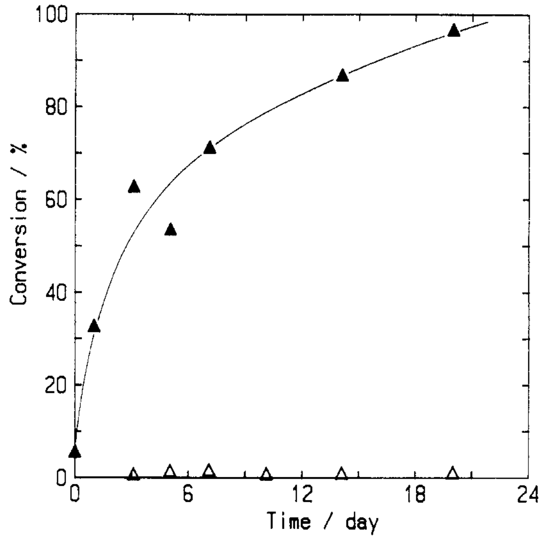

Figure 3. Amount of DAEG-2 covalently attached to PBLG (▲) and amount of free amino groups remaining in the gel (△), plotted against heating time at 70 °C. Molar ratio of the reaction mixture: PBLG/DAEG-2/DOX = 1/0.10/7.22.

In Figures 1–3, the amounts of free amino groups in the cross-linkers that are reacted with PBLG at only one of the two ends are also shown. The latter quantity will be 50%, if all the diamines are reacted with PBLG only at their single end. The amount of remaining amino group was very small for DAA-2 and DAEG-2. It appears that some of amino groups remained unreacted for DAEI-2. However, this may be due to the side reaction of TNBS with the secondary amino groups of DAEI-2, since the amount of amino group remained unchanged even after 20 days. The mixture of TNBS and di-*n*-butylamine did not form any product that shows a peak at 416 nm, but

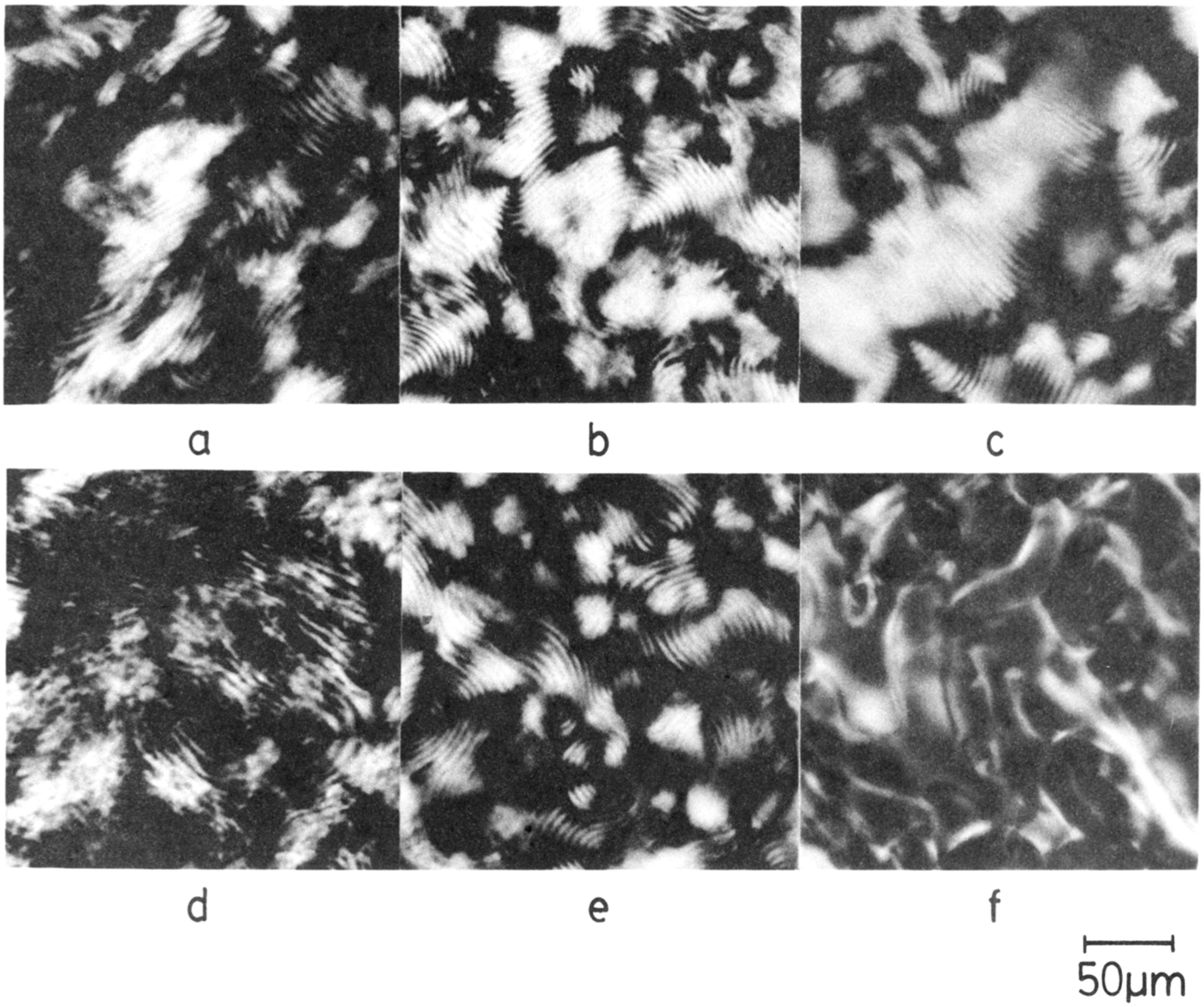

Figure 4. Textures of the reaction mixtures stored for 10 days with cross-linkers at 25 °C (a, DAA-2; b, DAEI-2; c, DAEG-2) and those after heating at 70 °C for 20 days (d, DAA-2; e, DAEI-2; f, DAEG-2). The mole percent of the cross-linkers was 10% with respect to the glutamate units.

the mixture showed an increase of base line at that wavelength.

It is concluded that the cross-linking with DAA-2 or DAEI-2 takes about 10 days at 70 °C. Almost all the cross-linkers bonded to PBLG participate in the cross-linking. The cross-linking with DAEG-2 is slower than that with DAA-2 or DAEI-2.

The change of the CLC texture during the cross-linking was followed by a microscope observation. Parts a–c of Figure 4 show the microscopic pictures of the reaction mixture stored at 25 °C for 10 days after mixing. Fingerprint textures characteristic of the CLC phase are seen for the three samples containing 10 mol % of DAA-2, DAEI-2, and DAEG-2, respectively. The texture of the mixture containing DAEG-2 is virtually the same as that containing no cross-linker. Those of the mixtures containing DAEI-2 and DAA-2 are somewhat changed from those in the absence of the cross-linkers. The structure change may be related to the extent of the cross-linking reaction that occurred during storage at 25 °C. No structural change was observed with DAEG-2, which did not react with PBLG at 25 °C. On the contrary, the CLC structure was somewhat disturbed in the cases of DAA-2 and DAEI-2, which reacted significantly during the storage.

The original texture was further disturbed with the progress of the cross-linking at 70 °C (Figure 4d–f). It is known that the cholesteric pitch becomes longer and finally a nematic structure appears upon heating the CLC of PBLG.[9] This is actually observed in the case of DAEG-2, in which no cross-linking was observed during the storage at 25 °C (Figure 4f). In this case the change of the CLC structure and its immobilization are occurring concurrently upon heating at 70 °C. In comparison to the DAEG-2 case, the CLC structures of the mixtures containing the other two cross-linkers remained unchanged during the progress of the cross-linking. Especially in the case of DAEI-2, the cholesteric pitch was kept constant as shown in Figure 5. The conservation of the original CLC structure may be a result of the substantial cross-linking occurring during storage at 25 °C.

Cross-linkers with different chain lengths were also tested. Cross-linking with DAEI-1 and DAEI-3 gave results similar to those with DAEI-2. Similarly, the cross-linking behavior with DAEG-1 was similar to that with DAEG-2. DAA-3 and DAA-4 behaved much like the DAA-2, but DAA-n's with $n > 5$ did not dissolve in the reaction mixture. Therefore, the chain length of the cross-linkers does not play an important role in determining the reactivity and the CLC order of the resulting gels. Incidentally, an average interhelix axis-to-axis distance between neighboring polypeptides has been estimated to be about 30 Å for 25 wt % of PBLG in dioxane.[2] This

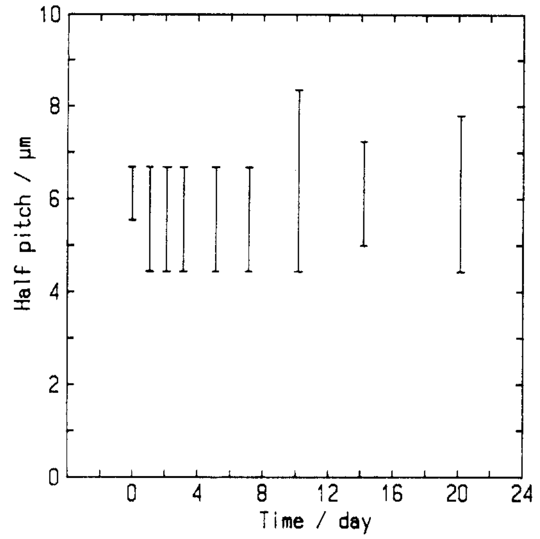

Figure 5. Cholesteric pitch measured by microscopic observation against reaction time. Molar ratio of the reaction mixture: PBLG/DAEI-2/DOX = 1/0.10/7.37.

Table I
Summary of Cross-Linking Reactions of PBLG in Three Different Solvents Using Three Different Cross-Linkers[a]

solvent	wt % of PBLG	cross-linking reagent		
		DAA-2	DAEI-2	DAEG-2
dioxane	25	○	○	○
DMF	25	×	○	×
chloroform	15	×	○	×

[a] Concentration of the cross-linker was 10 mol % with respect to the glutamate units.

corresponds to the nearest carbonyl-to-carbonyl distance of 18 Å. The chain lengths of the cross-linkers in their fully extended conformations are roughly estimated to be 3.9 (DAA-2), 5.2 (DAA-3), 6.5 (DAA-4), 6.5 (DAEI-1), 10.3 (DAEI-2), 14.2 (DAEI-3), 12.9 (DAEG-1), and 16.7 (DAEG-2) Å. Therefore, the chain lengths of the cross-linkers used mainly in this study are smaller than the average distance between carbonyl groups on the nearest polypeptide chains, and the extension of the length of the cross-linker did not improve the efficiency of the cross-linking and the ordering of the resulting gel.

The different behaviors of the three types of cross-linkers may be interpreted mainly in terms of their different reactivities of terminal amino groups. The results of the cross-linking using three different types of diamino compounds in three solvents are summarized in Table I. No gelation occurred when DAA-*n* or DAEG-*n* was mixed with PBLG in DMF or in chloroform. The DAA-*n* series with longer chain lengths than *n* = 4 were only partially soluble in chloroform and did not induce gelation even after 20 days at 70 °C. This contrasts the result of Aviram, who reported galation with DAA-6 in chloroform.[3] The DAEI-*n* series reacted with PBLG in the three solvents effectively. The high reactivity of the DAEI series may be due to the higher nucleophilicity of the terminal amino groups.

Properties of the Gels Having Various Degrees of Cross-Linking. Properties of the gels obtained at different heating periods were compared. The degree of swelling was calculated as the weight ratio of the gel equilibrated with DOX to that in the dry state, for three types of gels cross-linked by the three different cross-linkers. The degree of swelling decreased sharply with the heating period, but it became constant after about 10 days. From Figures 1–3, the degree of cross-linking, which is defined as the number of bonded cross-linkers divided by the total number of glutamate units, can be calculated. The degree of swelling was then plotted as a function of the degree of cross-linking in Figure 6.

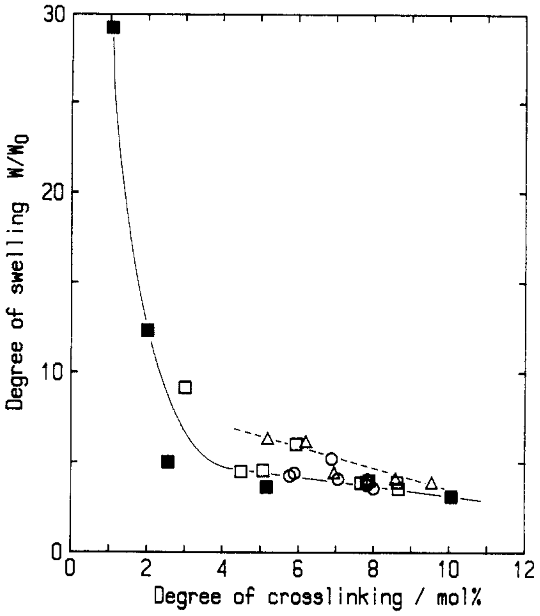

Figure 6. Degree of swelling of the PBLG gel plotted against the degree of cross-linking. Cross-linkers: DAA-2 (○), DAEI-2 (■, □), and DAEG-2 (△).

The degree of swelling increases with a decrease of the degree of cross-linking. Interestingly, the gels with a lower degree of cross-linking than 2 mol % swell more than the point where the concentration of PBLG is lower than the critical concentration for the LLC formation (PBLG = 10 wt %). In other words, the concentration range of the LLC phase is expanded by the cross-linking, or a LLC phase, which is thermodynamically unstable, was forced to exist by the cross-linking. The microscopic observation indicated that the highly swollen CLC gel consists of a homogeneous phase with a longer cholesteric pitch than that observed during the cross-linking. Typically, in the gel cross-linked with 1 mol % of DAEI-2, the original pitch was 4.2 μm and that of the swollen CLC gel was 19.4 μm.

The gels cross-linked with DAEG-2 show a higher degree of swelling than the other two types of gels having the same degree of cross-linking. As shown in Figure 4, the former gels show a CLC structure different from the other two gels. The different CLC structure may account for the different degree of swelling.

Cholesteric-Isotropic Transition Accompanied by Solvent-Induced Helix–Coil Transition. The helix–coil transition of PBLG may induce a large change in the CLC structure and the macroscopic shape of the cross-linked gel. Non-cross-linked PBLG in dichloroacetic acid (DCA)/DOX mixed solvent shows a helix–coil transition at a solvent composition of DCA/DOX = 90/10–95/5 at room temperature (Figure 7). In the same figure, the degree of swelling of the PBLG gel cross-linked with DAEI-2 is plotted as a function of the composition of the DCA/DOX mixed solvent. A sharp increase of the swelling ratio is observed at the helix–coil transition region, but the swelling ratio is insensitive to the DCA composition outside the helix–coil region. It is evident that the change in the molecular conformation leads to the macroscopic change of the gel shape.

The change in the swelling ratio was accompanied by the change in the CLC structure. Microscopic observation showed that the original cholesteric structure in the helix

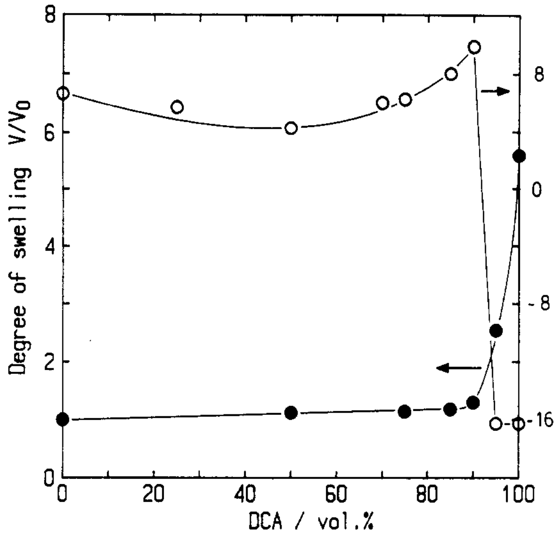

Figure 7. Degree of swelling of the PBLG gel cross-linked with 10 mol % of DAEI-2 plotted against the solvent composition in a DCA/DOX mixture (●). The specific rotatory power at 589 nm of PBLG ($M_w = 1.7 \times 10^5$) in the same solvent is also shown (○). In this figure, the swelling ratio, V/V_0, was calculated from the volume of the PBLG gel in DOX (V_0) and that in the mixture of DOX/DCA (V).

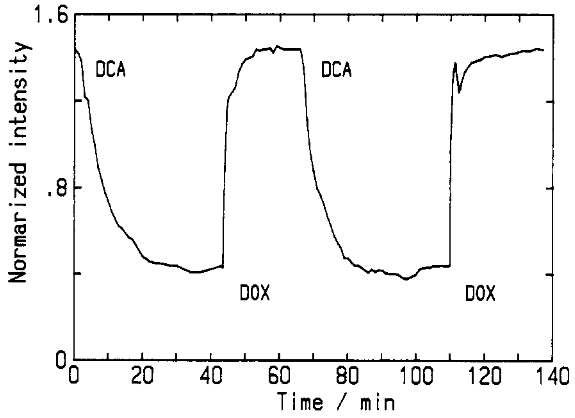

Figure 8. Reversible CLC–isotropic transition of the PBLG gel induced by the change of solvent composition. The ordinate is the intensity of transmitted light through the gel placed between cross-polarizers. The gel is cross-linked with 10 mol % of DAEI-2.

region was destroyed in the coil region. Very interestingly, the original CLC structure with the original cholesteric pitch was regenerated when the gel in the coil state was again immersed in DOX. Therefore, the original CLC structure is shown to be memorized in the cross-linked networks. The reversible process can be repeated by changing the solvent alternatively between DOX and DCA. In Figure 8, the reversible cholesteric–isotropic change was examined by following the light intensity transmitted through the gel placed between cross-polarizers. The transmitted light increases when the gel takes a CLC phase in DOX and decreases when it is isotropic in DCA.

Cholesteric–Isotropic Transition Induced by Thermal Helix–Coil Transition. Similar behavior was observed by changing temperature at a fixed solvent composition. PBLG in DCA/ethylene dichloride (EDC) (75/25) mixture shows a coil (low temperature) to helix (high temperature) transition as shown in Figure 9.[10] The thermal conformational transition also changed the CLC structure of the gel, as measured by the light intensity transmitted through the gel placed between cross-polarizers. In this experiment, a CLC gel prepared with 2% of DAEI-2 was used. Due to the low degree of cross-linking, this sample shows a much higher degree of swelling ($W/W_0 = 24$ at room temperature) in the mixed solvent than the former samples. At first, the temperature was set at 10 °C, and then it was raised stepwise to 60 °C. The system was thermally equilibrated at each temperature for 5 min. The increase of temperature induced the phase transition from isotropic (low temperature) to CLC (high temperature), as indicated by the increase of the intensity of transmitted light. The thermal transition with increasing temperature (forward process) was not as sharp as that of the PBLG molecule in the same solvent. The reverse process (high temperature to low temperature) was much sharper than the forward one. The hysteresis may be interpreted in terms of the stabilization of the helix conformation of PBLG in the CLC structure, since the CLC structure has been immobilized in the helical state of PBLG. The thermal phase change could be repeated many times by cycling the temperature between 10 and 50 °C, as shown in Figure 10.

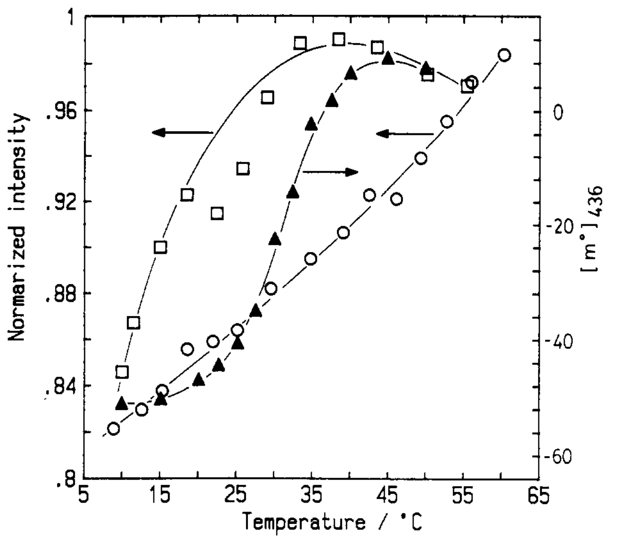

Figure 9. Temperature-induced phase change of the PBLG gel in a DCA/EDC (74/26) mixture: heating process (○); cooling process (□). The temperature-induced conformational change of a PBLG molecule in a DCA/EDC (75/25) mixture is also shown (▲) (data from ref 10). The PBLG gel is cross-linked with 2 mol % of DAEI-2.

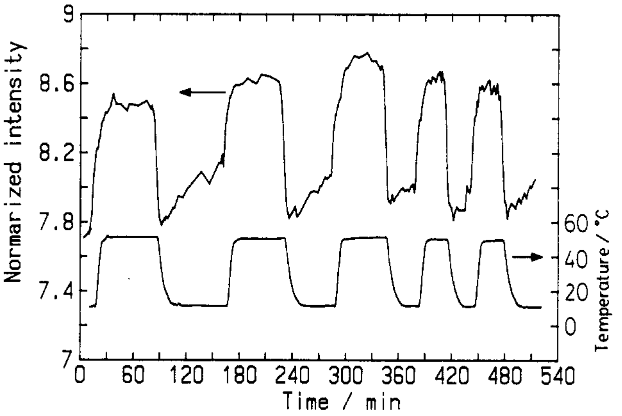

Figure 10. Reversible change of the phase of the PBLG gel by temperature in a DCA/EDC (74/26) mixture. The gel is cross-linked with 2 mol % of DAEI-2.

Conclusions

A polymer gel having the CLC order (CLC gel) was prepared by the cross-linking of PBLG in the CLC phase. The CLC gel showed reversible CLC–isotropic transition at the helix–coil transition region by the change of solvent or temperature.

References and Notes

(1) Robinson, C. *Trans. Faraday Soc.* **1956,** *52,* 571.
(2) Robinson, C.; Ward, J. C.; Beevers, R. B. *Discuss. Faraday Soc.* **1958,** *25,* 29.
(3) Aviram, A. *J. Polym. Sci., Polym. Lett. Ed.* **1976,** *14,* 757.
(4) (a) Samulski, E. T.; Tobolsky, A. V. *Nature* **1967,** *216,* 997. (b) Samulski, E. T.; Tobolsky, A. V. *Macromolecules* **1968,** *1,* 555.
(5) Mori, T.; Tanaka, R.; Tanaka, T. *Polymer* **1977,** *18,* 1041.
(6) Tsutsui, T.; Tanaka, T. *J. Polym. Sci., Polym. Lett. Ed.* **1977,** *15,* 475.
(7) Tsutsui, T.; Tanaka, R. *Polymer* **1981,** *22,* 117.
(8) Okuyama, T.; Satake, K. *J. Biochem.* **1960,** *47,* 454.
(9) Toriumi, H.; Yanagi, K.; Uematsu, I.; Uematsu, Y. *Mol. Cryst. Liq. Cryst.* **1983,** *94,* 267.
(10) Sayama, N.; Kida, K.; Norisuye, T.; Teramoto, A.; Fujita, H. *Polym. J.* **1972,** *3,* 538.

Registry No. DOX, 123-91-1; (DAA-*n*)(PBLG) (copolymer), 127943-51-5; (DAEI-*n*)(PBLG) (copolymer), 127971-09-9; (DAEG-*n*)(PBLG) (copolymer), 127943-52-6; DCA, 79-43-6.

Thermodynamic Theory of Network-Forming Polymer Solutions. 1

Fumihiko Tanaka

Department of Physics, Faculty of General Education, Tokyo University of Agriculture and Technology, Fuchu-shi, Tokyo, 183 Japan

Received December 5, 1989; Revised Manuscript Received February 15, 1990

ABSTRACT: This paper develops a lattice theory of strongly associating polymer solutions capable of forming macronetworks. The general procedure to deduce thermodynamic properties is presented and applied to thermoreversible gels. It is demonstrated that the multiple-equilibria conditions for molecular association caused by physical cross-linking can describe, when combined with traditional solution theory, the characteristic features of the temperature–concentration phase diagram. The central problem analyzed is the interference between gelation and two-phase separation.

1. Introduction

One of the few uninvestigated important subjects of polymer solutions is the spatial organization by strongly associative forces capable of forming bonds. It is clear that consideration of strong interpolymer interaction superposed on the familiar description of statistical chains can lead to the application of polymer science in numerous systems of practical interest. These include dimerization, solvation, and network formation. The purpose of this paper is to construct a thermodynamic theory of solutions, which include polymer chains carrying reactive groups capable of pairwisely forming bonds. We assume that the binding energy of a bond is, although strong enough to form specific spatial structures, of the order of thermal energy so that the entire system can readily reach thermal equilibrium. Association caused by such interaction can be classified into the following categories:

(1) Polymer chains A associate with each other in a solvent (S). We refer to this case symbolically as A·A/S. Homopolymer networks appear in this case.

(2) Polymer chains A associate with polymer chains B in a mixture of A and B. We refer to this case as A·B. Heteropolymer networks are formed in this case.

(3) Short polymer chains B (or solvent molecules (S)) cross-link long polymer chains A by conterminous reaction (or by forming a three-dimensional complex). We refer to this case as A·B·A (or A·S·A). Network properties are controlled by the chain length of the cross-linkers.

(4) Polymer chains A and polymer chains B can associate with each other within the same species but cannot form bonds between monomers of different species. We refer to this case as A·A/B·B. Interpenetrating polymer networks (IPN) are formed in this case.

The structure of a cluster formed in each category is schematically shown in Figure 1. We develop in this paper a thermodynamic theory that can treat all of these important categories. Extensive polydispersity inherent to such associating solutions is thermally controlled and strongly dependent on the composition of the system.

In the preceding papers,[1,2] we developed a thermodynamic theory of solutions belonging to category 1 and studied the phase behavior caused by the interference between gelation and phase separation. Comparison was made with experimental observations[3,4] for atactic polystyrene in the solvent of carbon disulfide. Present theory includes this theory as its special case.

Solution properties of a system belonging to category 2 were recently studied[5,6] in relation to the cluster formation by hydrogen bonding. Our theory includes this problem as another special case.

Thermodynamics of polymer solutions[7] and statistics of chain reaction (for example, polycondensation[8]) have so far been theoretically treated separately.[9] Our theory will attempt to unify these two mainstreams in the polymer science. In section 2, we will define our problem in more specific terms. Sections 3–5 are devoted to developing the theory. Some special applications and testing of the theory are presented in sections 6 and 7.

2. Definition of the Problem

Consider a binary mixture of linear polymers A and B. We assume for simplicity that polymer chains of each species consist of statistical units of the same size, a. The numbers of the statistical units on a chain are assumed to be n_A for A chain and n_B for B chain. We also assume that each chain carries a large number of reactive groups