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Heterogeneous Network Polymers. V. Heterogeneous Network Polymers from Poly(L-glutamic acid), Poly(acrylic acid), and Polyether Glycols

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ABSTRACT: The dynamic mechanical properties and the phase structures of some heterogeneous network polymers, such as poly(glutamic acid) [PGA]—poly(oxypropylene) glycol [PPG, $\bar{M}_n=400$], PGA—poly(oxyethylene) glycol [PEG, $\bar{M}_n=330$], and poly(acrylic acid) [PAA]—PEG were compared to each other to investigate the relationship between the mechanical properties and the aggregation state of the component polymers. When compared with PGA—PEG300 at the same PGA content, the PGA—PPG400 showed the following characteristics: (1) the dynamic mechanical $\tan\delta$ curves are much broader, (2) the $\tan\delta$ peak temperatures are higher, and (3) the E' values above the transition regions are lower. The most striking characteristics of PAA—PEG compared with PGA—PPG400 and PGA—PEG300 were: (1) E' in the rubbery plateau region increases in proportion to the crosslink density; (2) the $\tan\delta$ maximum values are as large as 1.0—1.5; and (3) the shape of the $\tan\delta$ curves is sharp and is little affected by the composition. The differences in the properties among the heterogeneous network polymers were discussed in terms of characteristic properties of PGA, the compatibility of the component polymers, and the reaction temperature.

KEY WORDS Poly(glutamic acid) / Poly(acrylic acid) / Poly(oxypropylene glycol) / Poly(oxyethylene) glycol / Network Polymer / Dynamic Mechanical Properties / Glass Transition /

The mechanical properties of composite polymers comprising quite different component polymers are greatly influenced by the mechanical, thermal, and morphological properties of each component. Furthermore, the compatibility of the components always governs the phase structure of the composites.

Recently, we synthesized a series of so-called heterogeneous network polymers by esterifying the γ-carboxyl groups of poly(glutamic acid) [PGA] with the hydroxyl groups of poly(oxyethylene) glycol [PEG]. Their mechanical properties were essentially determined by the relative amounts of PGA and PEG; individual factors such as compatibility, phase structure, crosslink density, free carboxyl group content, molecular weight of PEG, etc. were interdependent and collectively influenced the mechanical behaviors.[1-3]

Hydrogen bonds play an important role in the compatibility between the polymers with carboxyl groups and polyethers, especially in the case of an α-helical PGA because the rigid, rodlike core of an α-helix is surrounded by the carboxyl groups. A slight variation in the chemical structure in one of the component polymers, therefore, may induce a significant change in the compatibility and in the phase structure. For example, if we replace a methylene hydrogen of PEG with a methyl group, the resulting oxypropylene units are much less polar and have less hydrogen bonding tendency than the oxyethylene units.

Thus in this paper, heterogeneous network polymers were prepared from PGA and poly(oxypropylene) glycol [PPG]. Their dynamic mechanical properties and phase structure were compared with those of heterogeneous network polymers from PGA and PEG. PEG, HO-(-CH$_2$CH$_2$O-)$_{\bar{m}}$H, and PPG, HO-[-CH(CH$_3$)·CH$_2$O-]$_{\bar{n}}$H, having molecular weights of 330 (m=7.1) and 400 (n=6.8) respectively, were used to eliminate the effect of the chain length on the compatibility.

Studies on syntheses and properties of network polymers formed by different types of polymers have been reported also by Bamford, *et al.*,[4] Frish, *et al.*,[5] Allen, *et al.*,[6] Cook, *et al.*,[7] Ishikawa, *et al.*,[8] and Kito, *et al.*[9] The uniqueness of our heterogeneous network systems, compared with their studies lies in the fact that synthetic polypeptides were chosen as one of the component polymers. The synthetic polypeptides have two important features in contrast to the usual synthetic polymers: (1) synthetic polypeptides retain various conformations such as α-helix, β-coil, or random coil owing to strong intra- or inter-molecular hydrogen bonds in a solid film;[10] (2) rigid rodlike α-helical molecules of polypeptides form liquid crystal structures in concentrated solutions[11-15] and these structures persist in the solid films prepared by evaporation of solvents.[19-21] Similarly, we found in our heterogeneous network polymer systems that (1) the cholesteric liquid crystal structure is formed in the concentrated reaction mixtures of PGA and PEG; (2) this cholesteric liquid crystal structure was retained in the solid films of network polymers obtained by heating the mixture; and (3) these cholesteric domains affect the dynamic mechanical properties. In order to investigate the effect of the unique properties of polypeptides on the dynamic mechanical properties, the dynamic mechanical properties of amorphous network polymers from poly(acrylic acid) [PAA] and PEG were also measured.

EXPERIMENTAL

Materials

Poly(L*-glutamic acid*) [*PGA*]. PGA was prepared by saponification of poly(γ-methyl D-glutamate). PGA was confirmed by elemental analysis. *Anal.* Calcd: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.10; H, 5.42; N, 10.77 and optical rotation of 0.2-M NaCl aq PGA solution at pH 7.3; $[\alpha]_D^{25} = -105$.[22-24]

An infrared spectrum of a PGA film cast from N,N-dimethylformamide solution at 100°C showed that most of the PGA chains existed in α-helix form.

The weight-average molecular weight of PGA was estimated to be 48,000 from its intrinsic viscosity in 0.2-M NaCl aq solution at pH 7.3.[22,25]

Poly(*oxypropylene*) *glycol* [*PPG*] *and Poly*(*oxyethylene*) *glycol* [*PEG*]. PPG and PEG were supplied through the courtesy of Sanyo Chemical Industries. The number-average molecular

Table I. Characterization of PGA—PPG400 and PGA—PEG300[a]

	K[b]	g, %[c]	ρ, g/cm^3 [d]	$\nu \times 10^3$, mol/g[e]	$C \times 10^3$, mol/g[f]	$T_{E''\mathrm{max}}$, °C[g]
PGA—PPG400 (40/60)	1.0	86	1.18	2.7	0.8	−18
PGA—PPG400 (50/50)	1.6	91	1.21	2.3	1.8	18
PGA—PPG400 (60/40)	2.3	94	1.26	1.8	3.0	50
PGA—PPG400 (70/30)	3.6	86	1.28	0.9	4.6	65
PGA—PEG300 (40/60)	0.9	92	1.30	3.4	0	−7
PGA—PEG300 (50/50)	1.3	96	1.30	2.9	1.1	7
PGA—PEG300 (60/40)	1.9	99	1.31	2.3	2.3	40
PGA—PEG300 (70/30)	3.0	100	1.34	1.8	3.6	55

[a] Data for PGA—PEG300 were cited from ref 3.

[b] K=[—COOH]/[—OH], mol ratio of carboxyl groups in PGA to hydroxyl groups in PPG400 or PEG300 in reaction mixtures.

[c] Gel per cent, in DMF at 25°C.

[d] Density was measured by a flotation method using carbon tetrachloride and cyclohexane at 25°C.

[e] Crosslink density was calculated as in ref 3.

[f] Concentration of free carboxyl groups was calculated as in ref 3.

[g] Peak temperature of a E'' curve.

Table II. Characterization of PAA—PEG

	K[a]	g, %[b]	ρ, g/cm^3[c]	$\nu \times 10^3$, mol/cc[d]	T_g, °C[e]	E'_{150}, dyn/cm^2[f]
PAA—PEG300 (50/50)	2.1	97	1.255	3.6	33	2.0×10^8
PAA—PEG300 (60/40)	3.2	99	1.297	3.1	51	1.7×10^8
PAA—PEG300 (70/30)	5.0	94	1.310	1.9	57	1.2×10^8
PAA—PEG300 (80/20)	8.6	90	1.305	0.79	52	7.5×10^7
PAA—PEG600 (40/60)	2.6	91	1.251	2.3	−9	1.3×10^8
PAA—PEG600 (50/50)	4.1	99	1.272	2.1	22	1.5×10^8
PAA—PEG600 (60/40)	5.7	97	1.296	1.7	43	1.3×10^8
PAA—PEG600 (70/30)	9.4	96	1.312	0.89	44	5.8×10^7
PAA—PEG600 (80/20)	15.6	94	1.316	0.66	55	5.5×10^7
PAA—PEG1000 (40/60)	4.6	99	1.259	1.5	−18	1.2×10^8
PAA—PEG1000 (50/50)	6.9	98	1.268	1.2	3	8.0×10^7
PAA—PEG1000 (60/40)	10.4	99	1.292	1.0	36	6.8×10^7
PAA—PEG1000 (70/30)	15.9	99	1.310	0.76	46	5.1×10^7
PAA—PEG1000 (80/20)	29.4	97	1.307	0.41	50	3.8×10^7

[a] K=[—COOH]/[—OH], mol ratio of carboxyl groups in PAA to hydroxyl groups in PEG in reaction mixtures.
[b] Gel per cent, in water at 25°C.
[c] Density was measured by a flotation method using carbon tetrachloride and cyclohexane at 25°C.
[d] Crosslink density was calculated as in ref 3.
[e] Glass transition temperature was obtained by DSC measurements.
[f] Dynamic storage modulus at 150°C.

weights based on the determination of hydroxyl groups by acid-catalyzed acetylation[26] were 400 for PPG and 330, 583, and 1003 for PEG. They will be designated at PPG400, PEG300, PEG600, and PEG1000.

Poly(acrylic acid) [*PAA*]. Acrylic acid was polymerized in toluene with 0.2-wt% benzoyl peroxide at 80°C. Its molecular weight was 150,000, which was estimated from the intrinsic viscosity using the relation[27] $[\eta]=8.5 \times 10^{-4} M^{0.5}$.

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

Heterogeneous Network Polymers. The heterogeneous network polymers will be designated, for example, as PGA—PPG400 (70/30) to represent a heterogeneous network polymer made of PGA and PPG400 at 70 and 30% by weight, respectively.

PGA—PPG400, PAA—PEG300, PAA—PEG 600, and PAA—PEG1000 with systematically varied PGA or PAA content as 40, 50, 60, 70, and 80% by weight were synthesized as described in a previous paper except that the reaction temperature for PGA—PPG400 was 120°C because a macroscopic phase separation occurred at 100°C.

Characterization of the heterogeneous network polymers is shown in Tables I and II. In contrast to PGA—PEG300, gel per cents higher than 94% could not be attained for PGA—PPG400, presumably owing to the fact that PPG has a secondary hydroxyl group that is less reactive toward esterification than a primary one.

The densities of PGA—PPG400 are considerably lower than those of PGA—PEG300, and we shall discuss the densities in terms of the state of aggregation of PGA and PPG400, and the amount of the ordered domains.

The crosslink density, ν and the concentration of free carboxyl groups, C were determined as described in a preceding paper.[3]

The peak temperature of an E'' curve ($T_{E''\max}$) corresponds to the glass transition temperature.

Apparatus and Procedures

Dynamic Measurements. Dynamic measurements were made with a model DDV-IIc Rheovibron at 110 Hz in the temperature range of −120 to 200°C. The temperature was raised at a rate of 1.5—2.0°C/min.

Differential Scanning Calorimetry (*DSC*). The glass transition temperatures of PAA—PEG were determined using a Rigaku Denki differential scanning calorimeter under a heating rate of 10°C/min.

Polarizing Optical Microscopy. A Nikon polarizing optical microscope type LFG—Ke was used to observe the domain structure or optical anisotropy. Micrographs of thin specimens approximately 50 microns thick, sectioned parallel to the film surfaces with the use of a razor blade, were taken.

X-Ray Diffraction. Wide-angle X-ray diffraction patterns were obtained with a Rigaku Denki type D-3F X-ray generator. Nickel-filtered Cu—Kα radiation was used at 35 kV and 15 mA.

Infrared Absorption Spectroscopy. Infrared spectra of the heterogeneous network polymers were measured on a Perkin-Elmer Model 567 spectrophotometer using a multiple internal reflection (MIR) accessory.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of PGA—PPG400 and PGA—PEG300

The dynamic mechanical properties of a pure PGA film (hard component polymer) cast from DMF solution at 100°C were shown in a previous paper:[1] the peak temperature of a $\tan\delta$ curve was observed at around 130°C and E' at 200°C was about 1.2×10^9 dyn/cm^2.

PPG400 and PEG300 (soft component polymer), on the other hand, are in a liquid state at room temperature. According to Wetton, *et al.*,[28] poly(propylene oxide) ($\bar{M}_n=3\times10^5$) and

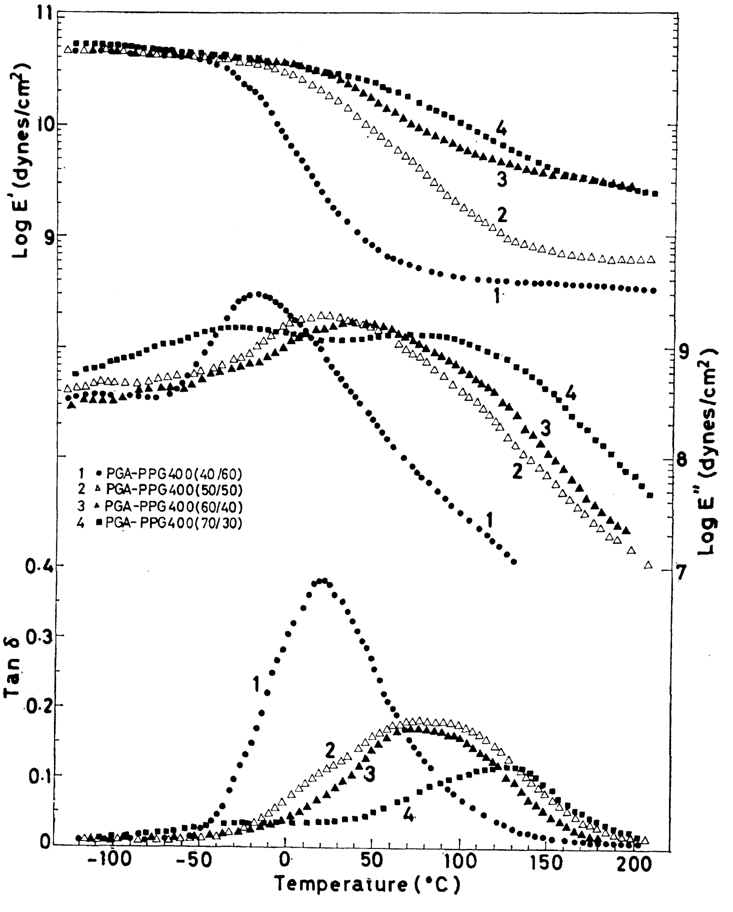

Figure 1. Dynamic mechanical properties of PGA—PPG400.

poly(ethylene oxide) ($\bar{M}_v=1.4\times10^6$) have glass transition temperatures of −75°C and −66.5°C, respectively.

The dynamic mechanical properties of PGA—PPG400 and PGA—PEG300 are shown in Figures 1 and 2, respectively.

With an increase in the PGA content (with a decrease in the crosslink density), the peaks of $\tan\delta$ and E'' shift to higher temperatures, $\tan\delta$ and E'' curves broaden and decrease in magnitudes, and E' above the transition region increases. These observations are interpreted as showing that the major factor that controls the dynamic mechanical properties of our PGA—polyether system is a copolymer effect and that the relaxation arises from the micro-Brownian motions of polyether segments and the PGA segments in the disordered region as mentioned in a previous paper.[3] These characteristic properties may be due to the existence of rigid PGA α-helices up to 200°C.

When the dynamic mechanical properties of PGA—PPG400 were compared with those of PGA—PEG300 at the same PGA contents, the following trends were recognized: (1) the peak temperatures of $\tan\delta$ and E'' shift to higher

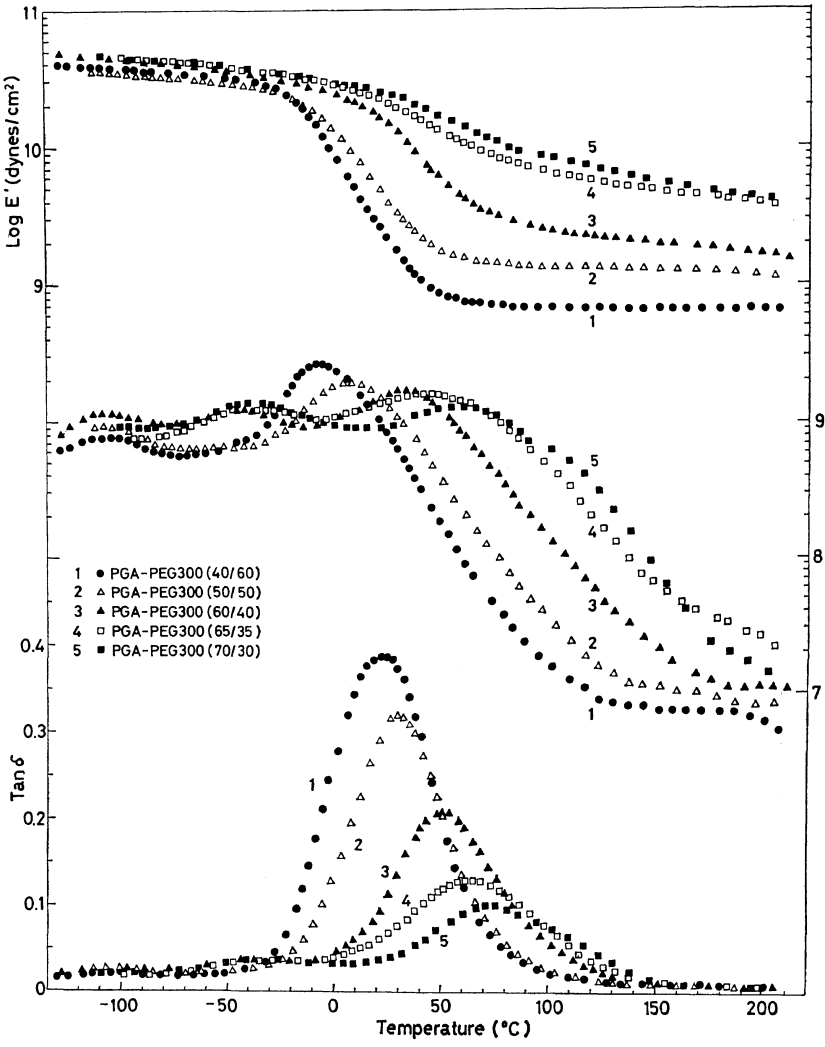

Figure 2. Dynamic mechanical properties of PGA—PEG300 (cited from ref 3).

temperatures; (2) tan δ and E'' curves broaden; (3) E' above the transition region decreases. These observations may be explained as follows. The reaction temperature of 120°C for the preparation of PGA—PPG400 was so high compared with 100°C for that of PGA—PEG300 that the proportion of the disordered region may have increased. This idea is supported by comparing the infrared spectrum of PGA—PPG400 (40/60) (Figure 9) with that of PGA—PEG900 (70/30) (prepared at 100°C) shown in a previous paper.[3] The amide V band, which is very sensitive to α-helix, β-form, and random coil conformations, varied little despite the difference in the composition, the reaction temperature, and the chemical structure of the soft component polymer. Thus, although we cannot differentiate α-helices in the ordered region from those in the disordered region, we may at least argue that the relative amount of α-helices did not vary much. Moreover, the polarizing micrographs shown in Figures 7 and 8 indicate that the fraction of disordered region in PGA—PPG400 is smaller than that in PGA—PEG300.

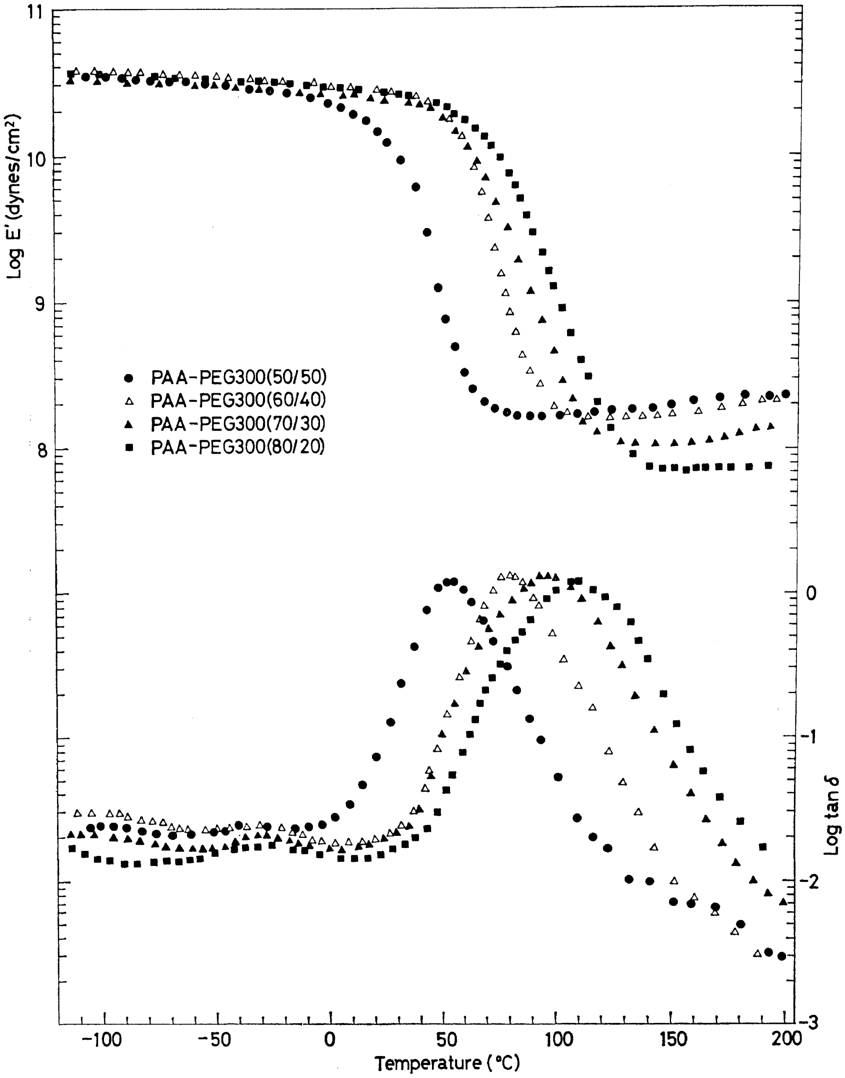

Figure 3. Dynamic mechanical properties of PAA—PEG300.

We may, therefore, conclude that the amount of α-helices in the ordered region decreased and that in the disordered region increased for PGA—PPG400.

Since it is almost certain that the relaxation arises from the micro-Brownian motions of PGA segments in the disordered region and PPG segments, the above observations (1) and (2) are attributed to the increase in the amount of PGA (hard component) in the disorderd region. Observation (3), however, may be due to the increase in the proportion of the disordered region to the whole polymer. Observation (2) may also be attributed to the poor solubility of PGA and PPG segments at the micro-structural level.

As Figure 1 shows, the relaxation curve of PGA—PPG400 (70/30) is very broad and similar to the curve of PGA.[1] On the other hand, the tan δ curve of PGA—PPG400 (40/60) is sharp and nearly symmetrical around the peak temperature. These results suggest that the phase inversion occurs at around 50-% PGA content. Each continuous phase is rich in PGA and PPG400 above and below the phase inversion region, respectively. This idea is supported by the polarizing microscopic photographs (Figure 7)

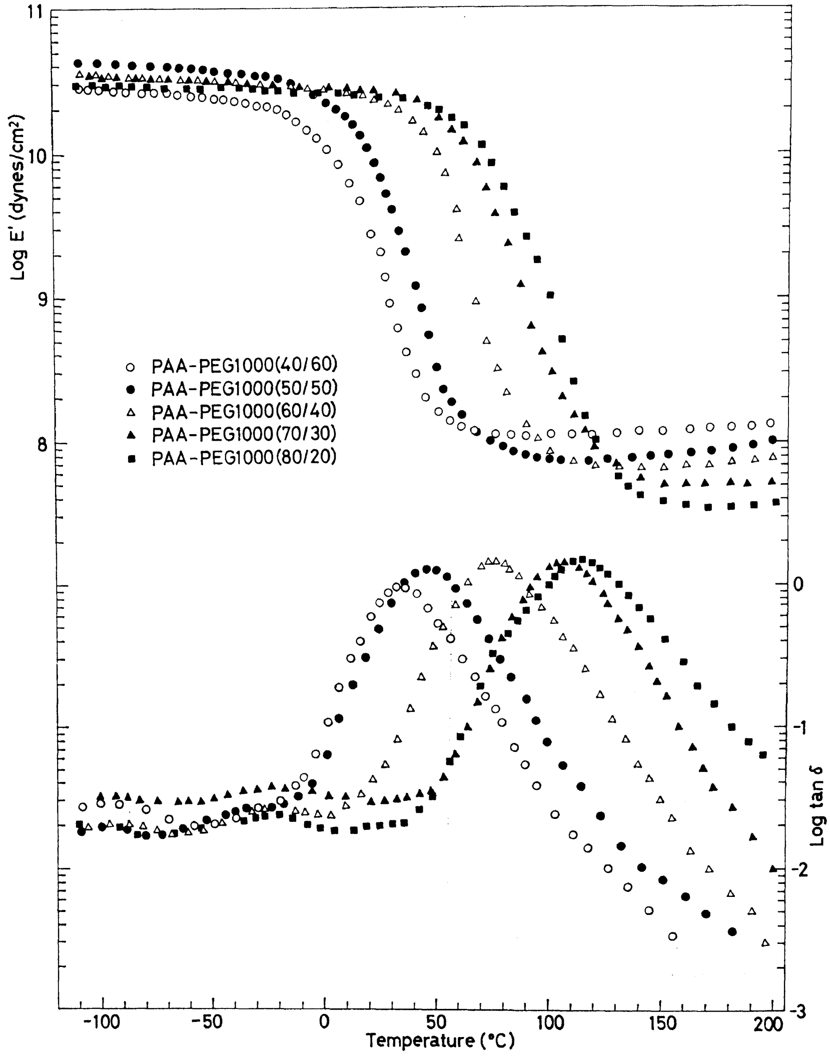

Figure 4. Dynamic mechanical properties of PAA—PEG1000.

and wide-angle X-ray analysis (Figure 10).

Dynamic Mechanical Properties of PAA—PEG300, PAA—PEG600 and PAA—PEG1000

The microscopic structures of PGA—PPG400 and PGA—PEG300 are very complicated, because PGA retains its various conformations such as α-helix or β- or random coils even after the heterogeneous networks are completed; moreover, the solid films of the heterogeneous network polymers are formed through a liquid crystalline state which is formed in the concentrated reaction mixtures. Some simplifying reference polymeric systems are, therefore, needed to unveil these complexities and to elucidate the role played by the "highly structured" PGA in the dynamic mechanical properties of the PGA—polyether heterogeneous network polymers.

Thus, amorphous network polymers were prepared from PAA and PEG. Their dynamic mechanical properties were studied with respect to the variations in composition and crosslink density; comparisons were made with the behaviors of PGA—PEG systems.

Some properties of the PAA—PEG polymers are given in Table II. The dynamic mechanical properties of PAA—PEG300 and PAA—PEG1000 are shown in Figures 3 and 4, respectively. The most striking characteristics of the properties are: (1) the dynamic storage moduli in the rubbery plateau regions E'_{150} are not dependent on the PAA content but vary almost in proportion to the crosslink density, as shown in Figure 5; (2) the magnitude of $\tan\delta_{\max}$'s ranges between 1.0 and 1.5 and is almost independent of the composition; (3) $T_{\tan\delta_{\max}}$ or the glass transition temperatures are primarily governed by the PAA contents, as shown in Figure 6——a similar tendency to that of PGA—PPG400 or PGA—PEG300. These observations were explained as follows. PAA—PEG are amorphous network polymers because PAA and PEG are compatible. In PAA—PEG, therefore, all of the PAA and PEG molecules are relaxed above the glass transition temperatures, and observations (1) and (2) are natural consequences. On the other hand, in PGA—PPG400 or PGA—PEG300, the rigid α-helical conformation of PGA in the ordered regions is retained even above the transition temperatures. The increase in the PGA (hard component) content, therefore, gives rise to the increase in E' above the transition region and the decrease in $\tan\delta_{\max}$. In general, T_g is affected by the composition (copolymer effect) and the crosslink density (crosslink effect). Based on observation (3), we may conclude that the copolymer effect predominates over the crosslink effect for our heterogeneous network polymers.

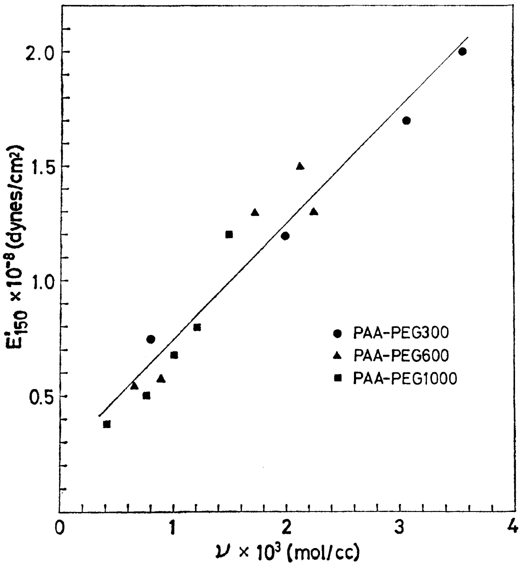

Figure 5. E' at 150°C versus crosslink density for PAA—PEG300, PAA—PEG600, and PAA—PEG1000.

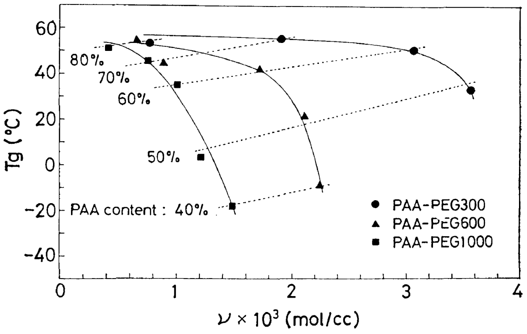

Figure 6. Effect of the composition and the crosslink density on T_g. T_g were measured by DSC.

Tobolsky, *et al.*,[29] synthesized amorphous network polymers by copolymerizing styrene, methyl methacrylate, and ethyl acrylate or octyl acrylate with tetraethyleneglycol dimethacrylate.

They discussed the dynamic shear modulus in the rubbery plateau region in terms of the equation of state for rubber elasticity. Our PAA—PEG is a system quite similar to their network polymers and, naturally, the E'_{150} values of PAA—PEG showed a tendency similar to theirs.

Polarizing Microscopy

In a previous paper,[3] we reported that PGA and PEG formed cholesteric liquid crystal phases in concentrated DMF solutions and these cholesteric liquid crystal phases were retained in the solid films of heterogeneous network polymers. Similar optically anisotropic regions were observed also in PGA—PPG400. The polarizing micrographs of PGA—PPG400 and PGA—PEG300 are shown in Figures 7 and 8, respectively. If a specimen of PGA—PPG400 (70/30) is rotated under crossed polarizers, most of the dark regions turn bright.

In PGA—PPG400 (40/60), on the other hand, most of the regions remained dark no matter how the specimen is rotated. Clearly the continuous phases are isotropic at 40-% PGA content and almost anisotropic at 70-% PGA content. In addition, the sizes of the anisotropic regions in PGA—PPG400 are small compared with those in PGA—PEG300 at the same PGA content. The densities of PGA—PPG400 shown in Table I are considerably smaller than those of PGA—PEG300 at the same PGA content. This may suggest that the amount of the anisotropic region decreases and/or the density of the anisotropic region becomes lower——seemingly contrary to our expectation. Because the compatibility of PGA with PPG400 is very poor, it is expected that PGA and PPG400 are apt to constitute separate domains, and the sizes of the anisotropic region should, therefore, become large and the amount of the anisotropic region should increase.

Actually, a macroscopic phase separation occurred when the reaction temperature was 100°C. But when the reaction temperature was raised to 120°C, the molecular motions of PGA

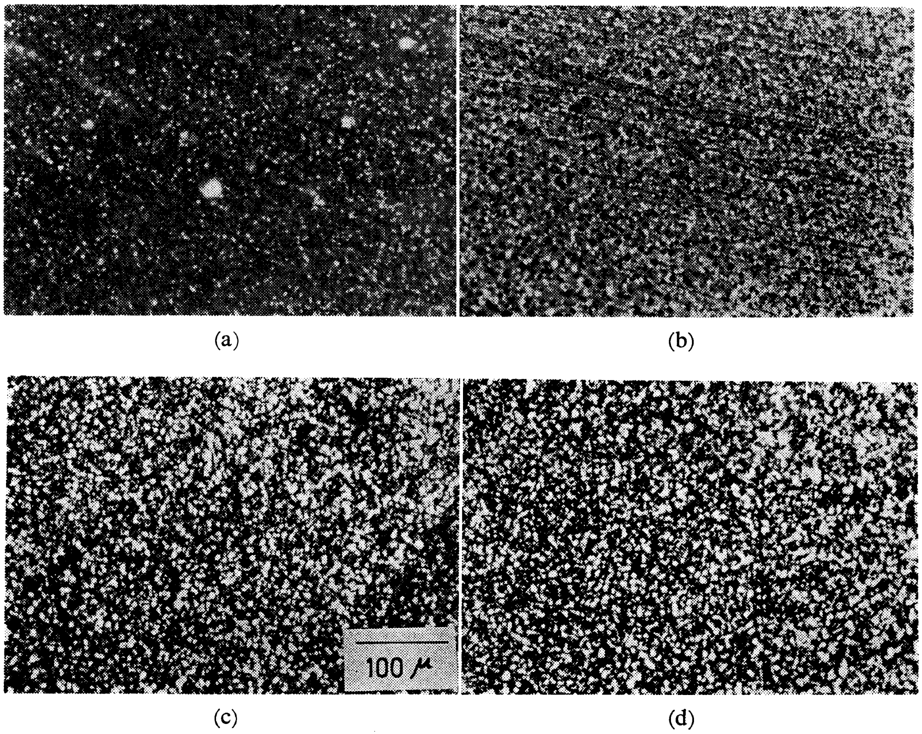

Figure 7. Polarizing micrographs of PGA—PPG400: (a) PGA—PPG400 (40/60); (b) PGA—PPG400 (50/50); (c) PGA—PPG400 (60/40); (d) PGA—PPG400 (70/30).

and PPG400 may become so vigorous that their ordering may become difficult and a macroscopic phase separation may not occur. This means that an increase in the compatibility of PGA with PPG400 caused by a rise of the reaction temperature from 100 to 120°C was more than enough to upset the expected decrease in the compatibility caused by the introduction of oxypropylene units.

Infrared Spectra

Figure 9 shows an infrared spectrum of PGA—PPG400 (40/60). Characteristic bands of α-helix appeared at $1645\,\mathrm{cm}^{-1}$ (amide I), $1540\,\mathrm{cm}^{-1}$ (amide II), and $610\,\mathrm{cm}^{-1}$ (amide V). There are also weak characteristic bands of β-form and random coil at $700\,\mathrm{cm}^{-1}$ and $650\,\mathrm{cm}^{-1}$, respec-

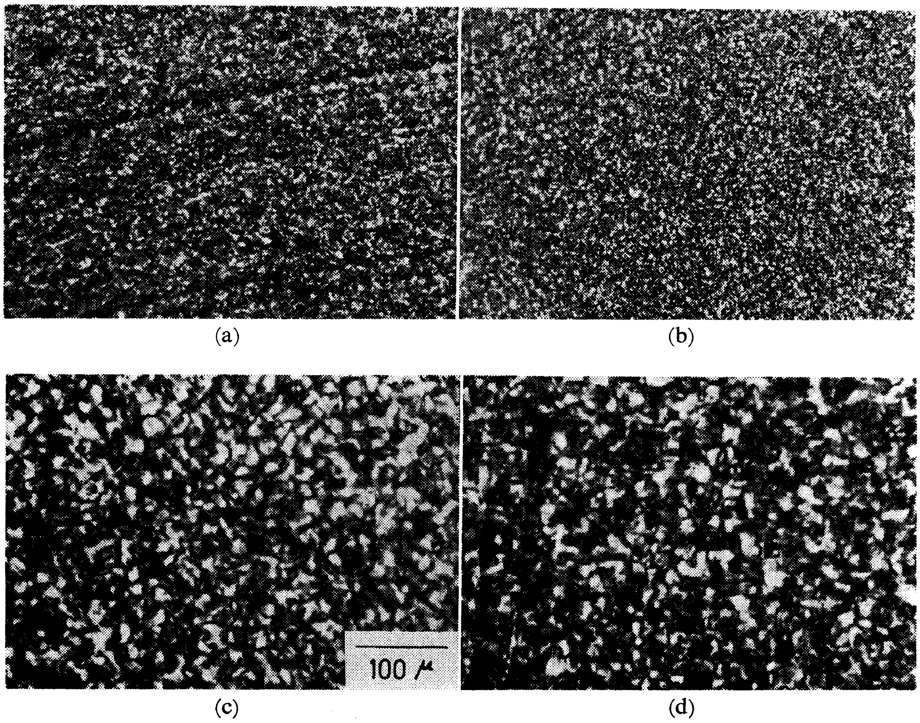

Figure 8. Polarizing micrographs of PGA—PEG300: (a) PGA—PEG300 (40/60); (b) PGA—PEG300 (50/50); (c) PGA—PEG300 (60/40); (d) PGA—PEG300 (70/30).

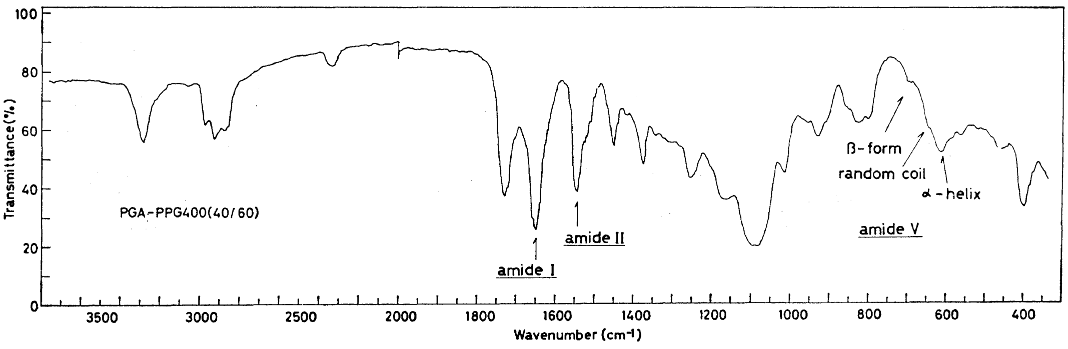

Figure 9. Infrared spectrum of PGA—PPG400 (40/60) measured by a multiple internal reflection method.

tively. A strong band at around 1090 cm^{-1} arises from C—O—C stretching vibration of PPG400. Thus most of the PGA chains retained the α-helical conformation.

X-Ray Diffraction

Wide-angle X-ray diffraction patterns of the heterogeneous network polymers were measured to investigate their microscopic structure. Every heterogeneous network polymer except PAA—PEG had a reflection at a Bragg angle of $2\theta = 5\sim9°$ which corresponded to the $(10\bar{1}0)$ plane of the hexagonal crystal lattice of PGA in α-helix. The lattice distance, $d_{10\bar{1}0}$, was plotted against the PGA content in Figure 10. Since $2d_{10\bar{1}0}/\sqrt{3}$ corresponds to the distance between neighboring α-helices, the inter-helix distance is shown to widen sharply with an increase in the PPG400 content up to *ca.* 50%; but above this content, the widening is only slight. Moreover, $d_{10\bar{1}0}$ of PGA—PPG400 is always longer than that of PGA—PEG300 at the same PGA content; at 40-% PGA content, the difference is 1—1.5 Å. This may be attributed to the geometrical difference of an oxyethylene unit and an oxypropylene unit, that is, a hydrogen atom with a van der Waals' radius of 1.2 Å is replaced by a methyl group with a radius of 2.0 Å in an oxypropylene unit. These observations indicate that both PEG and PPG chains are accommodated in the interstices among PGA α-helical chains, and this may account for the large difference in the densities between PGA—PPG400 and PGA—PEG300.

Structure of Heterogeneous Network Polymers

The chemical structure of the heterogeneous network polymers from PGA and PEG is represented schematically in Figure 11. The crosslinks are formed by esterification of the carboxyl groups of PGA with the hydroxyl groups of PEG.

The crosslink density and the content of free carboxyl groups vary with the relative content of PGA and PEG. A simplified model for the phase structure based on the dynamic mechanical properties, polarizing micrographs, X-ray studies, infrared spectra, etc., is illustrated in Figure 12. Most of the PGA chains are in α-helical conformation. The α-helices of PGA constitute the cholesteric liquid crystal domains by accommodating the PEG molecules among them. The α-helices in the cholesteric domains are packed

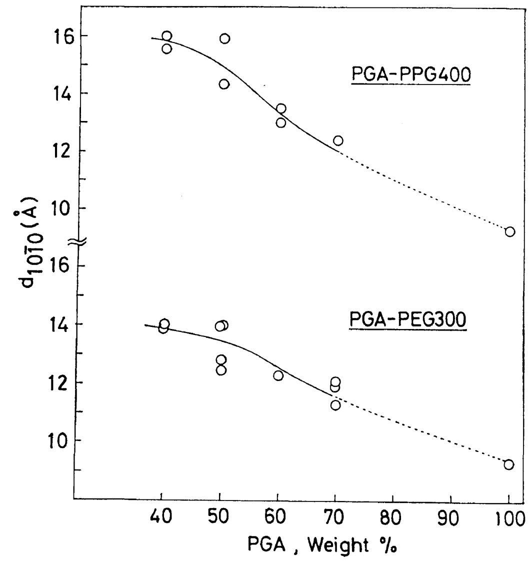

Figure 10. Plot of $d_{10\bar{1}0}$ *vs.* PGA content.

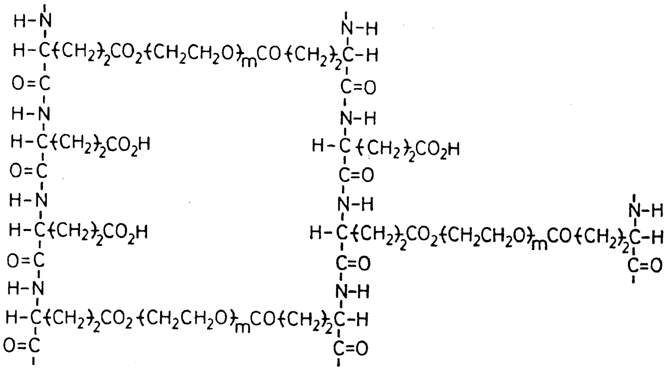

Figure 11. Chemical structure of PGA—PEG.

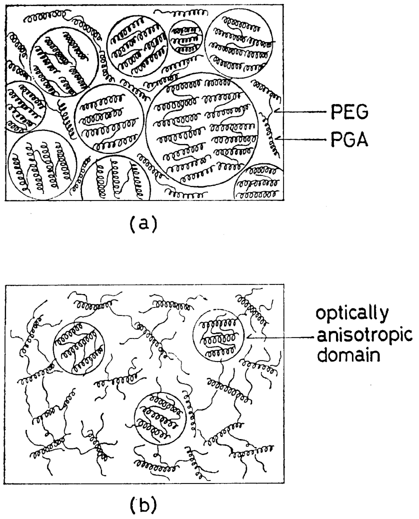

Figure 12. Schematic representation of the phase structure of PGA—PEG: (a) PGA content of 70%; (b) PGA content of 40%.

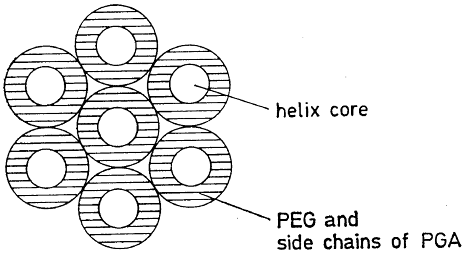

Figure 13. Schematic representation of α-helices packed on a hexagonal lattice.

on a hexagonal lattice, as shown in Figure 13.

PEG segments are accomodated among α-helices like the side chains of PGA. The size of the cholesteric domain varies from about 100 microns to below 1 micron with the PGA content, the molecular weight of PEG, the evaporation rate of DMF, etc. At the 70-% PGA content, the network polymers are composed of many cholesteric domains and, therefore, the PGA-rich phase constitutes the continuous phase. At the 40-% PGA content, on the other hand, the cholesteric domains are dispersed in the PEG-rich matrix.

CONCLUSIONS

Heterogeneous network polymers PGA—PPG400 were prepared from poly(L-glutamic acid) [PGA] and poly(oxypropylene) glycol [PPG, $\bar{M}_n=400$], systematically varying the PGA content to be 40, 50, 60, 70, and 80% by weight. Their dynamic mechanical properties and phase structure were compared with those of the heterogeneous network polymers PGA—PEG300 from PGA and poly(oxyethylene) glycol [PEG, $\bar{M}_n=330$] to study the effect of methyl groups of PPG400 on them.

When compared at the same PGA content, the PGA—PPG400 showed the following characteristics: (1) the dynamic mechanical $\tan\delta$ curves are much broader, (2) $\tan\delta$ peak temperatures are higher, and (3) E' above the transition regions are lower. These are explained by the difference in the compatibility between the component polymers and by the difference in the reaction temperatures.

X-ray diffraction patterns showed that every heterogeneous network polymer had crystallinity, and $d_{10\bar{1}0}$ corresponding to the distance between two adjacent PGA α-helices expanded with the increase in PPG400 content up to 50%; the widening almost ceased above this PPG400 content. The densities of PGA400 are considerably lower than those of PGA—PGA300.

Polarizing micrographs showed that optically anisotropic regions existed in the network polymers, and their sizes and amounts varied with the composition.

These observations indicate that the polyether chains are accommodated among the α-helices of PGA.

The dynamic mechanical properties of amorphous heterogeneous network polymers PAA—PEG from poly(acrylic acid) [PAA] and PEG were also compared with those of PGA—PPG400 and PGA—PEG300. The most striking characteristics of PAA—PEG were: (1) E' in the rubbery plateau region increases in proportion to the crosslink density; (2) the shape and the magnitude of $\tan\delta$ and E'' curves around T_g are not affected very much by the composition; and (3) the T_g is primarily affected by the PAA content. The main cause of the differences in the properties between PGA—polyether and PAA—PEG may be attributed to the existence of the α-helices of PGA or of the anisotropic regions.

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