

## Molecular Aggregation of Poly( $\gamma$ -Phenacyl L-Glutamate) in *N,N*-Dimethylformamide

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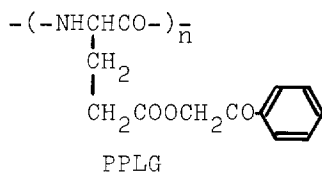
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### SUMMARY

Gel formation and the melting of solutions of poly( $\gamma$ -phenacyl L-glutamate) in DMF were investigated up to 40 wt% of polymer concentration. Two thermally reversible transitions were observed around 24°C and 55°C. The transition temperatures were almost independent of the concentration. The transition at 24°C was considered to be due to the collapse of the order in side-chain structures. The transition from gel into isotropic or cholesteric liquid-crystal phase occurred in the 50-60°C range, above which the gel rigidity and an X-ray reflection of about 40 Å suggesting a complex phase disappeared.

### INTRODUCTION

A right-handed  $\alpha$ -helical conformation was proposed for poly( $\gamma$ -phenacyl L-glutamate) (PPLG) in some solvents by Heitz et al. (1973 and 1975).



They reported that there is a sharp transition near 25°C in *N,N*-dimethylformamide (DMF) or pyridine, below which temperature strong interactions between side chains occur and gel formation is observed even at concentration as low as 0.002 g ml<sup>-1</sup>, while heating above 35°C leads to molecularly-dispersed solutions. Their work was confined to dilute solutions. In the present work, gel formation and the melting of PPLG solutions in DMF were studied up to 40 wt% of polymer concentration.

## EXPERIMENTAL

A polymer sample was synthesized by the N-carboxyanhydride method in dichloromethane by using triethylamine as the initiator. The intrinsic viscosity in DMF at 60°C was 120 ml g<sup>-1</sup>, corresponding to the molecular weight of about 140000 (Heitz et al. 1973). The solvent, DMF, was distilled and kept in a dry box. The polymer was dissolved in DMF by heating above 60°C.

X-ray diffraction patterns were taken by using the Ni-filtered Cu K $\alpha$  radiation for the solution sealed in a glass-capillary tube with a diameter of about 1 mm. Thermograms of differential scanning calorimetry (DSC) were recorded with a Perkin Elmer DSC II at a scanning rate of 10 deg./min. The rigidity of the solution was measured by the Schwedoff's concentric-cylinder method. The circular dichroism (CD) was measured with a JASCO J-20 Spectropolarimeter.

## RESULTS AND DISCUSSION

A typical thermogram of the solution of about 10 wt% is shown in Fig. 1, where two thermally-reversible transitions are observed. The transitions seem to be rather sharp from the reversibility. Fig. 2 shows the plots of the temperatures at the DSC peaks on the heating and cooling processes. The true transition temperature may be between the peak observed on heating and that on cooling. The transition temperature of 24°C is independent of concentration, while that of the another transition tends to rise from 50°C to 60°C as the concentration increases. The enthalpy was about 1 cal per gram of polymer for both transitions.

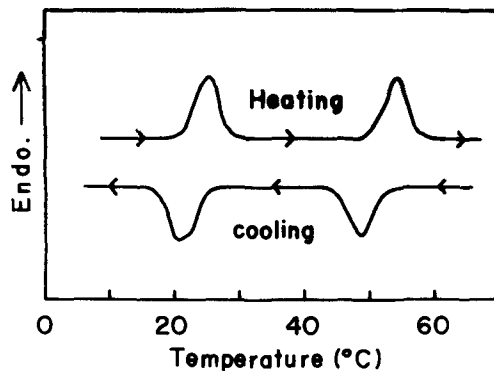


Fig. 1. A typical DSC thermogram of the PPLG-DMF solution.

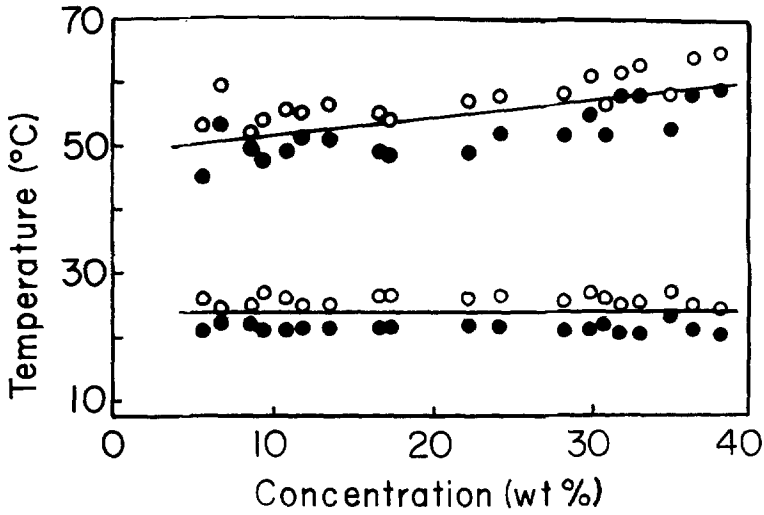


Fig. 2. Plots of the transition temperatures at the DSC peaks on heating (o) and cooling (●).

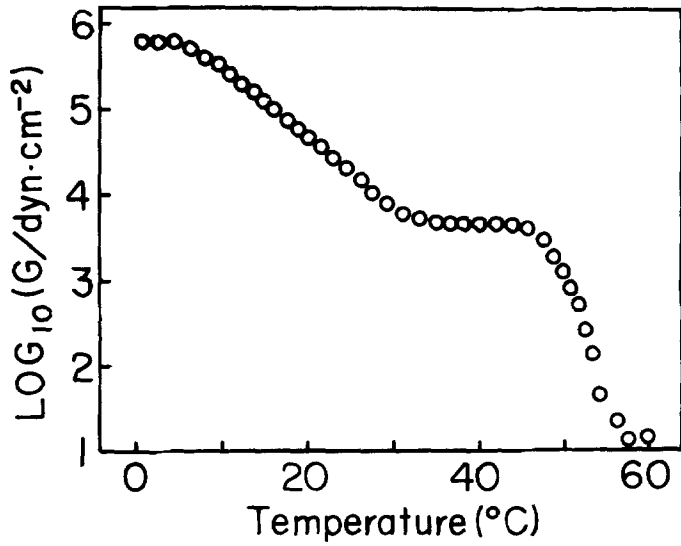


Fig. 3. Plot of the rigidity vs. temperature for a PPLG-DMF solution of 10 wt%.

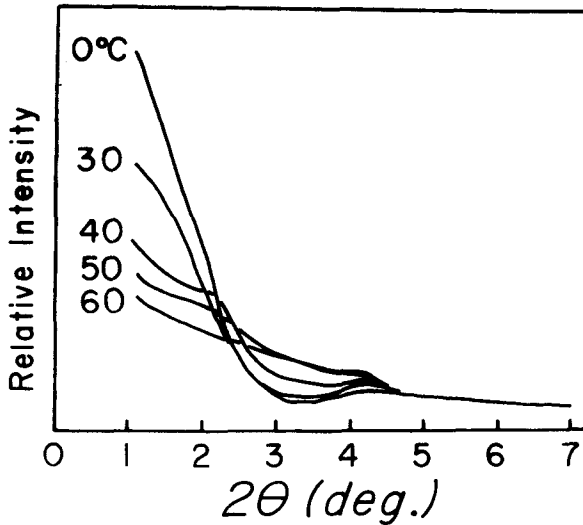


Fig. 4. Temperature dependence of the X-ray scattering pattern for a PPLG-DMF solution of 30 wt%.

A remarkable decrease of the rigidity (approximately to one hundredth) was observed in the 5-25°C range (Fig. 3), although the process seemed to be rather gradual. The transition at 24°C, however, does not correspond to the true melting of the gel, since the rigidity vanishes above 50°C. The rigidity is linearly related to the number of the effective cross-linkages in unit volume, that is, to the degree of the aggregation supporting the gel networks (Ferry 1970). The decrease of aggregation with rising temperature was also suggested by the X-ray scattering at small angles (Fig. 4). Intensities at smaller angles reflect the presence of larger scale of aggregates. The process of the intensity change with temperature did not seem to be so sharp.

As was reported by Heitz et al. (1973), the positive CD bands around 328 nm, corresponding to the  $n-\pi^*$  transition of the carbonyl of the phenacyl group, showed a sharp decrease in its intensity around 25°C. The same behaviour was observed even for concentrated solutions, as shown in Fig. 5. Accordingly, the transition at 24°C is probably due to the collapse of the order of side-chain structures in the gel-network aggregation.

The transition at 50-60°C corresponds to the melting of the gel into isotropic solution in the case of dilute concentrations. Solutions with concentrations higher than 20 wt% transform into birefringent solu-

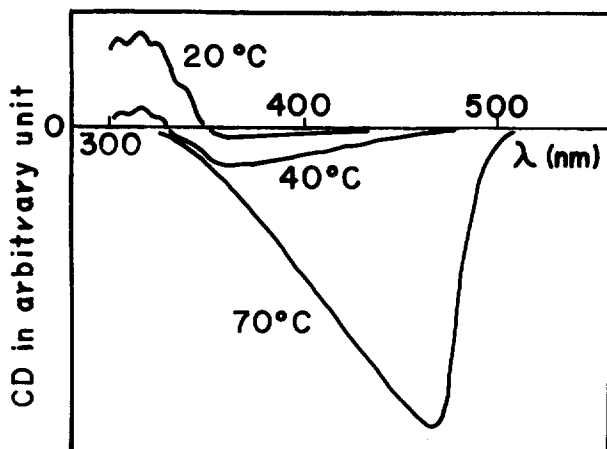


Fig. 5. CD spectra for a PPLG-DMF solution of 30 wt%.

tions above 50-60°C, showing a strong negative CD band in the 400-700 nm range of wavelength (Fig. 5). The peak position shifted linearly from 400 to 700 nm as the temperature increased from 60 to 80°C. This CD band was considered to be due to the selective reflection from the right-handed cholesteric liquid-crystal structure (Robinson 1966).

The melting of aggregated structures around 55°C was detected by X-ray diffraction. A broad reflection was observed at a diffraction angle of about 2° in the temperature range below 50°C for solutions of 20-40 wt%. The spacing of about 40 Å was almost constant in that concentration range, suggesting a PPLG-DMF complex. The structure was considered to be similar to that of the complex phase proposed for poly( $\gamma$ -benzyl L-glutamate)-DMF system (Parry and Elliott 1967; Sasaki et al. 1978), in which a special type of side-by-side arrangement of the  $\alpha$ -helical molecules has been assumed.

In conclusion, the transition at 24°C is due to structural changes in strong interactions between side chains, as was reported by Heitz et al. (1973). It is accompanied by the decrease of the molecular aggregation supporting gel networks. Some intermolecular interactions, however, still remain even above 24°C. Those interactions finally disappear above 50-60°C. The structure of aggregates may be a complex type.

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