Structure and Mechanical Properties of Poly(γ-methyl D-glutamate) Films. I. Influence of the Casting Solvents

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ABSTRACT: The effect of solvents on the structure and mechanical properties of cast films of poly(γ-methyl D-glutamate) (PMDG) was studied. The solvents used were chloroform, dichloromethane, 1,2-dichloroethane, and N,N-dimethylformamide. From X-ray diffraction measurements, it was found that films cast from chloroform and dichloromethane had a well-ordered structure consisting of α-helices packed on a regular hexagonal lattice, while films cast from N,N-dimethylformamide showed far less crystallinity. Circular dichroic studies showed that only those films cast from 1,2-dichloroethane maintained the same relative molecular disposition as in the cholesteric liquid crystal structure of the concentrated solution. The difference in the structure was reflected in the mechanical properties. Three types of relaxation phenomena were observed in the temperature range from 100 to 250°C, and they have been designated α_1, α_2, and α_3 dispersions in order of increasing temperature. These dispersions may be attributed to the molecular relaxation in the different phases, respectively.

KEY WORDS Casting Solvent / Poly(γ-methyl D-glutamate) / Cast Film / Cholesteric Twisted Structure / Mechanical Properties / Dispersion /

The concentrated solutions of PMDG in chloroform, 1,2-dichloroethane (EDC), dichloromethane (DCM), and *m*-cresol,[1] form mesomorphic phases akin to cholesteric liquid crystals. The molecules are packed approximately parallel, but with a small helical twist relative to one another about an axis perpendicular to the molecular axis. In consideration of the concentration dependence of pitch in cholesteric macrohelix,[1] it is easy to envisage that a somewhat similar structure is retained in the solid after all the solvent is removed. Tobolsky, *et al.*,[2] consider that poly(γ-benzyl L-glutamate) films cast from chloroform solutions contain paracrystalline and mesomorphic regions, and that in the latter region the cholesteric twisted structure is maintained.

Viscoelastic measurements have been carried out for several species of polypeptide films.[3-10] In the early studies of mechanical properties for PMG films, two dispersions have been observed,

and it has been presumed that a dispersion at about 0°C may be attributed to the side chain motion and another at 150°C to the segmental motion in the disordered part of main chains.[4] Recently, the relaxation mechanisms for two dispersions at about 160 and 180°C have been discussed on the basis of the molecular packing of α-helices.[7,10]

In spite of many investigations of structure and mechanical properties for PMDG films, systematical studies have not been performed in consideration of the casting process and/or in relation to the cholesteric liquid crystal structure in the concentrated solution. In this paper we report on the structure and mechanical properties of PMDG films cast from chloroform, DCM, EDC, and N,N-dimethylformamide (DMF) solutions, respectively.

EXPERIMENTAL

Materials

Films of PMDG (M_v=100,000) about 0.1—0.2 mm thick were cast from the solutions (about 3 vol%) in EDC, DCM, and chloroform. After casting, solid films were stripped off from the glass surface by immersing the film-covered glass plate into methyl alcohol, and were dried *in vacuo* at room temperature until all traces of solvent were removed. Observation by microscope showed that all films were obtained following formation of the cholesteric liquid crystal structure in concentrated solutions.

On the other hand, films cast from DMF were prepared after formation of the gel, since PMDG—DMF solution forms a thermally reversible gel on standing at room temperature. In this gel, the cholesteric liquid crystal structure was not observed throughout the concentration range. Therefore, the casting process of these films is very different from that of films cast from other solvents.

Methods

Dynamic mechanical measurements were performed with a Vibron viscoelastometer (Toyo Measuring Instrument Co., Ltd.), in the temperature range from −50 to 250°C at 110, 11, and 3.5 Hz. X-Ray diagrams were obtained by using Ni-filtered CuKα radiation. Infrared spectra were measured by use of JASCO Spectrophotometer over the region from 400 to 4000 cm^{-1}. Circular dichroism was measured by using a JASCO Automatic Recording Spectropolarimeter Model J–5. The incident light was irradiated at right angle to the film surface. Thermal measurements were made in a differential scanning calorimeter (Perkin-Elmer DSC–2) at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Structure of Cast Film

Figure 1 shows infrared spectra of thin films cast from chloroform, DCM, EDC, and DMF solutions. The spectra show a peak at 615 cm^{-1} (amide V), which indicates an α-helical conformation. The X-ray patterns are shown in Figure 2 and the interplanar spacings are listed in Tables I and II.

The X-ray diffraction diagram shows that PMDG films cast from chloroform solution are highly crystalline and α-helical molecules are packed into a hexagonal lattice.[11] The as-cast film shows, however, a 4.5-Å meridional reflection which was not reported by Bamford, *et al.*[11] As discussed by Johnson, *et al.*,[12] the existence of 4.5-Å reflection presumably assigned to 006 suggests that the side chains assume superstructure where the three residues make up an asymmetric unit as in the case of poly(L-alanine).[13,14] This is also supported by the fact mentioned below. The oriented film prepared by stroking the concentrated chloroform solution on a glass plate shows another new reflections corresponding to 111, 201, 211, and 104 reflections, as seen in the photographs of Figure 3. According to the diffraction theory of helical molecules by Cochran, *et al.*,[15] these reflections cannot be explained by the uniform α-helical conformation, but properly so by the side-chain structure mentioned above. These reflections, in addition to the 4.5-Å meridional reflection,
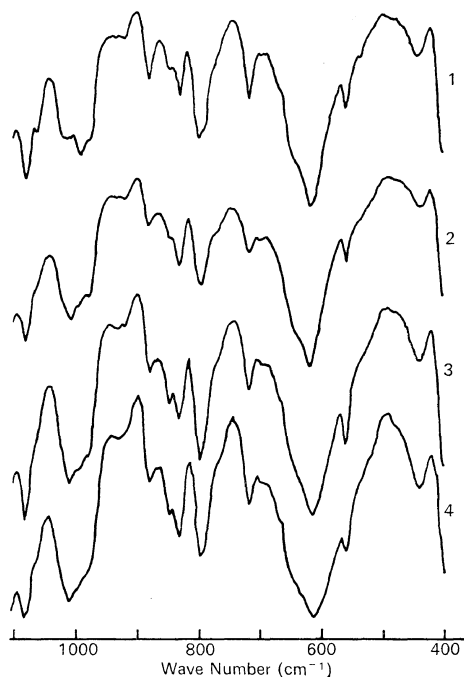

Figure 1. Infrared spectra for PMDG films. The code numbers, 1, 2, 3, and 4 show the films cast from chloroform, DCM, EDC, and DMF, respectively.

disappear by annealing the film at the temperature above 150°C (Figure 3). This result indicates that the side-chain structure mentioned above collapses around 150°C, although the 4.3-Å meridional reflection (appearing after annealing) cannot be elucidated very well. Furthermore, the original oriented film obtained by stroking the concentrated solution showed the layer-line streaks clearly, which were remarkably weakened by annealing above 150°C. These streaks are considered to be due to the translational disorder along the chain direction or due to the randomness of chain sense. Such types of disorder seem to remain to some extent, even in the annealed film.

Discussion of the molecular arrangement and packing of helical molecules in the solid state has been confined to the oriented films and
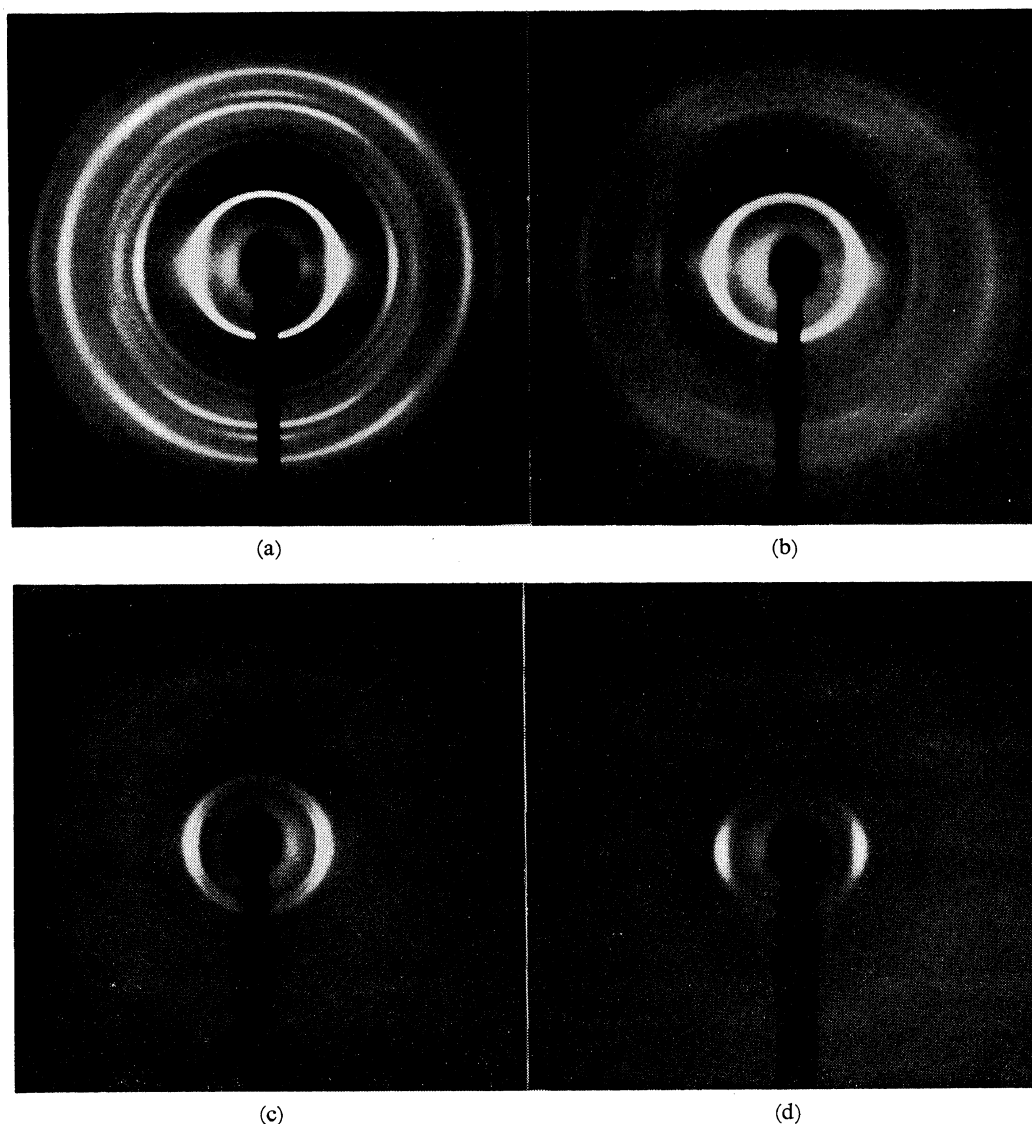
Figure 2. X-Ray diffraction photographs of (a) the film cast from chloroform, (b) the film cast from DCM, (c) the film cast from EDC, and (d) the film cast from DMF. CuKα radiation. The X-ray beam was irradiated parallel to the film surface.

fibers. Consequently, there has been no detailed discussion for the as-cast films. The structure of the as-cast films must be closely related to the cholesteric liquid crystal structure in the higher concentrated solution. We observed by a microscope uniform retardation lines due to the cholesteric twisted structure in the concentration range of 10 to 40 wt%. In this concentration range, the pitch (50 microns—few microns) de-

Table I. X-Ray diagram of PMDG film cast from chloroform

hkl	d_{calc}, Å[a]	Original d_{obsd}, Å	Annealed at 150°C for 10 min. d_{obsd}, Å
100	10.36	10.36	10.36
110	5.98	5.96	5.98
112	5.47	5.47	5.47
200	5.18	5.16	5.18
105	4.79	4.80	4.80
—	—	4.50	—
—	—	—	4.30
115	4.01	4.00	4.00
210	3.91	3.89	3.89
205	3.74	3.74	3.74
300	3.45	3.45	3.46

[a] Calculation is based on the hexagonal unit cell of $a=b=11.95$ Å and $c=27$ Å.

Table II. X-Ray diffraction pattern of PMDG films

(a) Film cast from DCM solution

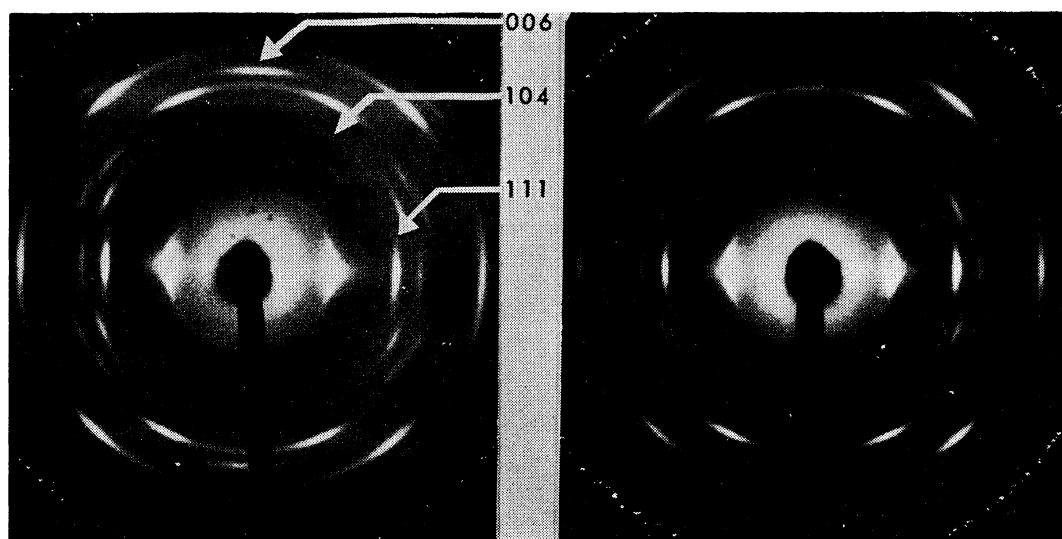| Original	Annealed at 130°C for 1 hr
d, Å	d, Å
11.20	—
10.33	10.36
8.16	—
5.98	5.95
5.52	5.52
5.16	5.17
4.91	4.83
4.52	4.51
3.91	3.89

(b) Film cast from EDC solution

d, Å
11.9
10.5
7.76
5.7 diff
5.2 diff

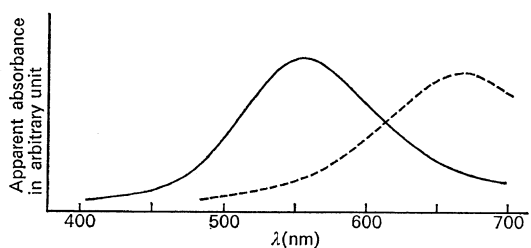(c) Film cast from DMF solution

d, Å
11.0
5.3 diff

Figure 3. X-Ray diffraction photographs of the oriented film prepared by stroking the concentrated chloroform solution: (a), the original film; (b), the film annealed at 200°C.

creased as the concentration increases. The well-defined hexagonal pattern of the film cast from chloroform solution, however, shows that no cholesteric twisted structure exists. Thus it is concluded that the cholesteric twisted structure must collapse at the higher concentration above 40 wt%.

The X-ray diagram of PMDG film cast from DCM solution is shown in Table II(a). The major reflections observed can be indexed on the basis of the same hexagonal unit cell as in the PMDG film cast from chloroform solution. Two reflections of 11.2 and 8.2 Å, however, cannot be interpreted in terms of the hexagonal unit cell. Moreover, these two reflections were found to disappear by heating at 130°C for 1 hr, while the hexagonal diffraction pattern was not affected. It is thus concluded that this film contains the hexagonal crystalline region and the region characterized by two reflections of 11.2 and 8.2 Å.

In Table II(b), the PMDG films cast from EDC solution show several diffuse reflections which have been explained by an orthorhombic or monoclinic unit cell by Sasaki, et al.[16] From circular dichroic measurements, we have found that these films have a cholesteric twisted structure.[17] The results of circular dichroism (CD) for the film cast from EDC solution are shown in Figure 4, where the CD is expressed as the apparent absorbance of the left circularly polarized light minus that of the right one. The CD curve indicates the large positive band with a peak in the region 500—600 nm. This band is due to the selective reflection of the left circularly polarized light caused by the uniform cholesteric twisted structure.[17-20] The wave-

Figure 4. Circular dichroism of the film cast from EDC solution: ——, the original film; ----, the film immersed in methyl alcohol. The incident light was cast at right angle to the film surface.

length at peak maximum, λ_m, in the CD curve was 550 nm. Using the equation $\lambda_m = n \cdot P$ where n and P are the average refractive index ($n=1.4$) and the pitch of the cholesteric twisted structure, respectively, we obtained 390 nm for P.

When this film is immersed in methyl alcohol, the CD peak shifts to the higher wavelength (Figure 4), and the pitch becomes longer by amount of 15—20%. This increase in the pitch corresponds to that of interchain distance estimated from X-ray measurements for the film immersed in methyl alcohol.[16] It can be thus concluded that the film cast from EDC solution has a uniform cholesteric twisted structure and that the several reflections in the X-ray diagram arise from such a cholesteric twisted structure on contrary to the explanation by Tobolsky, et al., for the structure of cholesteric mesophase of poly(γ-benzyl L-glutamate) film cast from chloroform solution.[2]

The PMDG film cast from DMF solution shows only one diffuse reflection as seen in Table II(c), and far less crystallinity compared to the other three films. It should be emphasized that this film was prepared after the gel formation of an isotropic solution and that in the whole concentration range the cholesteric liquid crystal structure was not observed by microscopy. The structure of this film, therefore, is free from the cholesteric liquid crystal structure.

As mentioned above, the structures of the PMDG films prepared in this experiment are classified into three types. The phases observed in the films cast from chloroform or DCM solution, from EDC solution, and from DMF solution are conveniently named phase C, phase M, and phase I, respectively.

DSC Thermograms

DSC thermograms for the PMDG film cast from chloroform solution are shown in Figure 5(a), in which two thermal transitions are observed. One endothermic peak which disappears in the second heating, is observed at about 140°C. The other peak is reproducibly observed at about 170°C. The former peak can be closely related to the breakdown of a superstructure in the side chains as predicted from X-ray measurements, since the sharp meridional reflection
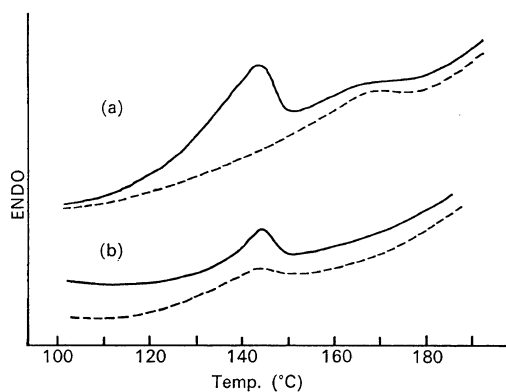
Figure 5. DSC thermograms of (a) the film cast from chloroform and (b) the film cast from DCM: ———, first heating; ———, second heating.

due to 006 planes does also disappear by heat treatment at 150°C (see Table I). Recently, from dielectric studies on the side-chain rotation, we have found that the dielectric increment, $\Delta\varepsilon$, estimated from Cole—Cole plots increases remarkably through heat treatment at a temperature above this transition.[21] These results suggest that in the original film cast from chloroform there exists a superstructure which may restrict the side-chain motion. On the other hand, we were not able to clarify what sort of the structural change corresponds to the latter peak at 170°C.

In Figure 5(b), similar endothermic peaks as in the film cast from chloroform are observed for the film cast from DCM, while no peaks can be observed for the films cast from EDC and DMF. Therefore, the structural changes corresponding to these endothermic peaks seem to occur in the phase C.

Dynamic Mechanical Properties

The results of dynamic mechanical measurements are shown in Figures 6, 7, 8, and 9 for the films cast from chloroform, DCM, EDC, and DMF, respectively, where tan δ are plotted against temperature. In all the films, a peak in tan δ is observed at about 0°C. This is attributed to the onset of the side-chain motion. However, there are notable differences in the temperature dependence of tan δ above 100°C. From IR measurements, we have already concluded that all of the films consisted of α-helical molecules. Therefore, the relaxations above

100°C could be attributed to the motion of α-helices in the region with the different melecular packing and to the mutual displacement of the crystallites,[7,10] since it is unlikely that they may be caused by the segmental motion in the disordered part of main chains.
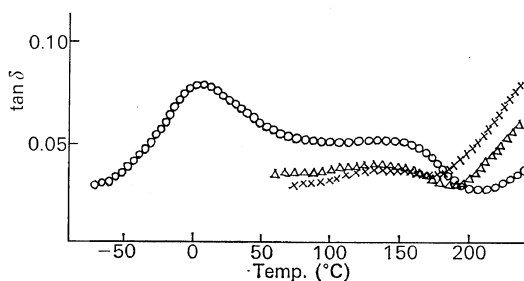
The film cast from DMF solution shows a
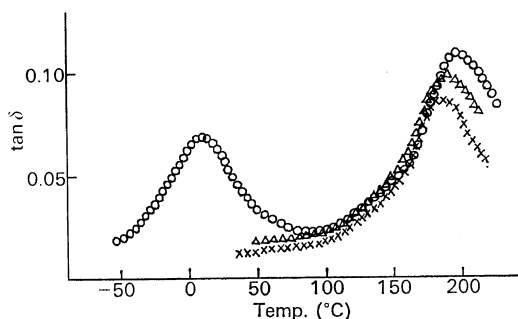
Figure 6. Plots of tan δ vs. temperature for the PMDG film cast from chloroform. The data were obtained at 110 Hz (○), 11 Hz (△), and 3.5 Hz (×).
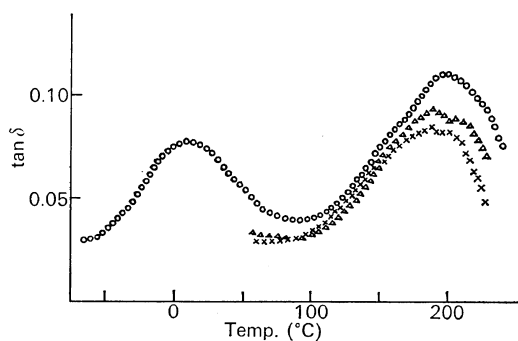
Figure 7. Plots of tan δ vs. temperature for the PMDG film cast from DCM. The data were obtained at 110 Hz (○), 11 Hz (△), and 3.5 Hz (×).
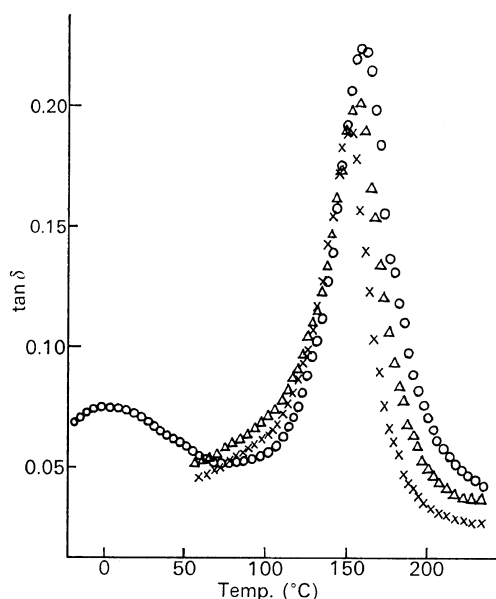

Figure 8. Plots of tan δ vs. temperature for the PMDG film cast from EDC. The data were obtained at 110 Hz (○), 11 Hz (△), and 3.5 Hz (×).

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Table III. High-temperature relaxation of poly(γ-methyl-D-glutamate) films

		High-temperature relaxation, °C		
		α_1 dispersion	α_2 dispersion	α_3 dispersion
Films cast from chloroform and dichloromethane	Phase C		190°C	
Films cast from 1,2-dichloro-ethane	Phase M	160°C		above 200°C
Films cast from N,N-dimethyl-formamide	Phase I	160°C		

Figure 9. Plots of tan δ vs. temperature for the PMDG film cast from DMF. These data were obtained at 110 Hz (○), 11 Hz (△), and 3.5 Hz (×).

large peak at 160°C (called α_1 dispersion), and the films cast from chloroform and DCM solutions show noticiably a peak at 190°C (α_2 dispersion). On the other hand, the film cast from EDC solution shows a very small peak at 160°C and a gradual increase of tan δ above 200°C (α_3 dispersion). The temperature at maximum peak of the α_3 dispersion was not determined, since a mechanical measurements could not be carried out above 250°C. In consideration of the dispersion temperature, the small peak at 160°C could be closely connected with the α_1 dispersion observed for the film cast from DMF, although there is a significant difference in the peak height. The increase of tan δ above 200°C

was not observed for the films cast from chloroform, DCM, and DMF, showing that this increase of tan δ is due not to the thermal decomposition, but rather to some kind of molecular relaxation. We have found that the cholesteric twisted structure of the phase M is stable on heating up to 180°C but this characteristic structure gradually collapses above 200°C as the result of the molecular rearrangement from twisted array to parallel one of α-helices.[17,22] Such a molecular rearrangement should be caused by the anharmonic molecular motion of α-helices in the phase M. Thus, the α_3 dispersion may be attributed to the molecular motion of α-helices in the phase M. The results show that the dispersions are classified as α_1, α_2, and α_3 dispersions, in order of increasing temperature, and that they are related to the molecular relaxation in the phase I, phase C, and phase M, respectively (Table III).

If the molecular motion responsible for the dispersion above 100°C may be confined to such a molecular motion of α-helices as pointed out by Kajiyama, et al.,[10] it is reasonable that the α_1 dispersion temperature is lower than that of the α_2 dispersion. However, it seems unreasonable that the α_3 dispersion temperature is higher than that of the α_3 dispersion, since the crystallinity of the phase C is much higher compared to that of phase M. This curious phenomenon may be explained by the fundamental difference between the molecular arrays of the α-helices in the phase C and phase M as mentioned above. If not so, it is necessary to consider the other type of the molecular relaxation for these dispersions.

The detailed examination for the mechanical properties of PMDG films is in progress. In the near future, the relationship between the

structure and these dispersions, and further the relaxation mechanism for them will be discussed.

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