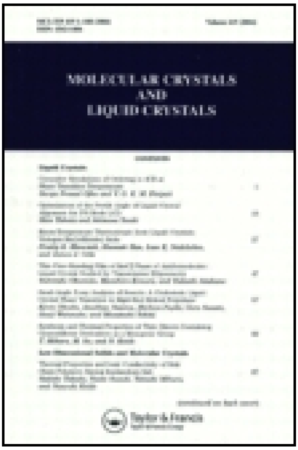

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Liquid Crystal Formation of Poly(γ-n-Alkyl D-Glutamate)S Having Long Alkyl Side Chains

Ryuichi Sakamoto [a] & Akito Osawa [a]

[a] Department of Textile Engineering, Faculty of Engineering, Gifu University, 1-1, Yanagido, Gifu, Gifu, 501-11, Japan

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LIQUID CRYSTAL FORMATION OF POLY(γ-*n*-ALKYL D-GLUTAMATE)S HAVING LONG ALKYL SIDE CHAINS

RYUICHI SAKAMOTO AND AKITO OSAWA
Department of Textile Engineering, Faculty of Engineering, Gifu University, 1-1, Yanagido, Gifu, Gifu 501-11, Japan

ABSTRACT Poly(γ-*n*-alkyl D-glutamate)s having alkyl side chains longer than decyl form a cholesteric liquid crystal phase in the solutions of helicogenic solvents. In the lower temperature range, the side chains of these polymers more or less crystallize, and above the melting temperature of the side chain crystallites the polymers are assumed to be in liquid crystalline state. It was found that these polymers form both lyotropic and thermotropic liquid crystal phases.

INTRODUCTION

It is well known that polyglutamic acid esters form lyotropic cholesteric liquid crystal in the solutions of various helicogenic solvents, and many investigations have been carried out[1].

On the other hand, the dynamic mechanical properties of polyglutamic acid esters have also been studied in solid state. Poly(γ-methyl L-glutamate) that has the shortest side chain shows three peaks of tan δ. The tan δ peak around 0°C (β-dispersion) is assigned to the glass transition of side groups of polymer and that around 150°C (α-dispersion) is assumed to be the motion of the rigid rod-like skeleton in rubber-like side groups[2]. The above results have suggested that poly(γ-methyl L-glutamate) in solid state consists of two phases; one is the rigid rod-like skeleton and the other is the flexible side chains. In the case of poly(γ-*n*-alkyl glutamate)s having longer alkyl groups than methyl, the temperature of β-dispersion decreases with the increase in the length of side chain from ethyl to octyl esters, and thereafter increases[3,4,5]. The alkyl side chains of the polymer having longer alkyl groups than decyl can crystallize and above the melting temperature of side chain crystallites the polymer becomes liquid crystalline state[5,6] .

In this study, the samples of poly(γ-*n*-alkyl D-glutamate)s having decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl side groups were prepared. The solution properties of the samples were measured and the formation of liquid crystal in solution was observed under a polarized microscope. And, then, the dynamic mechanical properties, the thermal analysis, and the observation under a polarized microscope were performed for the films of these polymers cast from solution. The possibility of the formation of the thermotropic liquid crystal was discussed on the basis of the experimental results.

EXPERIMENTAL

Materials

The samples of poly(γ-*n*-alkyl D-glutamate)s were prepared by the alcoholysis of poly(γ-methyl D-glutamate)(PMDG) with the corresponding higher alcohols. PMDG gel (Ajicoat-2000, provided by Ajinomoto Co.) was dissolved in dichloroethane or benzene, and excess of the corresponding alcohols and a small amount of sulfric acid were added. Then, the mixture was heated for a week under refluxing. The product was poured into a large amount of methanol and the polymer was precipitated. The precipitate was dried *in vacuo*. The purification of the polymer was made by the reprecipitation with benzene and methanol. The polymer was again dissolved in benzene and lyophilized. The degree of substitution was checked by NMR spectra of the resulting polymer in trifluoroacetic acid or in deuterized chloroform. Since the signal of the methoxyl group almost disappeared, the ester exchange reaction was assumed to be nearly completed.

Films of poly(γ-*n*-alkyl D-glutamate)s (PRDG) were cast on a glass plate floating on mercury from 4% chloroform solution. The resultant films were immersed in methanol, and then were dried *in vacuo* for several days.

Procedures

Number average molecular weight of the samples was determined using Wescan high-speed membrane osmometer in cyclohexanone at 40°C.

Vicosity measurements of the solutions of the samples were made using Ubbelohde type viscometer at 25°C.

Dynamic mechanical measurements of PRDG films were carried out using Rheovibron DDV-II (Toyo Baldwin Co.) at 3.5, 11, 35 and 110 Hz and in the temperature range from -170 to 200°C.

Thermal analysis of the samples was performed using a differential scanning calorimeter DSC-8230 (Rigaku Denki Co.).

Microscopic observation of the solutions and the films of PRDGs was made under a polarized microscope with a hot stage.

RESULTS AND DISCUSSION

It is found by the comparison of the intrinsic viscosity that PRDGs are almost molecularly dispersed in chloroform and cyclohexanone. Solution properties of the samples are shown in Table 1.

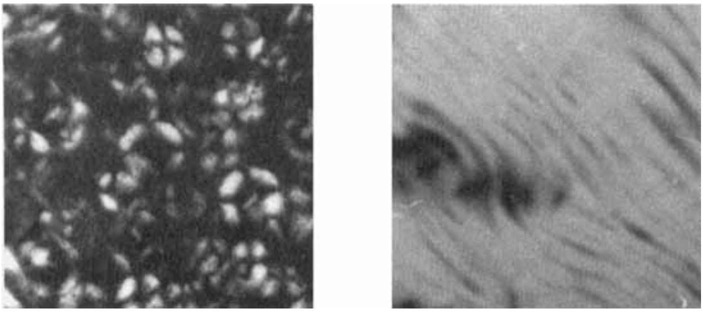
Table 1. Solution properties of PRDG samples.

Carbon No. of side chain	D.S.	$\overline{Mn}x10^4$	[η](g/dl) cyclohexanone	[η](g/dl) chloroform
10	0.91	11.3	3.00	4.40
12	0.88	12.5	2.88	3.80
14	0.80	19.7	2.54	3.05
16	0.90	9.0	2.79	3.60
18	-	9.2	1.68	2.50

D.S.: degree of substitution determined by NMR spectra.

Figure 1 shows the polarized microphotographs of the solutions of poly(γ-octadecyl D-glutamate). The photographs show the coexistence of the liquid crystal and the isotropic solution and also show the typical cholesteric texture. 4% chloroform solution used for the casting of films is isotropic, but there is the possibility of the liquid crystal formation in the process of casting.

Figure 2 shows the temperature dependence of tan δ of PRDG films. Three maxima of tan δ are found at least for each sample. They are called α, β and γ in order of



(a) 8% in cyclohexanone (b) 10% in chloroform

Figure 1. Polarized microphotographs of the solution of poly(γ-*n*-octadecyl D-glutamate).

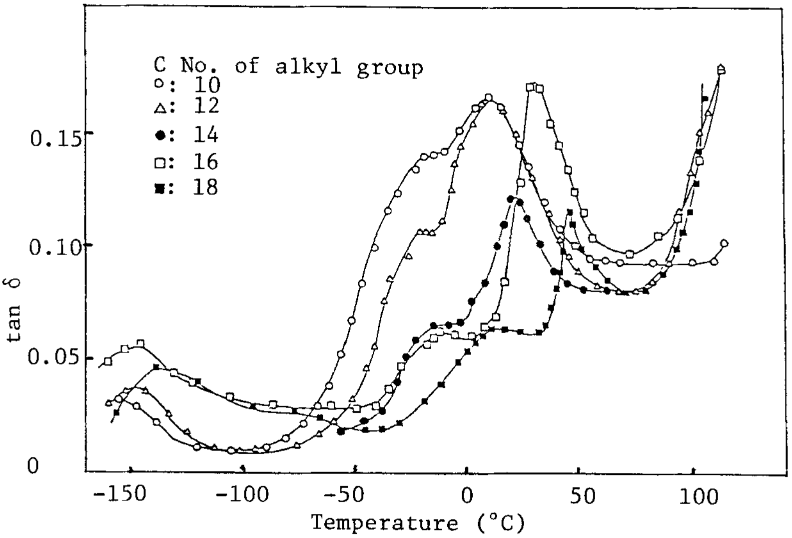


Figure 2. Temperature dependence of tan δ of PRDGs.

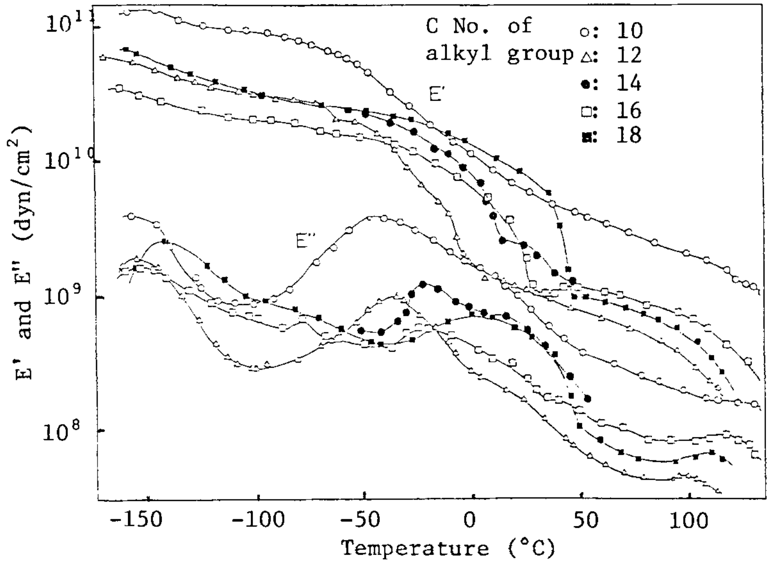


Figure 3. Temperature dependence of dynamic modulus E' and dynamic loss E" of PRDGs.

decreasing temperature. γ-dispersion found around -150°C does not depend on the side chain length. This dispersion is attributed to the onset of the rotation of the terminal methyl group of the side chain. The temperature of β-dispersion increases with the increase in carbon number of the side chain. This dispersion seems to be the glass transition of the side chain because the tan δ peaks are remarkably dependent on frequency. These results suggest that the intermolecular interaction in the polymer having longer alkyl groups than decyl becomes stronger with the increase in the carbon number of the side chains. The temperature of α-dispersion also increases with the increase in the carbon number of side chains. Figure 3 shows the dynamic modulus E' and the dynamic loss E" of PRDG films. Above the temperature of α-dispersion E' decreases strikingly to 1/10 of that below α-dispersion. From these results α-dispersion is assumed to be the melting of the crystal of the side chains. The peaks of E" appear in the similar temperature ranges as those of tan δ. Above results are almost similar to those reported by Watanabe *et al.*[5].

Figure 4 shows the DSC thermogram of PRDGs. The first order tran-

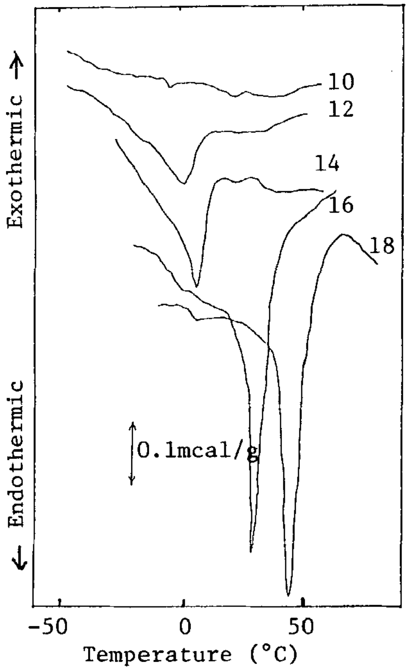


Figure 4. DSC thermogram of PRDGs.

Table 2. Tan δ peaks and DSC features of PRDGs having long alkyl side chains.

Carbon No. of side chains	tan δ			DSC	
	α	β	γ	Tm	Tg
10	13	-39	-150	-13.4	-49.2
12	14	-32	-150	-4.5	-35.5
14	17	-27	-	17.5	-
16	32	-24	-150	34.7	-6.8
18	47	3	-140	52.0	5.2

sition is observed for each polymer, and the transition temperature and the quantity of heat of transition increases with the increase in the carbon number of the side chains. The glass transition temperature Tg is also assigned from the shift tempereature of base line. In table 2 tan δ peak temperatures and Tm and Tg obtained by DSC measurement are shown. α-dispersion temperature almost agrees with Tm for tetradecyl, hexadecyl and octadecyl esters. For decyl and dodecyl esters, α-dispersion temperature does not show good agreement with Tm. This disagreement seems to be their low degree of crystallization. β-dispersion temperature also agrees with Tg approximately. The quantity of heat of transition increases with the increase in the length of side chain.

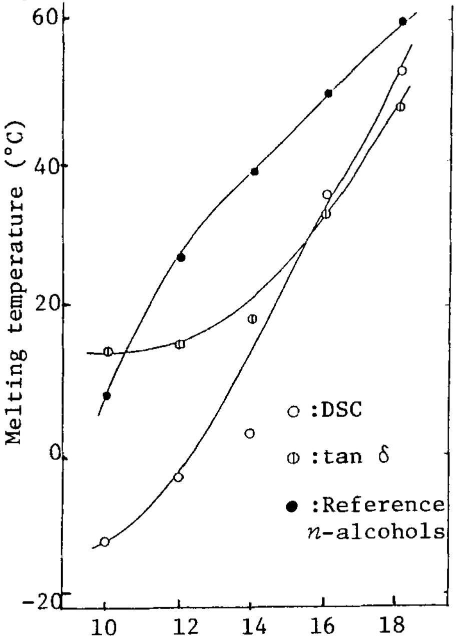
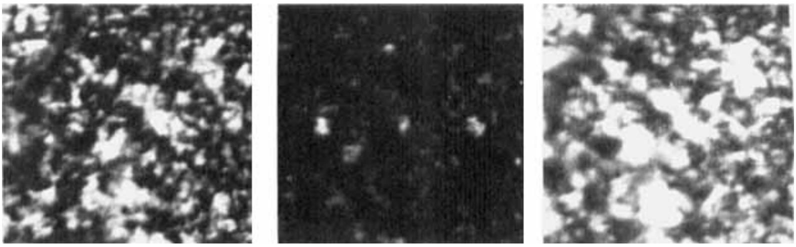


Figure 5. Melting temperature of PRDGs vs. carbon number of alkyl group.

This result means that the degree of crystallization increases with increasing side chain length. Figure 5 shows the comparison of the melting temperature of side chains of PRDGs obtained by the dynamic mechanical measurement with those obtained by DSC measurement. The melting points of the corresponding higher *n*-alcohols are added as a reference.

The films of PRDGs show birefringence both below and above the melting temperature. This result suggests that PRDGs become liquid crystalline state above their melting temperature of the side chains. The flexible side chains seem to behave as a solvent. In Figure 6 the polarized microphotographs of the film of poly(γ-*n*-octadecyl D-glutamate) are shown. The photographs show the same texture both below and above Tm, but the microscope field of view becomes dark around Tm. When the sensitive color plate is inserted in the light path of the microscope, each domain appears yellow or blue below Tm and the color of each domain becomes inverse above Tm. Around Tm the field of view becomes purple. The cause of these phenomena is unknown.



(a) below Tm (b) around Tm (c) above Tm

Figure 6. Polarized microphotographs of the film of poly(γ-*n*-octadecyl D-glutamate).

Thierry, Skoulios *et al.*[6] studied the thermotropic polynorphism of poly(γ-*n*-dodecyl L-glutamate) by X-ray diffraction. They found two transitions around room temperature and around 125°C. They assumed that in the lower temperature range the side chains are in crystalline state and the main chain is in β-form, and that above 125°C the polymer is in the nematic phase. In our study, the first-order transition has also been found around 140°C for poly(γ-*n*-dodecyl D-glutamate), but any evidence of the existence of β-form has not been observed in the lower temperature range. Thierry *et al.*[6] also observed a strong hysteresis of the melting temperature of the side chain crystallites. The authors have also observed similar hysteresis by the DSC measurement, but the difference between the melting temperature on heating and that on cooling has been only 4°C, whereas the same difference in the study of Thierry *et al.* was about 20°C.

From the results of this study and those of other investigators it is concluded that poly(γ-*n*-alkyl D-glutamate)s having long alkyl side chains form both lyotropic and thermotropic liquid crystalline phase.

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