

Heterogeneous Network Polymers. VI. Effects of Rate of Solvent Evaporation on Residual PGA Liquid Crystal Structure and its Dynamic Mechanical Properties

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Synopsis

Domains of cholesteric liquid crystal structures exist in films of heterogeneous network polymers from poly(L-glutamic acid) (PGA) and poly(oxyethylene glycol) PEG ($\bar{M}_n = 302, 1003$). The sizes and the amounts of the domains are dependent on the PGA content, the evaporation rate of the solvent, and the molecular weight of PEG. At the PGA content of 40% by weight, the sizes of the domains increase, the glass transition temperatures shift to higher temperatures, and the densities increase with increase in the rate of solvent evaporation. These observations suggest that the phase separation of PEG takes place at a PGA content of 40% when the evaporation rate is small. On the other hand, at a PGA content of 70% by weight, the sizes of the domains increase, the glass transition temperatures shift to higher temperatures, and the densities vary little with decrease in the rate of solvent evaporation. These observations suggest that PEG molecules are accommodated among α -helices of PGA and that the cholesteric liquid crystal phase grows at a PGA content of 70% when the evaporation rate is small.

INTRODUCTION

Since the early works of Elliott et al.¹ and Robinson et al.,²⁻⁵ the cholesteric liquid crystals formed by synthetic polypeptides in concentrated solutions have been extensively studied. Tobolsky et al.⁶⁻¹⁰ showed that the cholesteric liquid crystal structure was retained in solid polypeptide films cast from solutions and also in plasticized polypeptide films. Watanabe et al.¹¹ and Kajiyama et al.^{12,13} showed that the aggregated state of polypeptide molecules in solid films was greatly dependent on the casting solvent, and they investigated the relationship between the structure and the dynamic mechanical relaxation behavior.

We have been studying the properties of the heterogeneous network polymers from poly(glutamic acid) (PGA) and poly(oxyethylene glycol) (PEG) and their dependence on composition, phase structure, compatibility, crosslink density, etc.¹⁴⁻¹⁶ Two important findings were made: (1) phase inversion takes place in these composite polymers at ca. 50% PGA content, and it gives rise to the remarkable changes in the properties¹⁶; (2) cholesteric liquid crystal structure is formed in the PGA-PEG-dimethylformamide (DMF) system, and even when DMF is allowed to evaporate, the structure persists to varying degrees depending on the composition.^{16,17}

During the course of these studies we often suffered from the problem that the reproducibility of data such as dynamic mechanical properties, wide-angle x-ray diffraction patterns, polarizing micrographs, densities, etc., was not very

good. The fluctuations must at least be partly attributed to the microphase separation involving the retained cholesteric liquid crystal structure—this should, in turn, depend on the way how the solvent evaporates.

Thus, in this paper we discuss the effect of the evaporation rate of DMF on the dynamic mechanical properties, the phase structure, the densities, etc., of the heterogeneous network polymers prepared at three different evaporation rates. The PGA contents were 40% and 70% by weight where the PEG-rich and PGA-rich phases may constitute the continuous phases, respectively.

EXPERIMENTAL

Materials

Poly(L-glutamic Acid) (PGA). PGA was prepared by saponification of poly(γ -methyl L-glutamate). PGA was confirmed by elemental analysis (calcd: C, 46.10%; H, 5.46%; N, 10.85%; found: C, 46.02%; H, 5.42%; N, 10.81%), optical rotation of 0.2M NaCl aqueous PGA solution at pH 7.3; $[\alpha]_D^{20} = -105^{18-20}$, and an infrared spectrum. The weight-average molecular weight of PGA was estimated to be 48,000 from its intrinsic viscosity in 0.2M aqueous NaCl at pH 7.3.^{18,21}

Poly(oxyethylene Glycol) (PEG). PEG was supplied through the courtesy of Sanyo Chemical Industry. The number-average molecular weights obtained from the determination of hydroxyl groups by acid-catalyzed acetylation were 302 and 1003. They will be designated as PEG300 and PEG1000, respectively.

N,N-Dimethylformamide (DMF). DMF was of commercial origin and used without further purification.

Heterogeneous Network Polymers. Heterogeneous network polymers consisting of 70 and 40 wt-% PGA, in which the PGA-rich and PEG-rich phase, respectively, may constitute the continuous phase, were prepared. For example, 1.40 g PGA and 0.60 g PEG300 were dissolved in 14 ml DMF at 100°C. The clear solution was poured onto a mold (8.0 cm \times 5.0 cm \times 1.0 cm) coated with fluoride varnishes. The mold was placed in a metal box (10.5 cm \times 6.5 cm \times 2.0 cm) covered with a lid on which there were one, three, or ten holes of 2-mm diameter to vary the evaporation rate of DMF and heated in an oven at 100°C. It took about three days, one day, and 10 hr, respectively, until films were obtained. These heterogeneous network polymers thus obtained will be designated as PGA-PEG300(70/30)-s, PGA-PEG300(70/30)-m, and PGA-PEG300(70/30)-f, respectively. The films were kept further for three days at 100°C. A list of the heterogeneous network polymers is shown in Table I.

Apparatus and Procedures

Polarizing micrographs were taken using a Nikon polarizing optical microscope Type LFG-KE. A thin section approximately 50 microns thick was cut parallel to the film surface with the use of a razor blade.

Dynamic mechanical measurements were made with a Model DDV-IIc Rheovibron at 110 Hz in the temperature range of -140° – 205° C. The temperature was raised at a rate of 1.5° – 2.0° C/min. Wide-angle x-ray diffraction patterns were obtained with a Rigaku Denki Type D-3F x-ray generator. Nickel-filtered $\text{CuK}\alpha$ radiation was used at 35 kV and 15 mA.

TABLE I
 Characterization of Heterogeneous Network Polymers

Designation	K^a	\bar{g} % ^b	$\psi \times 10^3$, mole/g ^c	ρ^d , g/cm ³ d	$T^{\tan \delta_{\max}}$, °C, e	$d_{10\bar{1}0}$, Å ^f
PGA-PEG300(40/60)-s	0.78	87.5	3.1	1.269	-3	13.7
PGA-PEG300(40/60)-m	0.78	91.3	3.4	1.289	8	14.2
PGA-PEG300(40/60)-f	0.78	93.8	3.6	1.301	18	14.7
PGA-PEG1000(40/60)-s	2.59	81.0	0.8	1.269	-3	12.1
PGA-PEG1000(40/60)-m	2.59	82.9	0.9	1.280	5	12.7
PGA-PEG1000(40/60)-f	2.59	84.9	0.9	1.294	15	12.8
PGA-PEG300(70/30)-s	2.73	99.4	2.0	1.335	105	10.9
PGA-PEG300(70/30)-m	2.73	99.0	1.9	1.337	90	11.3
PGA-PEG300(70/30)-f	2.73	96.0	1.7	1.337	65	12.4
PGA-PEG1000(70/30)-s	9.07	98.8	0.6	1.333	85	11.3
PGA-PEG1000(70/30)-m	9.07	99.7	0.6	1.335	50	11.5
PGA-PEG1000(70/30)-f	9.07	99.8	0.6	1.335	50	12.0

^a $K = [-(\text{COOH})/(-\text{OH})]$, mole ratio of carboxyl groups in PGA to hydroxyl groups in PEG in reaction mixtures.

^b Gel percent, in DMF at 25°C.

^c Crosslink density, calculated as in reference 16.

^d Density, measured by a floatation method using carbon tetrachloride and cyclohexane at 25°C.

^e Peak temperature of $\tan \delta$ curve.

^f Bragg spacing obtained from wide-angle x-ray diffraction patterns, $d_{10\bar{1}0} \times 2/\sqrt{3}$ corresponds to the distance between neighboring α -helices of PGA.

RESULTS AND DISCUSSION

Polarizing Microscopy

As mentioned above, the fluctuation of properties that the heterogeneous network polymers exhibit may be ascribed to the domain structure arising from the aggregation of the component polymers. The resulting domain structure is affected by composition, molecular weight of PEG, thermal history, rate of solvent evaporation, etc.

Polarizing microscopy is a useful technique for studying the phase structure of films containing optically anisotropic regions. The polarizing micrographs shown in Figures 1 and 2 indicate that the phase structure of heterogeneous network polymers are greatly dependent on the rate of DMF evaporation and the molecular weight of PEG. Regularly spaced lines or retardation lines were seen in Figure 1(c) and Figure 2(a). This is strong evidence that a cholesteric liquid crystal structure exists in these networks polymers.

PGA-PEG300(40/60) and PGA-PEG1000(40/60). When the rate of DMF evaporation is large, the cholesteric color and the optical retardation lines characteristic of a cholesteric liquid crystal structure were observed in the polarizing micrographs of PGA-PEG300(40/60)-f as shown in Figure 1, though the retardation lines could not be observed in a PGA film made by casting from DMF solution at 100°C. The spacing S between retardation lines was about 5 microns. These observations are similar to the following results: Elliott et al.¹ could not observe retardation lines in a film of poly(γ -benzyl L-glutamate) (PBLG), but Samulski et al.^{7,9} reported that the retardation lines could be observed in PBLG films swollen in benzene and plasticized with 3,3'-dimethylbiphenyl. Robinson² reported that S varies in proportion to $1/C^2$, where C is the volume fraction of PBLG in the cholesteric phase. According to this experimental rule, we interpreted that one of the reasons that the retardation lines could be observed in PGA-PEG300(40/60)-f was that PEG lowered the concentration of PGA acting as a diluent. When the rate of evaporation is small, on the other hand, the finely dispersed anisotropic regions were observed as shown for PGA-PEG300(40/60)-s in Figure 1.

The variation of the phase structure resulting from the change in evaporation rate of the solvent is explained in terms of phase separation of PEG. The evaporation process is considered to involve the following steps: isotropic solution \rightarrow point A (isotropic phase + cholesteric liquid crystal phase) \rightarrow point B (cholesteric liquid crystal phase) \rightarrow solid film. Namely, the isotropic solution of PGA and PEG is concentrated as the DMF evaporates. Above the concentrations corresponding to points A or B, the solution changes to the cholesteric liquid crystal phase. When the evaporation rate is large, the cholesteric structure will be retained in the solid film; but when the evaporation rate is small, the PEG molecules will separate out and the anisotropic regions may be finely dispersed. This idea is supported by the results shown in Table I that the density ρ becomes lower and the distance between neighboring α -helices of PGA, $d_{10\bar{1}0} \times 2/\sqrt{3}$, becomes shortened when the evaporation rate is small.

Compared with PGA-PEG300(40/60), the phase structures of PGA-PEG1000(40/60) were not so affected by the evaporation rate within this experimental range. This may be because PEG1000 is apt to separate out even when the evaporation rate is fast, because PEG1000 is not as miscible with PGA as PEG300 is. Therefore, the fine anisotropic regions are observed.

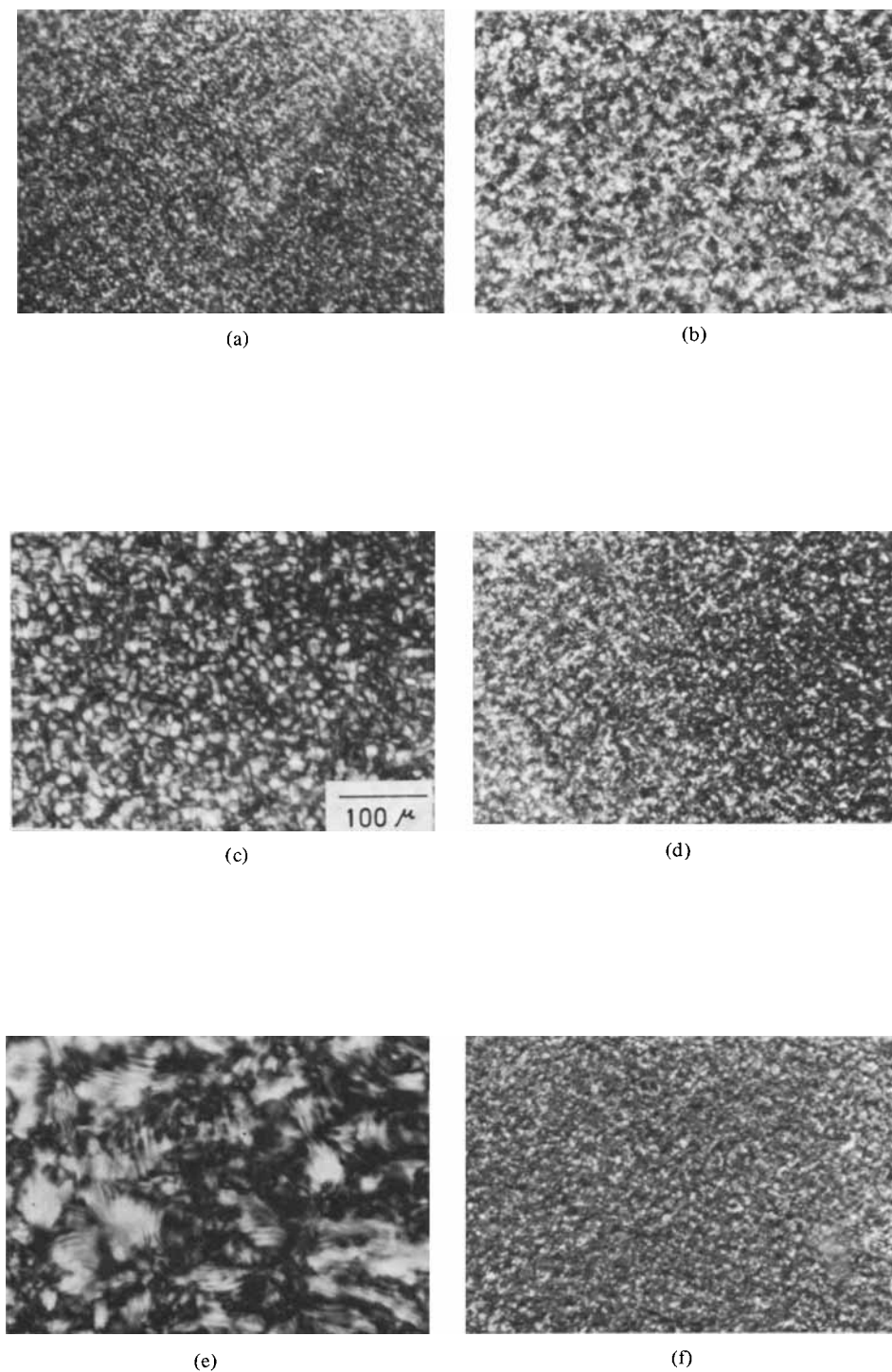


Fig. 1. Effect of evaporation rate of DMF on polarizing micrographs of PGA-PEG300 (40/60) and PGA-PEG1000(40/60): (a) PGA-PEG300(40/60)-s; (b) PGA-PEG300(40/60)-m; (c) PGA-PEG300(40/60)-f; (d) PGA-PEG1000(40/60)-s; (e) PGA-PEG1000(40/60)-m; (f) PGA-PEG1000(40/60)-f.

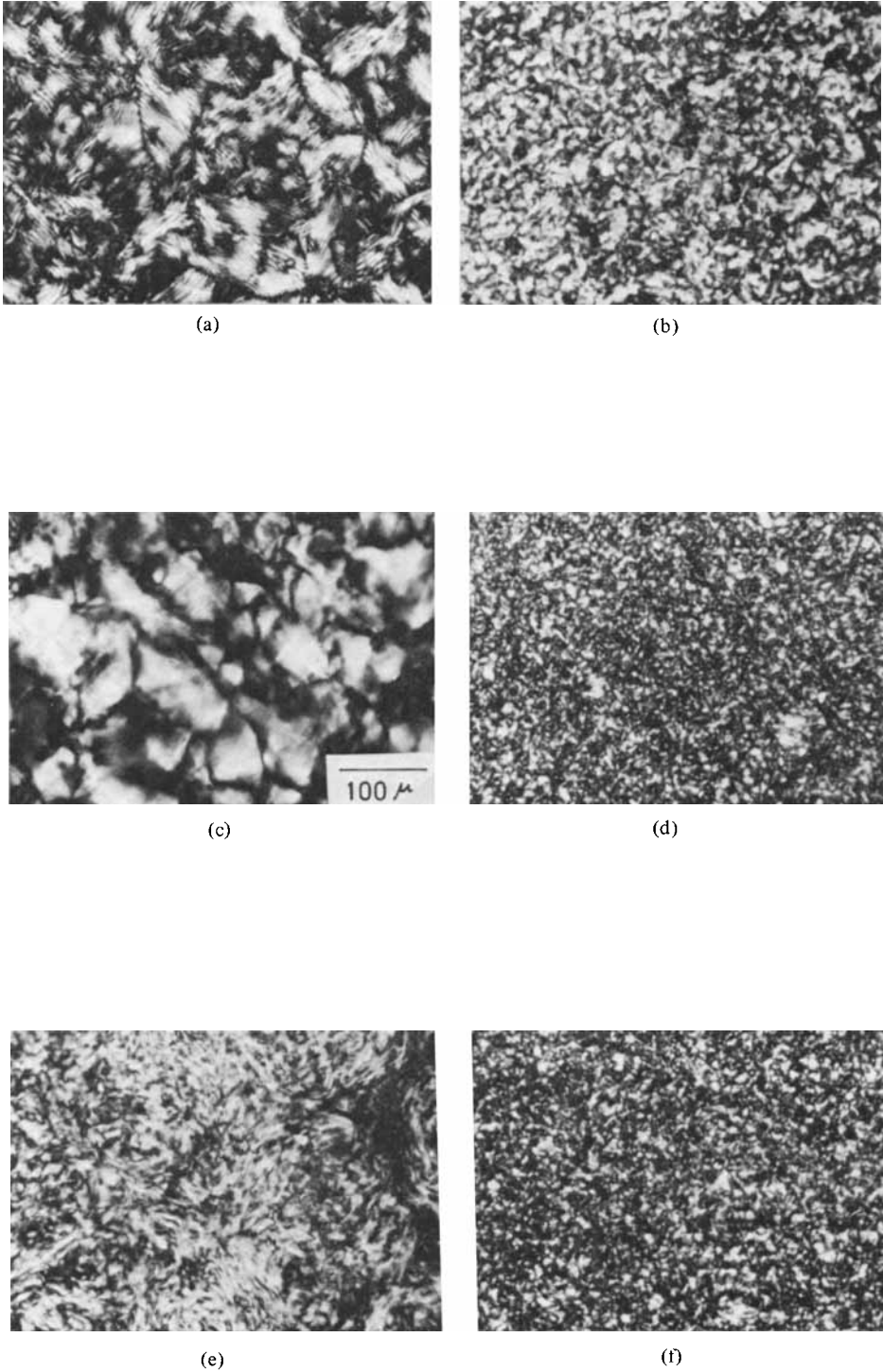


Fig. 2. Effect of evaporation rate of DMF on polarizing micrographs of PGA-PEG300(70/30) and PGA-PEG1000(70/30): (a) PGA-PEG300(70/30)-s; (b) PGA-PEG300(70/30)-m; (c) PGA-PEG300(70/30)-f; (d) PGA-PEG1000(70/30)-s; (e) PGA-PEG1000(70/30)-m; (f) PGA-PEG1000(70/30)-f.

PGA-PEG300(70/30) and PGA-PEG1000(70/30). Films of heterogeneous network polymers containing 70% PGA are composed of many cholesteric liquid crystal domains as shown in Figure 2. The sizes of the domains of PGA-PEG300(70/30) vary from about 10 microns to about 100 microns with a decrease in the evaporation rate of DMF. Optical retardation lines were observed in PGA-PEG300(70/30)-s, and the spacing S was about 4 microns, which was smaller than that of PGA-PEG300(40/60)-f. This may be attributed to an increase in PGA content in the cholesteric liquid crystal phase of PGA-PEG300(70/30)-s compared with that of PGA-PEG300(40/60)-f. In PGA-PEG300(70/30)-f, on the other hand, optical retardation lines were not observed though a cholesteric color was observed. This may be explained as follows. As the density is little affected by the rate of evaporation (Table I), the separation of PEG probably does not take place. The cholesteric liquid crystal phase formed above points A and B is expected to grow into large cholesteric liquid crystal domains when the rate of evaporation is small. In contrast, films become composed of small cholesteric liquid crystal domains when the rate of evaporation is fast because there is not enough time for liquid crystal growth.

PGA-PEG1000(70/30) showed a similar tendency, but the effect of the rate of DMF evaporation was small within this experimental range and the optical retardation lines were not observed in PGA-PEG1000(70/30)-s. The reason for this result is obscure at present, but one explanation may be as follows. The concentrations of PGA at points A and B for PGA-PEG1000-DMF at which a cholesteric liquid crystal appears may be low compared with those of PGA-PEG300-DMF. Therefore, even the lowest evaporation rate of this experiment may not give enough time for liquid crystal growth.

These observations collectively suggest that at the 70% PGA content, phase separation of PEG does not occur and the time allowed for liquid crystal growth may be a main factor governing the phase structure.

Dynamic Mechanical Properties

In the previous paper¹⁶ we described the effects of composition, phase structure, molecular weight of PEG, etc., on the dynamic mechanical properties of the heterogeneous network polymers. In the course of the study it became apparent that the dynamic mechanical properties were dependent on the rate of solvent evaporation.

PGA-PEG300(40/60) and PGA-PEG1000(40/60). The dynamic mechanical properties of the heterogeneous network polymers containing 40% PGA were shown in Figures 3 and 4. The $\tan \delta$ curves were nearly symmetrical around the peak temperatures, and the intensities of the peaks were fairly large. The relaxation was attributed to the micro-Brownian motions of PEG segments because the PEG-rich phase constitutes the continuous phase.¹⁶ This assignment is supported by the dynamic mechanical properties of PEG or poly(ethylene oxide) (PEO) reported previously^{14,22-24}: the major relaxation occurs at -60° to -20°C depending on the molecular weight, and PEG and PEO melt below 66°C . The assignment is supported also by the dynamic mechanical properties of segmented polyurethane block copolymers reported by Huh et al.²⁵; these copolymers are very similar systems to our heterogeneous network polymer systems because (1) they are composed of a hard component (urethane segments) and a soft component (polyether segments), and (2) the hard component domains are dispersed

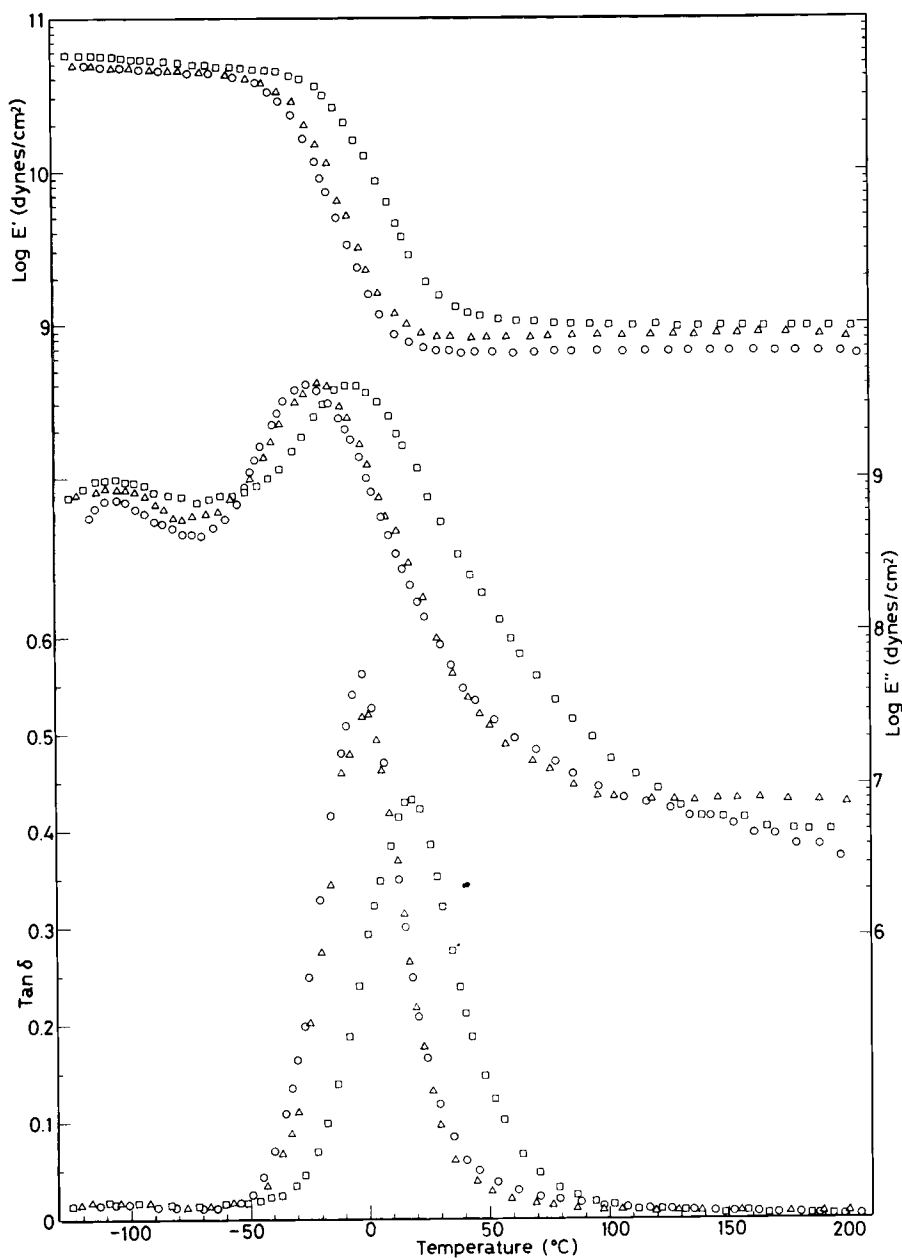


Fig. 3. Effect of evaporation rate of DMF on dynamic mechanical properties of (O) PGA-PEG300(40/60)-s; (Δ) PGA-PEG300(40/60)-m; (\square) PGA-PEG300(40/60)-f.

in the soft component matrix. The major relaxation process that occurs at about -10°C was attributed to the micro-Brownian motions of polyether segments.

With a decrease in the rate of evaporation, (1) peak temperature ($T_{\tan \delta_{\max}}$, $T_{E''_{\max}}$) shifted to lower temperatures; (2) the magnitude of $\tan \delta$ at the peak temperature ($\tan \delta_{\max}$) increased; (3) E' above the transition temperature decreased. This may be explained by the increase in the PEG content in the continuous phase (PEG-rich phase) because the more PEG is expected to separate out from the cholesteric liquid crystal phase to the continuous phase when

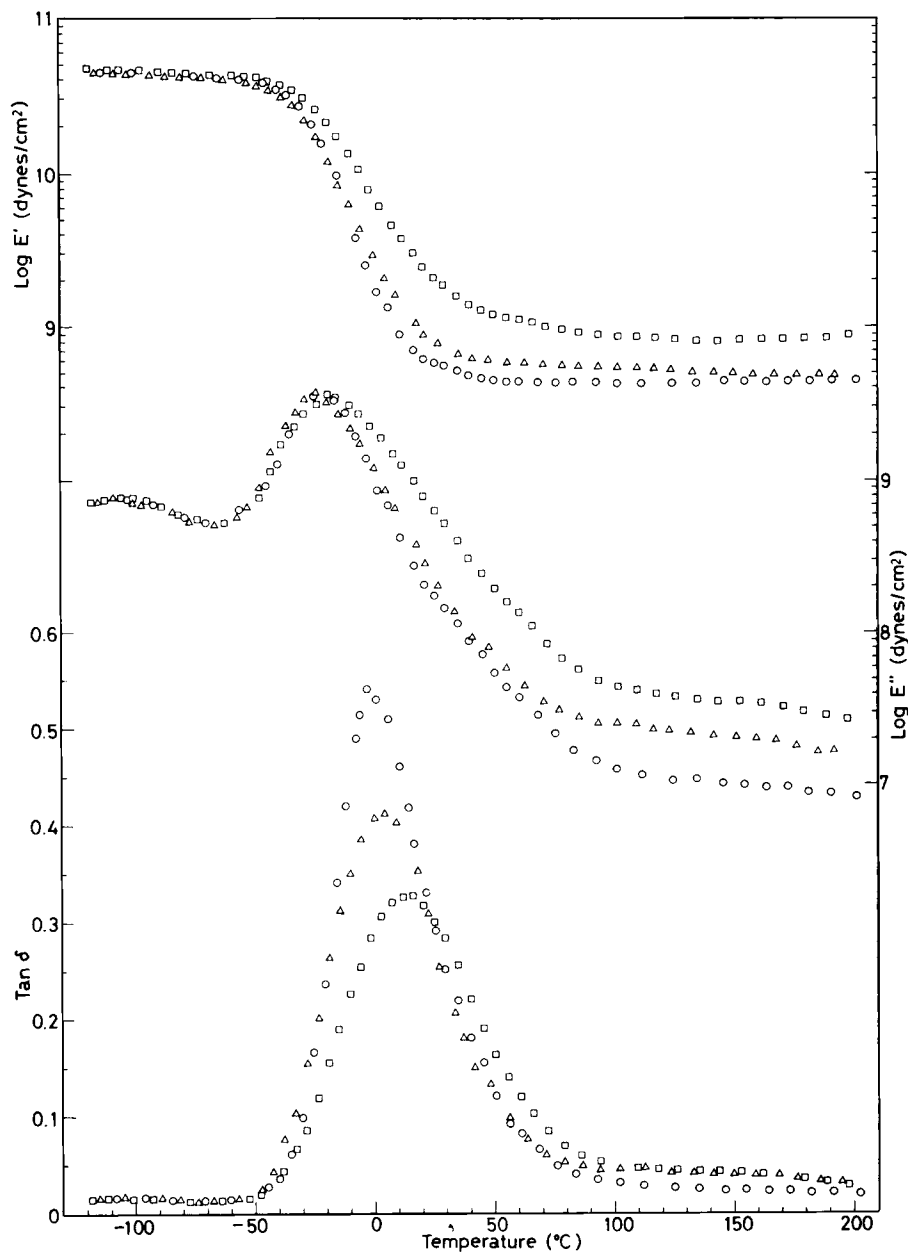


Fig. 4. Effect of evaporation rate of DMF on dynamic mechanical properties of (O) PGA-PEG1000(40/60)-s; (Δ) PGA-PEG1000(40/60)-m; (\square) PGA-PEG1000(40/60)-f.

the evaporation is slow. When the rate of evaporation is large, however, PEG molecules consisting the cholesteric liquid crystal structures with PGA cannot effectively separate out. The decrease in PEG content in the continuous phase may shift the $T_{\tan \delta_{\max}}$ to higher temperatures and decrease the $\tan \delta_{\max}$, because the relaxation may arise mainly from the micro-Brownian motions of PEG.

PGA-PEG300(70/30) and PGA-PEG1000(70/30). The rate of DMF evaporation influences the dynamic mechanical properties of heterogeneous

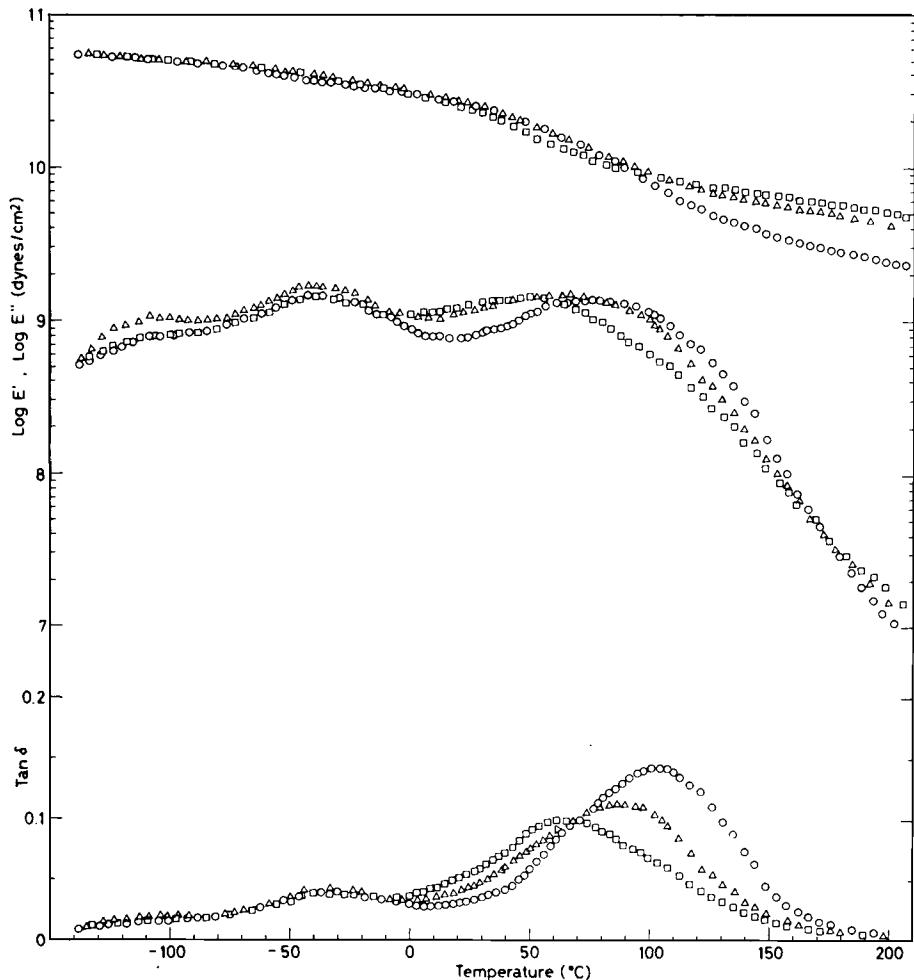


Fig. 5. Effect of evaporation rate of DMF on dynamic mechanical properties of (O) PGA-PEG300(70/30)-s; (Δ) PGA-PEG300(70/30)-m; (\square) PGA-PEG300(70/30)-f.

network polymers containing 70% PGA in the reverse direction, compared with those containing 40% PGA as shown in Figures 5 and 6. Namely, with a decrease in the rate of evaporation, (1) $T_{\tan \delta_{\max}}$ and $T_{E'_{\max}}$ shifted to higher temperatures; (2) $\tan \delta_{\max}$ increased; (3) E' above the transition temperature decreased. It is certain that the relaxation is associated with PGA molecules because the PGA-rich phase constitutes the continuous phase at the PGA content of 70%. But it is obscure what kinds of motions of PGA are responsible.

Two types of relaxation mechanisms may be attributable to this relaxation. One is the micro-Brownian motions of PGA in the disordered region and PEG. The other is the rotational or slipping motions of PGA in the ordered region. At present we consider that the former is the case based on the following observations: (1) Since the density is little affected by the rate of evaporation, the PEG molecules are by and large accommodated among the α -helical PGA molecules. (2) The relaxation curve of PGA-PEG300(70/30)-s varied little with annealing at 150°C for 10 hr. (3) PGA homopolymer shows its $\tan \delta$ maximum at ca. 135°C as reported in the previous paper,¹⁴ and the relaxation curve was little affected

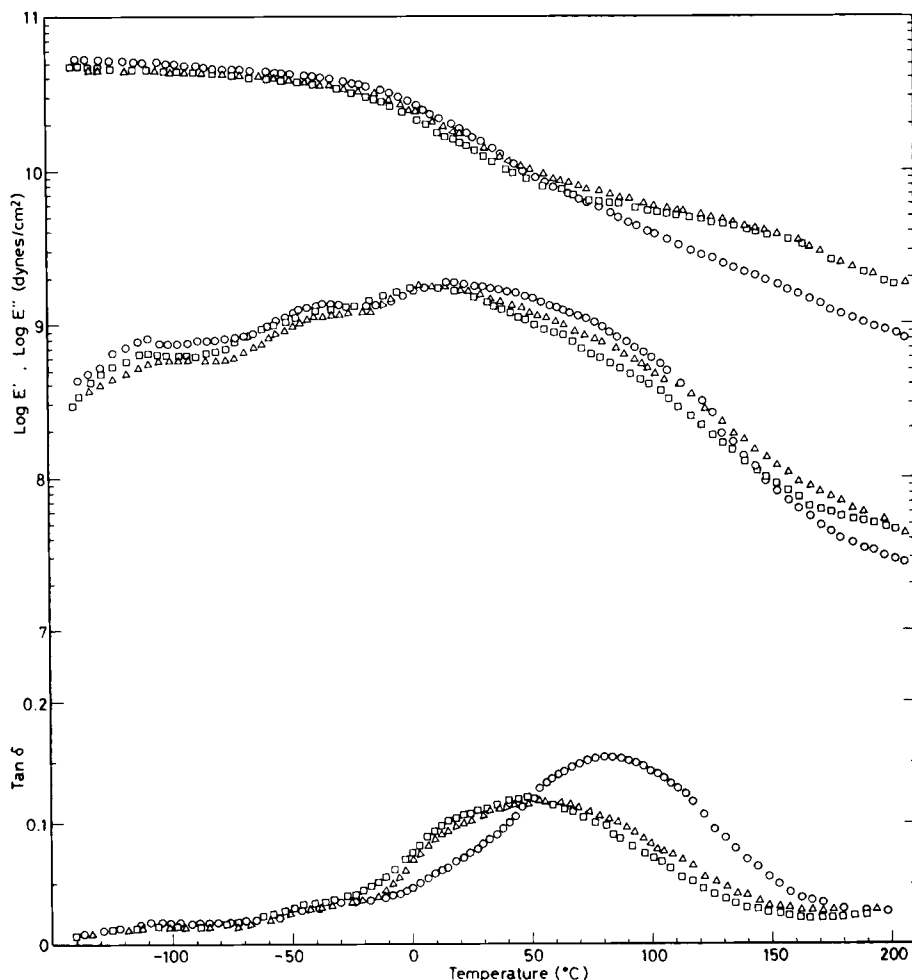


Fig. 6. Effect of evaporation rate of DMF on dynamic mechanical properties of (O) PGA-PEG1000(70/30)-s; (Δ) PGA-PEG1000(70/30)-m; (\square) PGA-PEG1000(70/30)-f.

by annealing at 150°C for 2 hr although the $\tan \delta_{\max}$ at ca. 135°C increased with annealing at 150°C for 48 hr (thermal degradation of PGA may occur). In the light of the relaxation mechanisms of poly(γ -methyl D-glutamate) reported by Kajiyama et al.,^{12,13} we assumed that the relaxation of PGA homopolymer arises from the micro-Brownian motions in the disordered region. To further elucidate this and to correlate with the behaviors of heterogeneous network polymers, a study of dynamic mechanical behavior of PGA homopolymer is being continued.

X-Ray Diffraction

The aggregation state of PGA and PEG in a microstructural level was further studied by x-ray diffraction analysis. Every heterogeneous network polymer had a reflection at a Bragg angle of $2\theta = 6^\circ$ – 9° which corresponded to the (10 $\bar{1}$ 0) plane of the hexagonal crystal lattice of pure PGA in α -helical conformation. The lattice distance, $d_{10\bar{1}0}$, is shown in Table I; $d_{10\bar{1}0} \times 2/\sqrt{3}$ is equal to the dis-

tance between neighboring α -helices. The $d_{10\bar{1}0}$'s of heterogeneous network polymers are longer than the $d_{10\bar{1}0}$ of PGA (9.7 Å) by 1–1.5 Å. Moreover, the $d_{10\bar{1}0}$'s of heterogeneous network polymers containing 40% PGA are longer than those of 70% PGA content. And with the same compositions, the slower the solvent evaporation, the smaller became the $d_{10\bar{1}0}$'s.

Thus, we propose that the interhelical space of the PGA liquid crystal that is formed in DMF in the presence of PEG has a certain capacity to hold the PEG chains even after DMF is completely gone. When the PGA content is only 40% by weight, there is simply not enough PGA to accommodate all the PEG that amounts to 60%—and the excess PEG is ejected depending on the rate of DMF evaporation. On the other hand, the PGA content of 70% by weight is still unsaturated with respect to the interhelically accommodated PEG—the variation in the rate of solvent evaporation only results in the difference in the mutual aggregation mode of the liquid crystal domains.

SUMMARY

Heterogeneous network polymers composed of PGA and PEG300 or PEG1000 were prepared at three different evaporation rates of DMF, and their dynamic mechanical properties, phase structure, density, etc., were investigated. With increase in the evaporation rate of DMF, at 40% PGA content, (1) the sizes of the cholesteric liquid crystal domains became larger, (2) $T_{\tan \delta_{\max}}$ and $T_{E''_{\max}}$ shifted to higher temperatures; (3) $\tan \delta_{\max}$ decreased; (4) $d_{10\bar{1}0}$ increased; (5) ρ increased. At 70% PGA content, (1) the sizes of the cholesteric liquid crystal domains became smaller, (2) $T_{\tan \delta_{\max}}$ and $T_{E''_{\max}}$ shifted to lower temperatures, (3) $\tan \delta_{\max}$ decreased; (4) $d_{10\bar{1}0}$ increased; (5) ρ varied little. The correlation among the evaporation rate, the phase structure, and the dynamic mechanical properties was discussed.

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