

# Differential scanning calorimetry and modulus measurements of poly( $\gamma$ -benzyl-L-glutamate) gels

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When poly( $\gamma$ -benzyl-L-glutamate) is dissolved in benzyl alcohol, it forms a gel at room temperature that is optically anisotropic. Studies on gels of five different concentrations are reported here. Differential scanning calorimetry and rigidity modulus measurements have been carried out to examine the transitions that occur upon heating and cooling the gels. The transition temperatures recorded are in good agreement between the two techniques, but the behaviour of the gels cannot simply be related to the Flory phase diagram.

(Keywords: poly( $\gamma$ -benzyl-L-glutamate); gel; differential scanning calorimetry; rigidity modulus; liquid crystal; transition temperature)

## INTRODUCTION

Poly( $\gamma$ -benzyl-L-glutamate) (PBLG) was the first liquid-crystalline polymer (LCP) to be discovered<sup>1</sup>, and has been the focus of many studies. It is often regarded as an ideal model LCP and its behaviour in a range of solvents has been extensively studied by several workers<sup>2-5</sup>. Such studies have included a comparison of the phase diagram with that predicted by Flory<sup>6</sup> for a set of rigid-rod molecules, with the PBLG-dimethylformamide system in particular showing a phase diagram in good agreement with the theoretical prediction<sup>2</sup>. However, gelation in toluene<sup>7,8</sup>, dimethylformamide (DMF)<sup>5</sup> and benzyl alcohol (BA)<sup>9</sup> has also been reported, although it is not yet clear how the sol-gel transition relates to the phase diagram, nor what the mechanism of gelation is.

In this paper we explore the sol-gel transition in the PBLG-BA system using two techniques: differential scanning calorimetry (d.s.c.) and rigidity (shear) modulus measurements. One of the major problems in identifying the mechanism of gelation is actually locating the transition temperature. Some methods, such as that based on the temperature at which a small ball starts to fall through the gel, are not only subjective in the measurement but also depend on the particulars of the apparatus (i.e. the nature of the ball). Other methods, although more quantitative, may be subject to some uncertainty due to rate (e.g. d.s.c.) or frequency (e.g. dynamic mechanical testing) effects. Such techniques have at least the advantage that a consistent set of experiments may be performed on a series of samples, permitting direct comparisons, and in principle it is also possible to obtain some estimate of the magnitude of the effects by systematically varying the rate or frequency.

In this study a comparison is made of results obtained from d.s.c. with measurements of the rigidity modulus obtained via the technique of Saunders and Ward<sup>10</sup>.

Some preliminary measurements were carried out using the falling-ball technique, but these experiments were not pursued because of the impossibility of obtaining quantitative information. In the Saunders and Ward technique, a small volume of gel is placed in the arm of a U-tube containing mercury, and is subjected to hydrostatic pressure. The rise in height of the mercury column as the gel deforms permits the modulus of the gel to be determined. The technique, which has previously been applied to gelatin gels<sup>11,12</sup>, has the advantage of using relatively small amounts of gel, and the same sample can be used repeatedly as the temperature is raised or lowered over the range of interest. A plot of modulus *versus* temperature indicates the position of any transitions present. Transitions can be observed on both heating and cooling, unlike the falling-ball technique mentioned above, which can only be used for heating cycles.

The comparison shows good agreement for the observed transition temperatures between the two techniques. However, the transitions so measured do not correlate with those observed in a parallel study using optical microscopy<sup>13</sup>. The phase diagram derived from the microscopy observations is not dissimilar to that predicted by Flory, but it seems that the gel-sol transition is quite separate, and is tentatively assigned to the melting of small crystallites.

## EXPERIMENTAL

Concentrations of 5, 8, 10, 15 and 15.7 vol% were prepared using spectroscopic-grade benzyl alcohol (BA) (<0.65% water) from BDH Chemicals Ltd. The BA was further dried with KCO<sub>3</sub> and filtered before use. The polymer had a  $M_w$  of 345 000 and was obtained from Sigma Chemical Co. Ltd. Samples were prepared by mixing the polymer and BA at room temperature, and then heating the mixture, with stirring, to temperatures between 70 and 80°C (depending on concentration).

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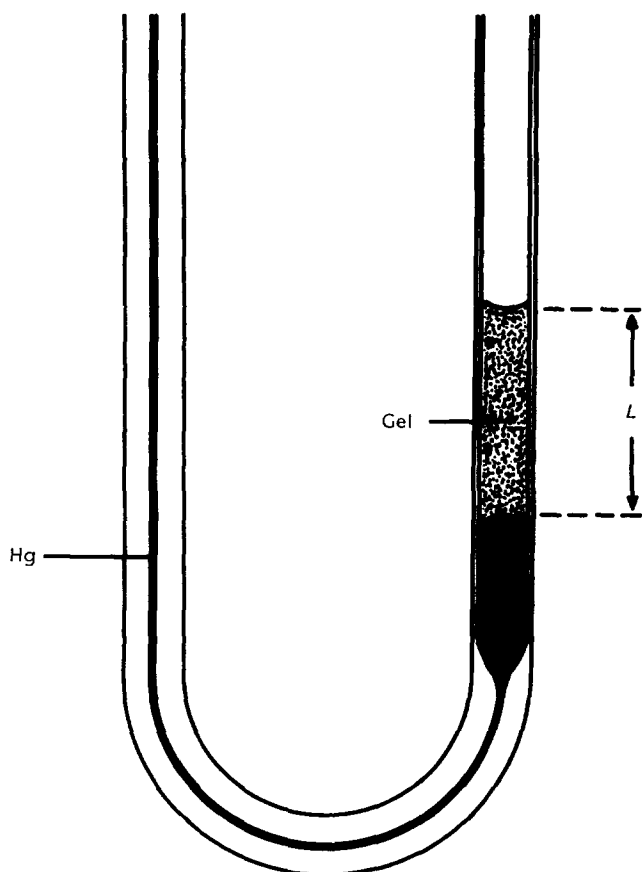


Figure 1 U-tube apparatus used in the measurement of rigidity modulus

Complete dissolution of the polymer was taken to be the point at which uniform transparency was achieved. The solutions were then allowed to cool slowly ( $< 1^{\circ}\text{C min}^{-1}$ ) to room temperature, during which process the gel formed. Initially, all of the cooled gels were transparent except the 15 and 15.7%, which became slightly translucent on cooling. Within a day, the turbidity of these two concentrations had increased and the 10% had also become slightly turbid. Turbidity increased with increasing concentration. The 8% gel eventually became slightly turbid whereas the 5% gel always remained almost perfectly transparent. Gels were stored at  $25^{\circ}\text{C}$ , small amounts being removed at intervals for the d.s.c. measurements. Larger amounts ( $\sim 1\text{ cm}^3$ ) were required for the rigidity modulus measurements.

The rigidity modulus measurements were made using a U-tube of which one arm is a capillary of 0.5 mm diameter and the other a precision-bore glass tube of 6.0 mm diameter (Figure 1). The U-tube was cleaned with acid solution and thoroughly rinsed and dried before use. A gel sample was introduced into the large-diameter tube above a column of mercury and then heated to between  $70$  and  $80^{\circ}\text{C}$ , so that the gel sample became fluid enough to make contact with the tube wall. After cooling, the filled tube was stored at  $25^{\circ}\text{C}$  for not less than 15 h prior to the experiment.

The experiments were performed by lowering the U-tube vertically into an oil or water bath so that the gel column was well below the surface. The large-diameter tube was connected to an air compressor and mercury manometer; the pressure  $P$  did not exceed 0.5 atm ( $5 \times 10^7\text{ Pa}$ ). The volume displacement  $V$  was calculated by

measuring the rise of mercury in the capillary with a travelling microscope. The length of gel  $L$  was measured for each recorded temperature using the microscope, and the gel was also checked at intervals to see whether any slippage was occurring at the tube wall. As long as end effects are negligible, i.e.  $L \gg R$  ( $R$  is the tube radius), then it can be shown<sup>10</sup> that the shear modulus  $G$  is given by:

$$G = \frac{\pi PR^4}{8LV}$$

The bath was heated with an immersion heater and the heating rate controlled to be about  $0.25^{\circ}\text{C min}^{-1}$  by varying the supply voltage to the heater. The rate was slow enough to allow measurements to be taken at intervals of  $1^{\circ}\text{C}$ , or less if necessary, up to a maximum temperature of between  $70$  and  $80^{\circ}\text{C}$ . At this temperature, the heater was removed and the bath allowed to cool. The cooling rate was uncontrolled but sufficiently slow to allow readings to be taken at intervals of  $1^{\circ}\text{C}$  or less as the temperature dropped; at  $40^{\circ}\text{C}$  the rate was less than  $0.2^{\circ}\text{C min}^{-1}$ . The bath was continuously stirred to maintain an even temperature, and a complete experiment took around 10 h to perform. Experiments were performed within a week of preparing the U-tube and at least three times on each concentration with an interval of at least two days between experiments. In order to check for ageing effects, two concentrations (5 and 10%) were left for 3 and 6 weeks respectively at  $25^{\circ}\text{C}$  before performing a further experiment.

Differential scanning calorimetry experiments were performed on a Mettler 2000 having possible heating rates down to  $0.1^{\circ}\text{C min}^{-1}$ . Gel samples were sealed in small aluminium crucibles and weighed before and after experiments to check for weight loss. The majority of experiments were performed at a heating or cooling rate of  $1^{\circ}\text{C min}^{-1}$ ; the highest rate used was  $3^{\circ}\text{C min}^{-1}$ .

## RESULTS

### Modulus measurements

The modulus measurements provide a complete profile of the shear modulus as the temperature is cycled. An example of such a profile is shown in Figure 2a for the 5% gel. This has a modulus of  $3.5 \times 10^5\text{ Pa}$  at room temperature, which decreases as the temperature is raised; between  $40$  and  $48^{\circ}\text{C}$  the decrease becomes more rapid. A transition temperature,  $T_{1m}$ , is identified as the temperature at which a straight line through the lower-temperature points crosses a straight line through the higher-temperature points, as shown in the figure.  $T_{1m}$  is about  $45^{\circ}\text{C}$  for the 5% gel. The kink in the curve between  $57$  and  $62^{\circ}\text{C}$  is not reproducible. At  $62^{\circ}\text{C}$  the modulus has fallen to  $1 \times 10^3\text{ Pa}$  and this is maintained at higher temperatures. On lowering the temperature, no change is observed until  $37^{\circ}\text{C}$ , when the modulus rises sharply. The temperature at which the sharp increase in modulus is observed is designated  $T_{3m}$  (also shown on Figure 2a). By  $30^{\circ}\text{C}$ , the two curves of increasing and decreasing temperature are virtually coincident, and remain so down to room temperature. The 5% gel aged for 3 weeks behaved similarly except that it had a slightly lower room-temperature modulus of  $2.5 \times 10^5\text{ Pa}$ .

Table 1 lists the initial room-temperature modulus of all the gels studied, the value of the modulus at  $70^{\circ}\text{C}$ , above

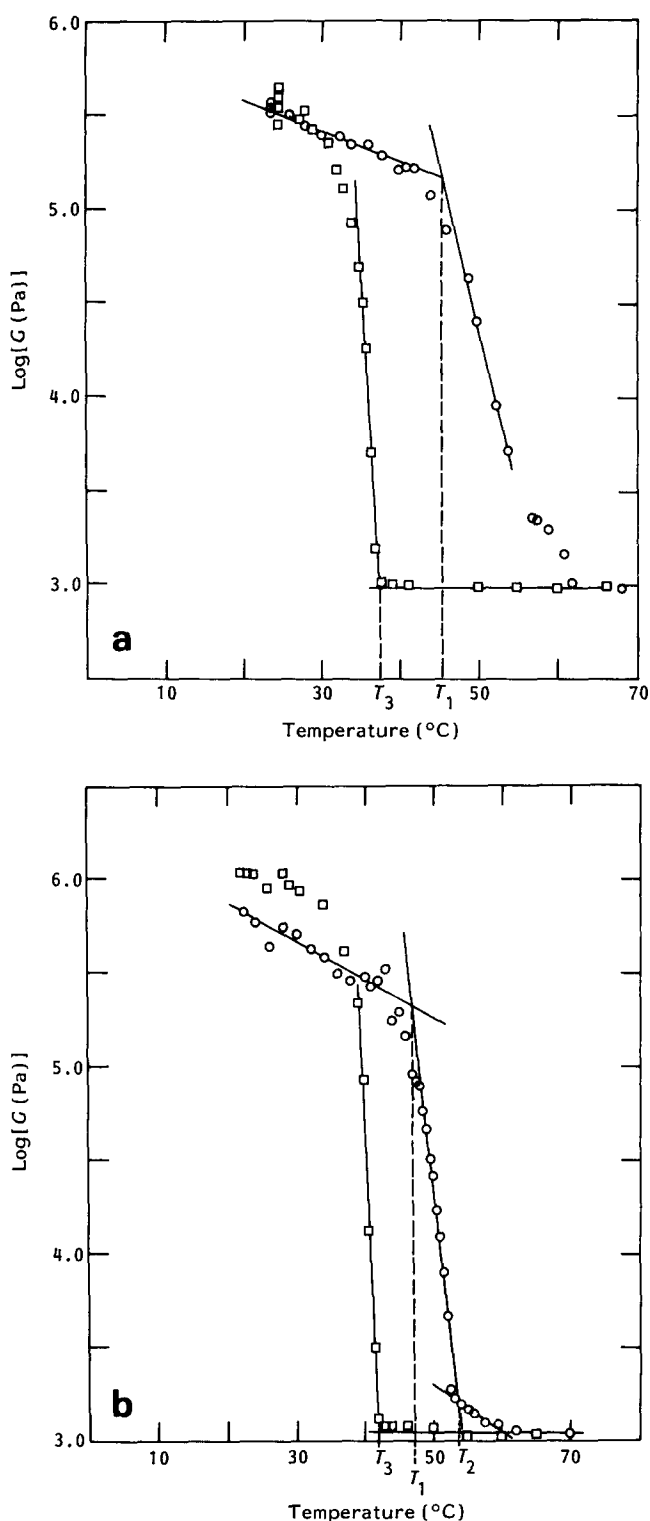


Figure 2. Temperature profile for the rigidity modulus for (a) 5% and (b) 10% gels:  $\circ$ , heating cycle;  $\square$ , cooling cycle. The transition temperatures are indicated, together with the construction for locating them

the gel melting point, and the room-temperature modulus measured immediately after cooling. For the 8 and 10% gels, two transitions are recorded on heating. The position of the second transition,  $T_{2rm}$ , is obtained in the same way as  $T_{1rm}$  by extrapolation of the lines drawn through the low- and high-temperature points. An example of this construction is shown in Figure 2b, which is the modulus profile for the 10% gel. Figure 2b also shows that still only a single, sharp transition is measured

on cooling. The value of the modulus immediately after cooling is higher than the initial room-temperature modulus (see Table 1), but returns to the lower value within 2 days. A similar effect was also observed for the 8% gel.

By comparison with the behaviour of the 10% gel shown in Figure 2b, the aged (6 weeks) 10% gel had a much-reduced modulus. After pressurizing the gel, the mercury level in the capillary continued to rise very slowly after its initial increase, and between 30 and 42°C no steady level was achieved; this seems to suggest that some slippage of the gel is taking place. Above 42°C, pressurizing resulted in a steady mercury level and measurements were possible, yielding a  $T_{2rm}$  of 51°C, with the modulus falling to  $1.1 \times 10^3$  Pa by 64°C. On lowering the temperature it was possible to measure the modulus right down to room temperature, with a  $T_{3rm}$  of 41°C being identified.

It was also found to be impossible to measure a room-temperature modulus for the 15.7% gel: if left at room temperature for only a few hours after preparation, the gel visibly exuded a liquid that caused it to slip within the tube when pressurized. If the temperature was raised, this effect persisted until 63°C, when a modulus could first be measured, with a value of  $1.5 \times 10^3$  Pa. On decreasing the temperature, the modulus started to increase at 50°C and a  $T_{3rm}$  of 50°C was measured. Summaries of all the results described here are given in Tables 1 and 2, the latter including a list of all the transition temperatures measured.

#### Differential scanning calorimetry experiments

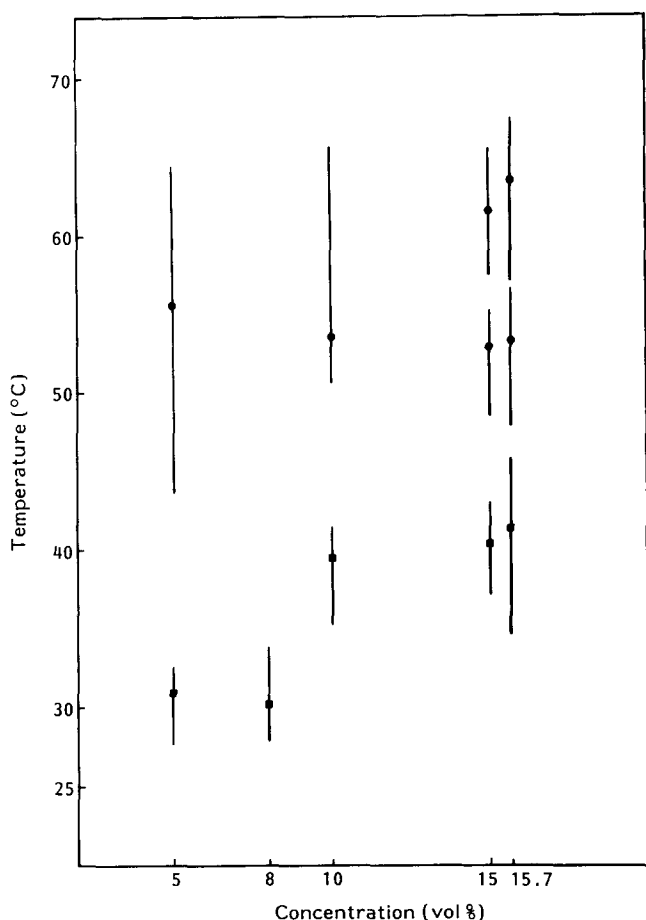
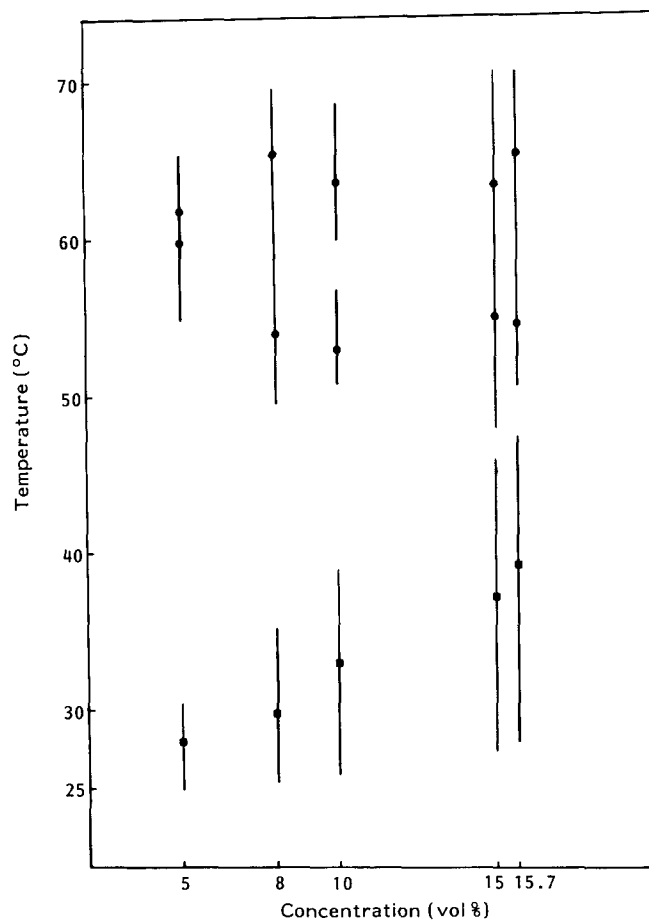
Figure 3 is a schematic representation of average values of peak positions and widths for all concentrations using small amounts of gel (<25 mg). Averages were taken from three or four experiments for each concentration except in the case of the 8%, where only one experiment was performed, no heating transition being observed in this case. Errors in temperature are estimated to be  $\pm 1^\circ\text{C}$ . In the heating portion of the cycle, a single broad peak is observed with difficulty for the 5 and 8% specimens and two peaks for the 15 and 15.7% gels. Cooling cycles exhibit much sharper single peaks, which start between 2 and 10°C below the start of the heating peaks. The use of large amounts of sample allows the resolution of smaller transition peaks, but with less accurate values of peak temperature position owing to a heat transfer effect. Using larger masses (>50 mg) two peaks are observed for the 15, 8 and 10% gels, and a hint of two peaks, virtually inseparable, in the 5% gel. A summary of results for these specimens is shown

Table 1 Rigidity moduli for various gels

Sample	Modulus (Pa)		
	Room temperature (initial)	70°C	Room temperature (after cooling)
5%	$3.5 \times 10^5$	$1.0 \times 10^3$	$3.0 \times 10^5$
Aged 5%	$2.5 \times 10^5$	$1.0 \times 10^3$	$3.0 \times 10^5$
8%	$9.0 \times 10^5$	$1.5 \times 10^3$	$2.0 \times 10^6$
10%	$6.0 \times 10^5$	$1.0 \times 10^3$	$1.0 \times 10^6$
Aged 10%	slippage	$1.1 \times 10^3$	$1.0 \times 10^6$
15.7%	slippage	$1.5 \times 10^3$	$1.4 \times 10^6$

**Table 2** Sol-gel transitions ( $^{\circ}\text{C}$ ) for various methods

Conc. (%)	D.s.c.										
	Ave. small mass			Large mass			Rigidity modulus			Clearing range	
	$T_1$	$T_2$	$T_3$	$T_1$	$T_2$	$T_3$	$T_1$	$T_2$	$T_3$	Heating	Cooling
5	44	—	33	55	—	31	45	—	37		
8	—	—	34	50	56 <sup>a</sup>	35	45	53	41	44–50	40–42
10	51	—	42	51	60	39	47	54	41	50–62	40–42
15	48	57	43	48	57 <sup>a</sup>	46	—	—	—		
15.7	48	57	46	51	59	47	—	—	50	60–62	49–51

<sup>a</sup>  $\pm 2^{\circ}\text{C}$ **Figure 3** Schematic representation of peak temperatures of the transitions observed by d.s.c. for small amounts of gel: ●, heating cycle; ■, cooling cycle. Bars represent the widths of the peaks**Figure 4** Schematic representation of peak temperatures of the transitions observed by d.s.c. for large amounts of gel: ●, heating cycle; ■, cooling cycle. Bars represent the widths of the peaks

schematically in *Figure 4*. In all cases, if the experiment was immediately repeated, the higher-temperature heating transition peak was substantially reduced in magnitude, and the cooling transition remained essentially unchanged (*Figure 5*). The lower temperature of the two heating transition peaks was essentially unchanged on this second heating in the higher concentrations.

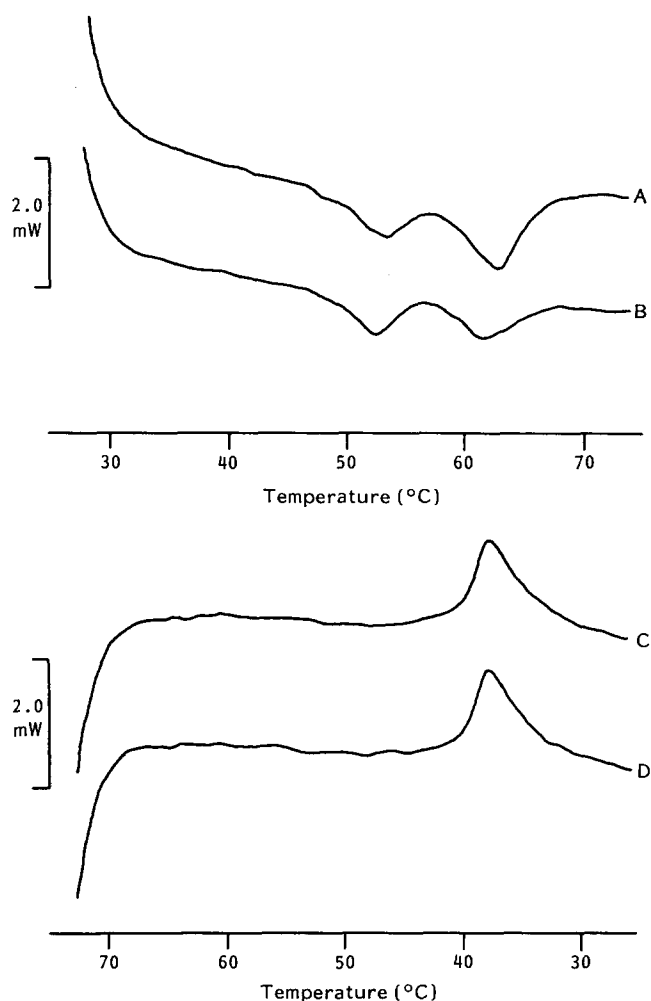
$T_{1\text{dsc}}$  and  $T_{2\text{dsc}}$  were chosen as the start of the lower- and higher-temperature peaks on heating and  $T_{3\text{dsc}}$  as the start of the transition on cooling. In the case of the 8 and 15% gels, the two heating transitions overlapped and  $T_{2\text{dsc}}$  was estimated with a error of  $\pm 2^{\circ}\text{C}$ . Experiments were also performed at sub-ambient temperatures, when no

transitions that might be evidence of water content<sup>14</sup> were observed.

A summary of the results from the d.s.c. experiments is included in *Table 2*. During the course of the rigidity modulus experiments, initially opaque gels were observed to clear as the temperature was raised. *Table 2* also contains a synopsis of these clearing temperatures. In all cases, clearing was not instantaneous.

## DISCUSSION

Whereas the temperature  $T_1$  does not seem to vary significantly or systematically with concentration, there does seem to be a clear trend for  $T_3$  to increase, as revealed by both techniques. There are insufficient data to comment on the behaviour of  $T_2$ . Furthermore, the



**Figure 5** Heating and cooling d.s.c. cycles of 15% gel, 99.1 mg: A, first-run heating; B, repeat heating; C, first-run cool; D, repeat cool

modulus does not increase monotonically with concentration, the 8% gel having a higher value than the 10% at all temperatures. This effect was also observed by Murthy and Muthukumar, in their recent study of the dynamic mechanical properties of similar gels<sup>15</sup>. They suggested that the effect could in some way be related to the 8% sample being the only one to enter the so-called biphasic chimney of the Flory phase diagram (a similar effect is seen in rheological properties of lyotropic polymers), but further evidence is needed to clarify this point.

Both the d.s.c. and modulus techniques suggest that there are two separate mechanisms contributing to the gel-sol transition, characterized by the temperatures  $T_1$  and  $T_2$ . The higher-temperature mechanism becomes more prominent as concentration is increased (thus  $T_2$  is not detectable in the lower concentrations). The two techniques are in good agreement and produce reliable and reproducible measurements of the transition temperatures. It is now necessary to consider the possible sources of the transitions.

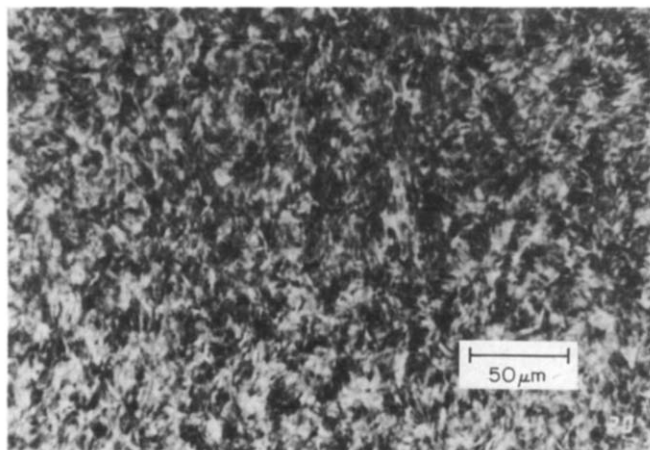
PBLG is a rod-like polymer that is capable of forming liquid-crystalline phases in many solvents, including BA. As was stated in the introduction, this has led people to study its phase diagram and its relationship with the theoretical predictions of Flory<sup>6</sup>. However, these theoretical predictions take no account of any possible crystallinity or gelation, and simply consider the regimes

of coexistence of isotropic and anisotropic phases, including the possibility of there being more than one of the latter. Optical micrographs show that all the concentrations of PBLG in BA studied here appear anisotropic at room temperature, as seen in *Figure 6* (although it is anticipated that the material is actually biphasic, with the presence of a finely distributed isotropic phase being masked by the anisotropic). Thus one has the intriguing system of an optically anisotropic gel. Whether this gel is also mechanically anisotropic<sup>16</sup> remains to be seen. One fundamental question that has to be addressed is the relationship (if any) between the existence of a liquid-crystalline phase, its transition to an isotropic phase, and the gelation phenomenon. In other words, is there any structure inherent in the liquid-crystalline phase that is capable of conferring rigidity on the gel and giving it a finite modulus, or is the gel state actually unrelated to this phase?

Several mechanisms for gelation in anisotropic systems containing PBLG have been considered. A mechanism based on spinodal decomposition was proposed by Miller *et al.*<sup>7,8</sup> for the toluene system, whereas both Ginzburg *et al.*<sup>5</sup> for the DMF system, and Sasaki *et al.*<sup>9</sup> for the BA, have postulated the existence of some type of crystallite acting as the gel junction points. In the Ginzburg approach, the low-temperature gel is envisaged as a three-phase system: isotropic, liquid crystalline and crystalline. At higher temperatures the isotropic phase is assumed to transform to a second liquid-crystalline phase, but the crystallite junction points remain. Sasaki *et al.*<sup>9,17,18</sup> use X-ray evidence to identify two so-called 'complex phases', which lead to two types of gel (produced by different thermal histories) with slightly different melting points. The precise nature of these complex phases is not spelt out in their papers.

In the present work several points indicate the presence of crystallization:

(1) All the gels at room temperature exude a liquid, the amount of exudate increasing with concentration and time. If this exudate were the isotropic phase of the wide biphasic region in the Flory phase diagram, then one would expect the amount to *decrease* with increasing concentration. On the other hand, syneresis is a typical effect of crystallization in gels and is due to the thickening of crystals after their formation<sup>19,20</sup>, so the amount of



**Figure 6** Optical micrograph of the 10% gel at room temperature under crossed polars, indicating the anisotropic nature of this gel

solvent rejected in this case will increase with polymer concentration, as observed. Thus the exudate is thought to be due to syneresis. It is the presence of this liquid in sufficient quantity that prevents the measurement of modulus in the aged 10% and the 15.7% specimens.

(2) On cooling, the d.s.c. traces exhibit only one sharp peak at a much lower temperature than the heating transition. The modulus measurements also exhibit a single sharp transition on cooling, at a temperature well below the heating transitions. Melting point depression is a characteristic of crystallization, as the crystalline state develops at a finite rate only at temperatures well below the melting temperature<sup>21</sup>.

(3) Clearing of the gels is not instantaneous. This could be due to the presence of different sized crystallites, which melt at different temperatures. The broadness of the d.s.c. heating transition is consistent with this. Clearing occurred uniformly in the gels so that local temperature differences can be ruled out.

Thus it seems extremely probable that some type of crystalline aggregates are present in the gel.

Recent X-ray work on the PBLG-BA gels confirms that at room temperature some crystallinity is present<sup>16,22</sup>, but work is continuing to explore changes in the diffraction pattern as the system passes through the sol-gel transition. However, the data do seem to confirm that for this system the gel junction points can be associated with the crystals. It is clear from parallel optical microscopy studies<sup>13</sup> that the transitions observed by that technique are quite distinct (i.e. transitions of the type liquid crystal-isotropic, etc., which must be between macroscopic phases to be observable in the light microscope), although they may be described well by the Flory phase diagram. At room temperature this means that the material appears optically anisotropic, as seen in *Figure 6*.

If this distinction is the case, then it follows that the gel-sol transition must be superimposed on the standard Flory diagram, with additional phase boundaries corresponding to crystal melting to demarcate the limit of gel stability, as suggested by Sasaki *et al.*<sup>18</sup>. That the gel is optically anisotropic can therefore be regarded as a consequence of the fact that the crystals are embedded in a liquid-crystalline, rather than the normal isotropic, matrix. This fact must, however, be regarded as coincidental to the gel state. Above the gel melting temperature, micrographs show that the liquid remains liquid crystalline (anisotropic). A further discussion of this will be given in a subsequent paper in which the optical evidence of the different (macroscopic) phases present will be described<sup>13</sup>.

This study should be compared with a recent dynamic mechanical study of PBLG-BA gels<sup>15</sup>, using PBLG of the same nominal molecular weight. In this it was found that the gel point could be characterized by the drop in the storage modulus. However, this drop was sharp only for isotropic solutions, i.e. for low concentrations. An attempt was made to relate the transition to the Flory phase diagram, but this rests on the assumption, disputed above, that the gel transition corresponds to the phase boundary of that diagram. In this study we find that, even in solutions that we know are anisotropic, the  $T_1$  transition is sharp, which makes the identification of the 'gel-point' more straightforward than in their work. Secondly, because the drop in modulus is steep, it is

possible to pick up the  $T_2$  transition for the more concentrated solutions. In fact there is a hint of a second transition in the curves presented by Murthy and Muthukumar, particularly for the 10% sample. Finally, we note that the transition temperatures measured by the quasi-static technique described in this paper are in good agreement with those measured dynamically by Murthy and Muthukumar, but our values for the modulus are systematically lower, as might be expected.

With this identification of the gel junction points as being some kind of crystal, further thought needs to be given to what these crystals are. Without further X-ray evidence, this can only be speculated on. One possibility is that they can be identified as some type of crystallosolvate complex (i.e. a crystal formed from polymer plus solvent bound on a lattice). This is presumably the type of 'complex' implied by Sasaki *et al.*<sup>9,17,18</sup>, although it was not explicitly so identified. Thus the biphasic region of the Flory phase diagram becomes triphasic: liquid crystal, isotropic and crystallosolvate phases being present.

Crystallosolvate phases have previously been identified in other rigid-rod polymer systems, notably polybenzamide<sup>23</sup>, poly(*p*-phenylene benzobisthiazole)<sup>24</sup> and nitrocellulose<sup>25</sup>, and an association of their appearance with the onset of gelation noted<sup>26</sup>. For aromatic polyamides, which are rather rigid molecules, solubility only occurs in strongly interacting solvents and this will tend to promote the formation of crystals where the two components are cocrystallized. In other cases where the polymer is more readily soluble (e.g. PBLG), specific interactions such as hydrogen bonding may play a key role.

The behaviour of the PBLG-BA gel upon heating can therefore be described in summary as follows. According to the Flory phase diagram, as the temperature is raised, the volume and concentration of the isotropic phase increase, and the volume of the anisotropic phase decreases. Assuming that the crystalline junctions are maintained intact up to the gel melting temperature, the polymer concentration in the isotropic phase must increase at the expense of the liquid-crystal phase, i.e. there is an exchange of polymer between these two phases, the amount of polymer exchange increasing as the temperature is raised. At a temperature  $T_1$  the crystalline junctions melt to leave a simple biphasic system, but this transition would appear not to be related in any way to the Flory diagram. This temperature  $T_1$  is clearly shown by both the d.s.c. ( $T_{1\text{dsc}}$ ) and rigidity modulus ( $T_{1\text{rm}}$ ) measurements, with good agreement between the two.

For the higher-concentration gels, a second transition  $T_2$  is observable on heating, from both d.s.c. and modulus measurements. The modulus decrease at  $T_{2\text{rm}}$  is much less marked than at  $T_{1\text{rm}}$ , and the magnitude of the endotherm at  $T_{2\text{dsc}}$  is reduced if a second heating run is carried out immediately after the first. Thus it appears that some second type of 'crystal' is present, which confers less rigidity to the gel than the first and takes time to re-form. If the lower-melting crystal is a crystallosolvate phase, the higher may be associated with the polymer chains alone. Because of the comparatively low mobility of the macromolecules, compared with the solvent, these crystals are likely not to re-form instantaneously, thus explaining the d.s.c. results. Annealing experiments are likely to cast further light on this matter. Again, this transition is not detectable optically. The next phase

transition discernible in the optical microscope is at a much higher temperature when a second liquid-crystalline phase appears followed by the disappearance of the isotropic phase<sup>1,3</sup>.

## CONCLUSIONS

It is proposed that the optically anisotropic gels exhibited by the PBLG-BA system are most easily considered as consisting of two parts: a liquid-crystalline/isotropic component that behaves as predicted by Flory, within which are crystallites that confer rigidity upon the gel. The former occupies by far the greater volume. The gel-sol transition  $T_1$  is identified as crystal melting and there is no evidence to connect this transition with any of the phase transitions in the Flory phase diagram. A higher-temperature transition  $T_2$  can also be identified.

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