Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Phase behaviour of poly-(λ-benzyl-L-glutamate) in benzyl alcohol

Alyson Hill[ab]; Athene M. Donald[a]
[a] Cavendish Laboratory, University of Cambridge, Cambridge, England [b] Minnesota 3M Research Ltd, Harlow, Essex, England

To cite this Article Hill, Alyson and Donald, Athene M.(1989) 'Phase behaviour of poly-(λ-benzyl-L-glutamate) in benzyl alcohol', Liquid Crystals, 6: 1, 93 — 110
To link to this Article: DOI: 10.1080/02678298908027326
URL: http://dx.doi.org/10.1080/02678298908027326

LIQUID CRYSTALS, 1989, VOL. 6, NO. 1, 93–110

Phase behaviour of poly-(γ-benzyl-L-glutamate) in benzyl alcohol

by ALYSON HILL† and ATHENE M. DONALD
Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, England

(*Received 21 July 1988; accepted 25 January 1989*)

Polarized optical microscopy has been used to investigate phase transitions in the poly-(γ-benzyl-L-glutamate) benzyl alcohol system and these have been compared with the predictions of Flory. All of the samples studied form gels at room temperature. The behaviour of the lowest concentration studied, 5 per cent by volume, shows transitions in the optical microscope compatible with the Flory phase diagram, becoming isotropic at elevated temperatures. Gels of higher concentrations exhibit bulk phase separation into an isotropic liquid phase and an anisotropic phase at room temperature, also in accord with the Flory predictions; the texture of the anisotropic phase varies with concentration. At higher temperatures these concentrations exhibit two coexistent anisotropic phases.

1. Introduction

Flory [1] has predicted the phase behaviour of rod-like particles in solution using a lattice model. The resultant phase diagram (sketched in figure 1) is composed of a curve for isotropic solutions at low concentrations and a second curve encompassing ordered phases at higher concentrations and temperatures, separated by a biphasic region which extends into a chimney. The presence of a maximum in the curve for the ordered phase prompted Flory to postulate the coexistence of two anisotropic phases in this region.

The phase equilibria of the poly-(γ-benzyl-L-glutamate) (PBLG)-dimethylformamide (DMF) system has been studied in some detail [2–5]. The experimental phase diagram, constructed by Wee and Miller [2], is generally comparable to the Flory predictions, observation of the chimney region being a notable feature. The effect of molecular weight was also studied by these workers and shown to be as predicted, i.e. an increase in molecular weight caused a narrowing of the chimney region and a shift to lower concentration. By investigating the temperature dependence of the periodicity of the cholesteric pitch, more recent work [4] has shown the region of the ordered phase curve at concentrations just above the chimney region to have the curvature predicted by Flory, thus implying that two liquid-crystalline phases do indeed coexist.

The PBLG-benzyl alcohol (BA) system has been investigated by Ginzburg *et al.* [6] using optical methods. They propose a phase diagram similar in shape to the Flory prediction but in which the phases are considerably more complex; notably the wide biphasic region is divided into an isotropic–liquid crystal–crystallite phase at low temperatures and a region composed of two liquid crystal phases and a crystallite phase at higher temperatures. The addition of a crystallite phase was, in their opinion, necessitated by the observation of gelation around room temperature.

† Present address: Minnesota 3M Research Ltd, Pinnacles, Harlow, Essex, England.

0267-8292/89 $3.00

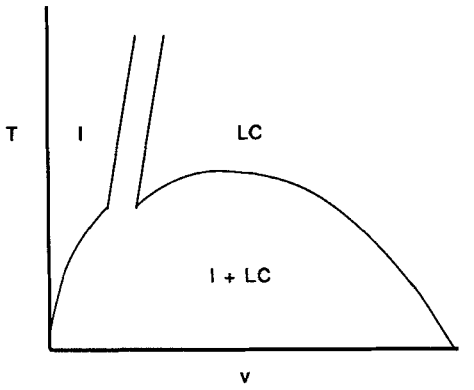


Figure 1. Phase diagram for rigid rod molecules, after Flory. T is the temperature and V is the volume fraction of polymer.

The optical microscopy work presented here forms part of a wider programme of research intended to explore in more detail the different phases of the PBLG-BA system, to correlate them with the gelation phenomenon and to identify the gelation mechanism. Benzyl alcohol was chosen because of the lack of aggregation of PBLG in this solvent [3] and its suitability for studies of gelation near room temperature. Discussion of the mechanical properties of the gel and the transitions observed by D.S.C. are presented elsewhere [7].

2. Experimental

Four solutions were made up: 5, 8, 10 and 15 per cent by volume. Spectroscopic grade benzyl alcohol from B.D.H. Chemicals Ltd. (< 0·65 per cent water), was further dried with KCO_3 and filtered. Several ml of each concentration were made by measuring a volume of solvent into a clean, dry glass jar and adding the appropriate weight of polymer. The PBLG was obtained from the Sigma Chemical Company Ltd. and had a molecular weight of 345 000. A density of 1·264 g/ml was used in calculating the polymer volume. The jar was heated to between 70°C and 80°C for one or more hours depending on the concentration. A magnetic stirrer facilitated the dissolution process. When all of the polymer had dissolved, determined by its uniform transparency, the solution was allowed to cool slowly (< 1°C/min). All solutions formed gels at room temperature which initially were completely transparent, but on aging the 10 and 15 per cent solutions became milky although not opaque; the 5 per cent gel becomes slightly cloudy. Solutions were stored at 25°C and allowed to equilibrate for a minimum of three weeks prior to study. The rigidity of the gels increased noticeably with concentration. The polarizing microscope used was a Carl-Zeiss Jenapol equipped with a 35 mm Olympus camera and a Stanton Redcroft heating stage. Maximum viewing magnification was × 32 due to physical restrictions on the hot stage. It was also possible to hold the temperature at any point within the heating or cooling cycle.

Specimens for the microscope were prepared by compressing a small quantity of gel onto a clean, dry slide with a 25 μm spacer and glueing a cover slip on top. Two types of glue were used, one a high temperature cement, the other a single phase cyanoacrylate adhesive. Behaviour of the gels was independent of the type of glue used. Each gel was subjected to heating cycles at low rates (2°C/min unless otherwise

stated) to a maximum of 180°C and cooled at the same rate. Over a period of 6 months specimens were regularly made up from the stock gels for observation on the microscope in order that any ageing effects might be determined. Gels of any one concentration aged for longer than three weeks behaved qualitatively in much the same way; hence only representative results are reported for each concentration here.

3. Results

All stock gels in their sealed glass jars exuded a liquid which coated the walls and lid above the gel as droplets. We have tried to identify the composition of this exudate by D.S.C. and infra-red techniques but so far it has not been possible to determine whether it is a distinct phase, an effect of polydispersity or a syneresis effect due to crystallization. In addition, this phenomenon is present in a specimen (of any concentration) prepared for microscopy some time before an experiment. Figure 2 shows isotropic droplets on the surface of a 10 per cent gel in a dimple slide. The specimen had been prepared three days prior to this photograph and in this time (during which the specimen had been kept at 25°C) the droplets had appeared. Similarly, if the gel was squashed between cover slip and slide with a spacer, droplets developed in the surrounding space. Thus the exudate and droplets visible in the specimens result from the same phenomenon and seem to be due to the formation of a vapour-saturated atmosphere which subsequently condenses. Upon heating the droplets grow and coalesce.

Some higher concentration specimens were seen, immediately on removal from the stock solution, to consist of a gel within a pool of (isotropic) liquid, this being more common in the longer-aged gels. In this case the liquid was not associated with the

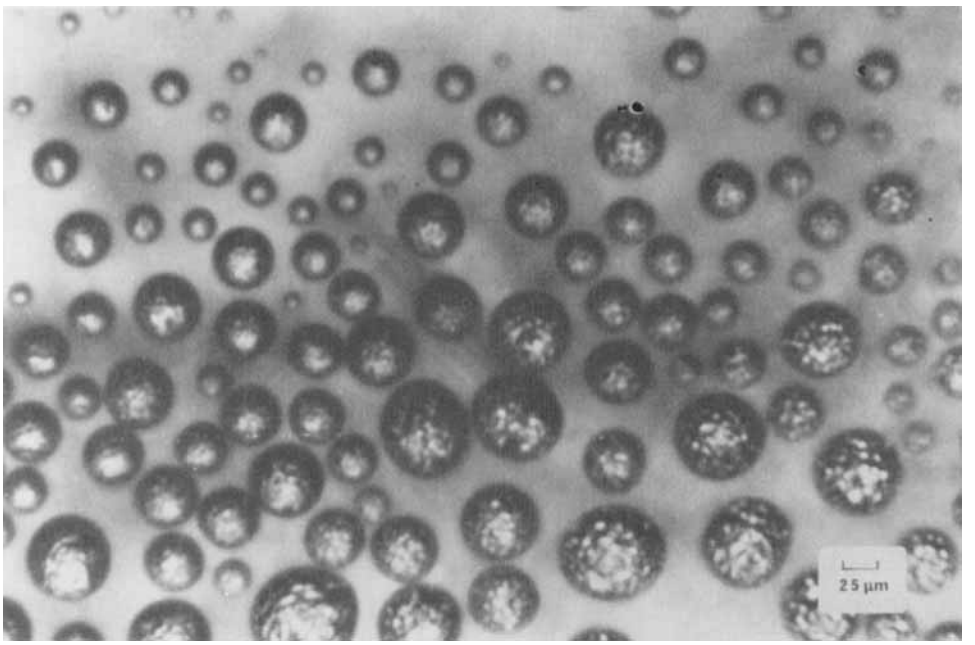
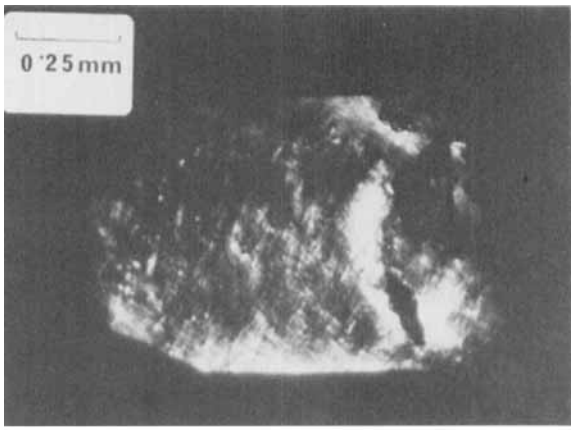
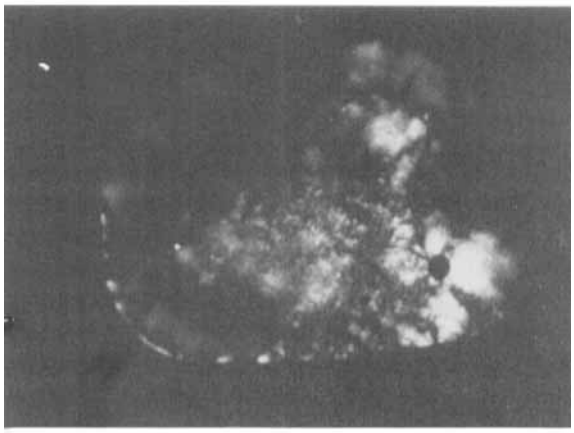


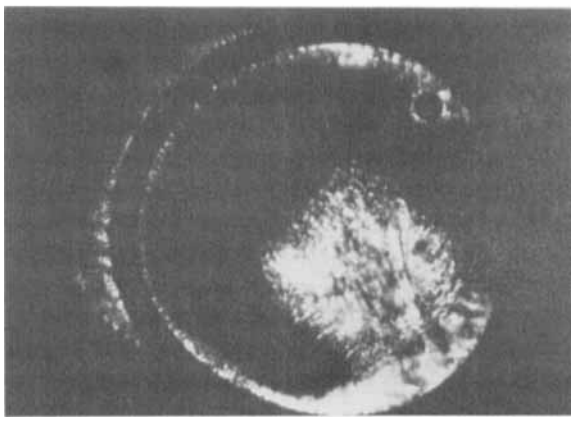
Figure 2. Isotropic droplets over the anisotropic phase in a 10 per cent gel; under crossed polars.



(*a*)



(*b*)



(*c*)

Figure 3. Sequence of events on heating an 8 per cent gel (*a*) 24°C; (*b*) 71°C; (*c*) 110°C.

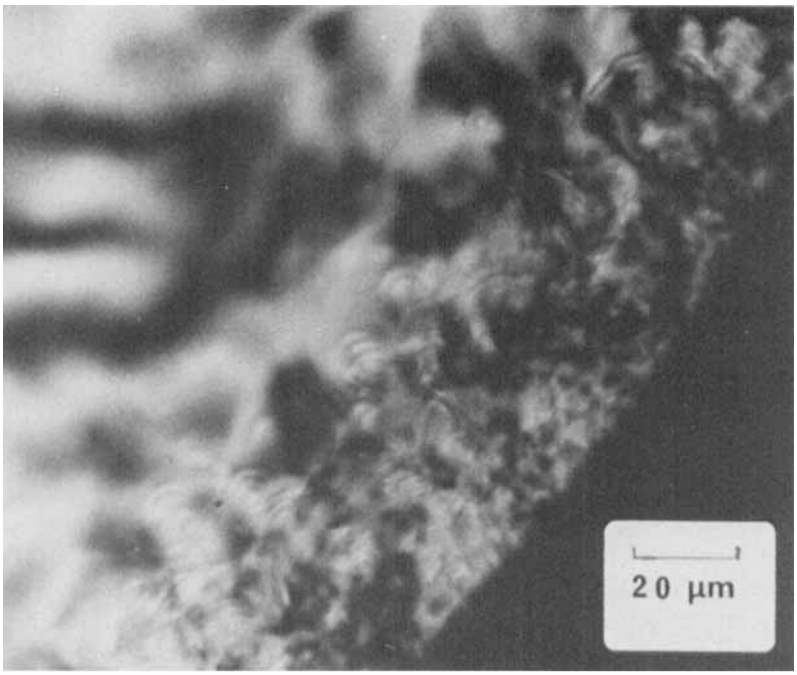
surface but on the contrary was a bulk phenomenon. Heating such specimens also led to a growth in volume of the isotropic pool. It seems likely that the exudate and isotropic pool are not due to the same phenomenon. Because of its behaviour during heating, the isotropic pool may be identified as the isotropic phase in the wide biphasic region of the phase diagram.

At room temperature all specimens of the 5 per cent gels aged from three weeks to six months appeared anisotropic and were uniformly milky in appearance under crossed polars. A continuous liquid phase was seen to spread across the field of view at a temperature of between 60°C and 68°C. (There was no apparent correlation between clearing temperature and age.) When the gel was left to cool anisotropic regions were observed, with a black and white texture under crossed polars. However distinct isotropic regions rather than a continuous phase also remained so that, on the time scale of these experiments, the effect of heating appears irreversible.

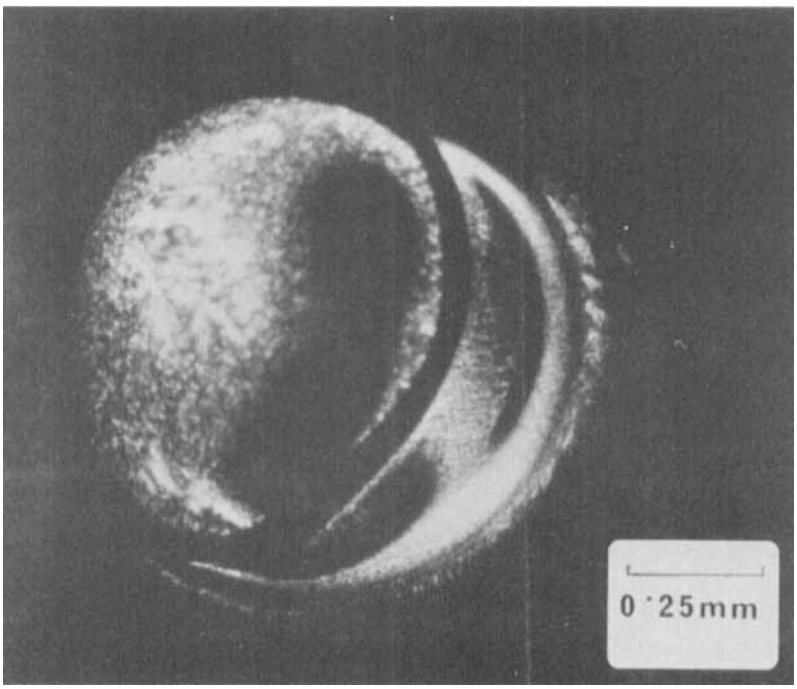
At ambient temperature 8 per cent specimens appear anisotropic with some isotropic regions, see figure 3 (*a*). On raising the temperature, the isotropic material increases in volume and between 60°C and 70°C the original irregular boundary of the gel becomes smoother, see figure 3 (*b*). Simultaneously, a thick, dark boundary forms, outside of which further anisotropic material appears, designated LC1, see figure 3 (*c*). The boundary is dark both in transmitted light and under crossed polars. Darkening, between crossed polars, continues and the volume of LC1 increases as the temperature is raised further. Held at 110°C the dark boundary contracts but no fingerprinting is observed. Cooled at 2°C/minute, the boundary contraction is arrested and a fingerprint texture appears in the interior anisotropic material, LC2, at about 80°C, see figure 4 (*a*). Simultaneously, LC2 grows at the expense of the isotropic material. Figure 4 (*b*) shows the appearance following cooling to 59°C. The isotropic volume has decreased and LC1 (outside) and LC2 (inside the boundary) have both grown relative to that in figure 3 (*c*). Note that a vestige of the original boundary is still visible. Growth is by the appearance and coalescence of spherical entities bearing a dark cross. During cooling some fingerprinting remains but this region appears to become increasingly separated from the dark boundary by the growth of fresh anisotropic material which does not have a fingerprint texture.

On reheating, the volume of LC2 gradually reduces, the fingerprint texture disappears and by about 95°C no evidence of the cholesteric fingerprinting remains, see figure 5 (*a*), (*b*). For one sample the temperature was kept constant at 105°C for 50 min. During this time the volume of LC2 (without fingerprinting) began to grow at the expense of the isotropic material, but the fingerprint texture did not reappear. On cooling at 20°C/min the fingerprint texture reappeared at 90°C accompanied by an increase in volume of the anisotropic LC2 at an accelerating rate as the temperature was lowered. Fingerprinting first appeared at the edge of LC2 but was again seen to recede from the boundary as growth continued, see figure 6.

The two types of anisotropic material, LC1 and LC2, seem to be quite distinct. Once the polymer has transformed to the LC1 phase it does not appear to change subsequently. Thus the total volume of LC1 grows during successive cycles. Repeating the heating cycle led to similar behaviour within the boundary (i.e. where LC2 is in contact with the isotropic phase). A slight temperature rise in general occurred between repeated runs. This is probably a real effect due to changes in composition as more and more material is transformed to LC1; however it could possibly be due to the fact that although the heating rate was maintained fixed, the pattern of temperature holds (e.g. to take a series of photographs) was not necessarily the same.

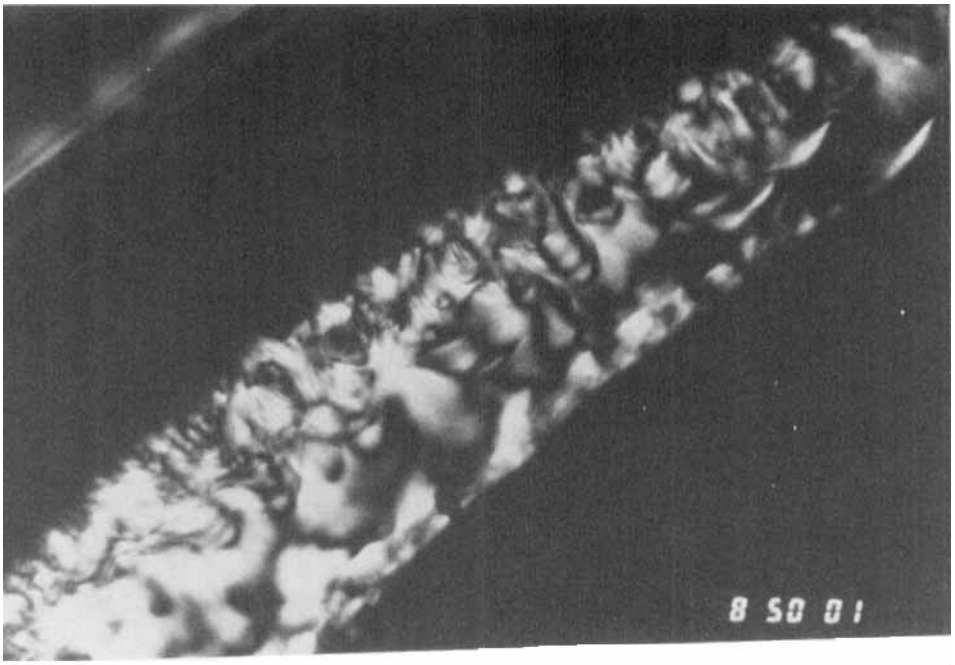


(*a*)

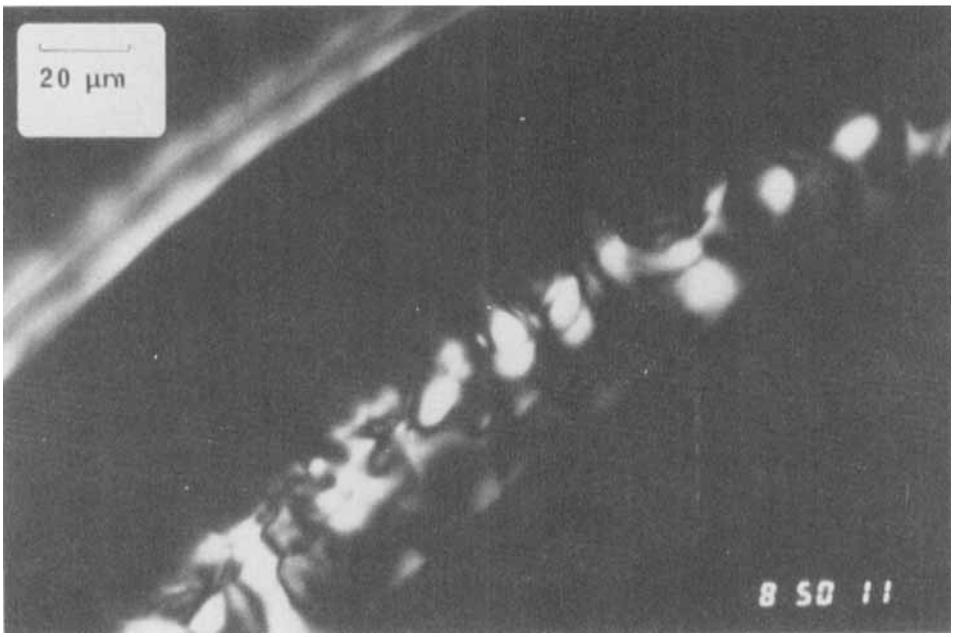


(*b*)

Figure 4. Sequence of events on cooling an 8 per cent gel (*a*) 81°C; (*b*) 59°C.

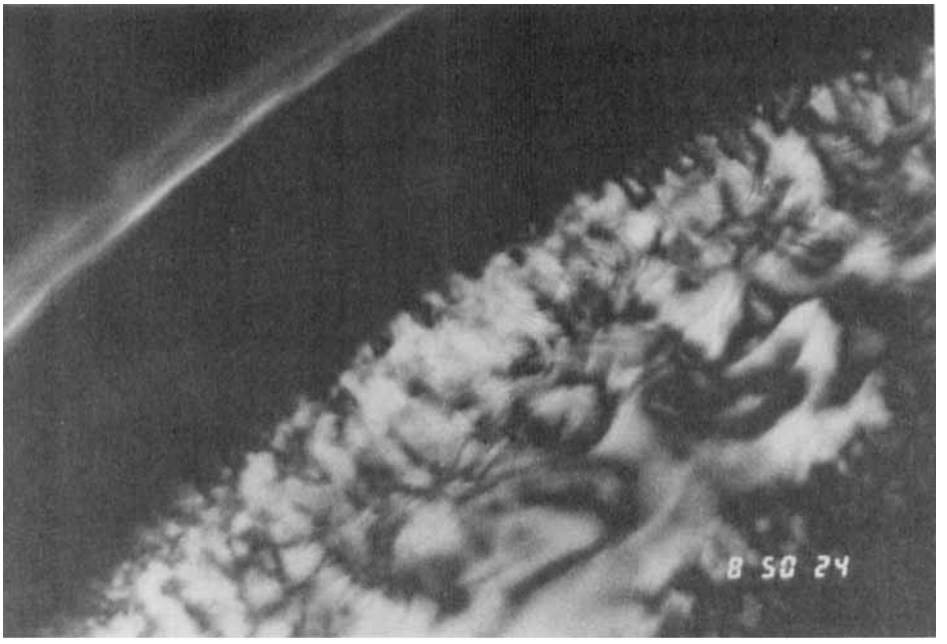


(*a*)

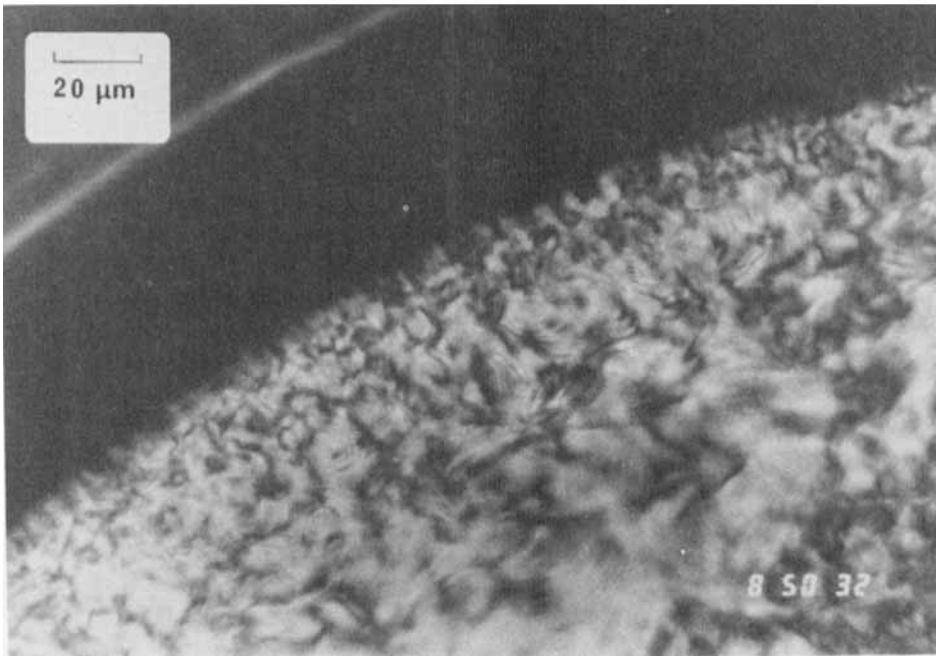


(*b*)

Figure 5. Second heating of an 8 per cent gel (*a*) 21°C; (*b*) 95°C.



(*a*)



(*b*)

Figure 6. Second cooling of an 8 per cent gel (*a*) 60°C; (*b*) 26°C.

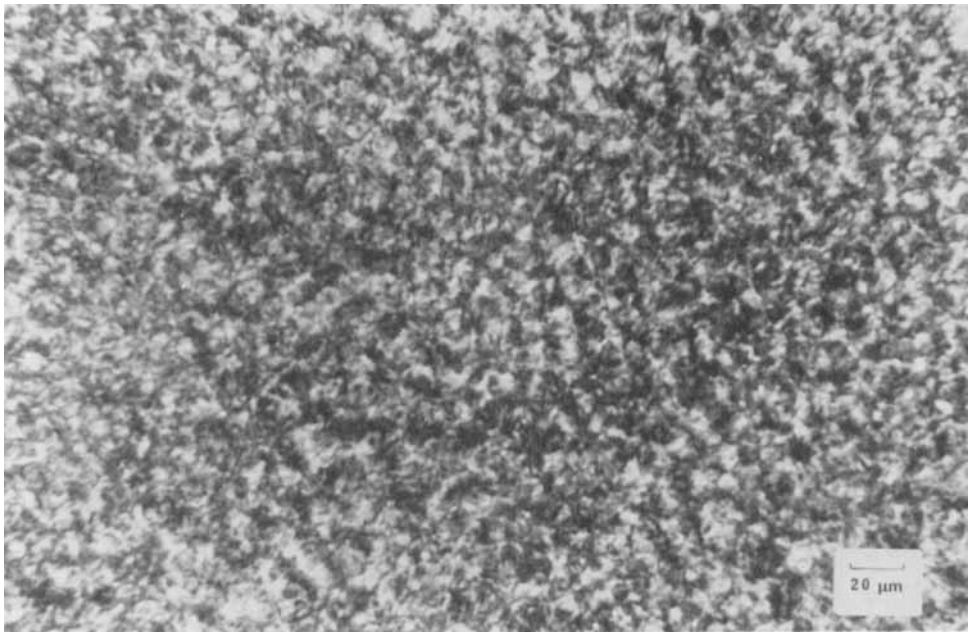


Figure 7. Typical texture of a 10 per cent gel under crossed polars at room temperature.

The as-prepared gels of 10 per cent concentration are always of a black and white mottled appearance under crossed polars (see figure 7). If prepared on the slide a few days before the experiment a liquid pool develops around the gel, which nevertheless retains its shape. Again, as in the 5 and 8 per cent gels, droplets of an isotropic liquid phase are present in the surrounding volume, and these grow and coalesce on heating. Gel samples taken three weeks and six months after the stock gel was prepared behaved in much the same manner.

At 36°C the pool perimeter is observed to contract towards the anisotropic material. At 63°C the anisotropic regions within the pool are reduced in volume; the dark perimeter changes shape becoming more or less circular by 78°C. At 75°C further anisotropic material (LC2) appears on the inner perimeter, building up as the temperature is increased further. At 92°C anisotropic material (LC1) is observed outside the dark perimeter and at 102°C the perimeter itself contracts (see figure 8). A fingerprint texture is observed in LC2 and this region begins to show colour. If held at 102°C the perimeter collapse continues, reducing the volume of isotropic material and increasing the volume of LC2. Outside the perimeter LC1 increases in volume. After about 15 minutes the isotropic material has completely disappeared and a dark bordered coloured anisotropic region, LC2, surrounded by the black and white textured LC1 remains (see figure 8 (*c*)). The coloured crescent appears quite dark in transmitted light which suggests that it scatters strongly. Again two types of anisotropic material seem to have developed, a black and white texture which occupies the larger volume at 102°C (LC1) and a black bordered crescent of coloured material exhibiting a fingerprint texture (LC2).

The 15 per cent gels as prepared show a slightly less granular texture (see figure 9). They are usually coloured, however, perhaps due to greater thickness as this concentration is much more difficult to compress. In a six month aged specimen the two

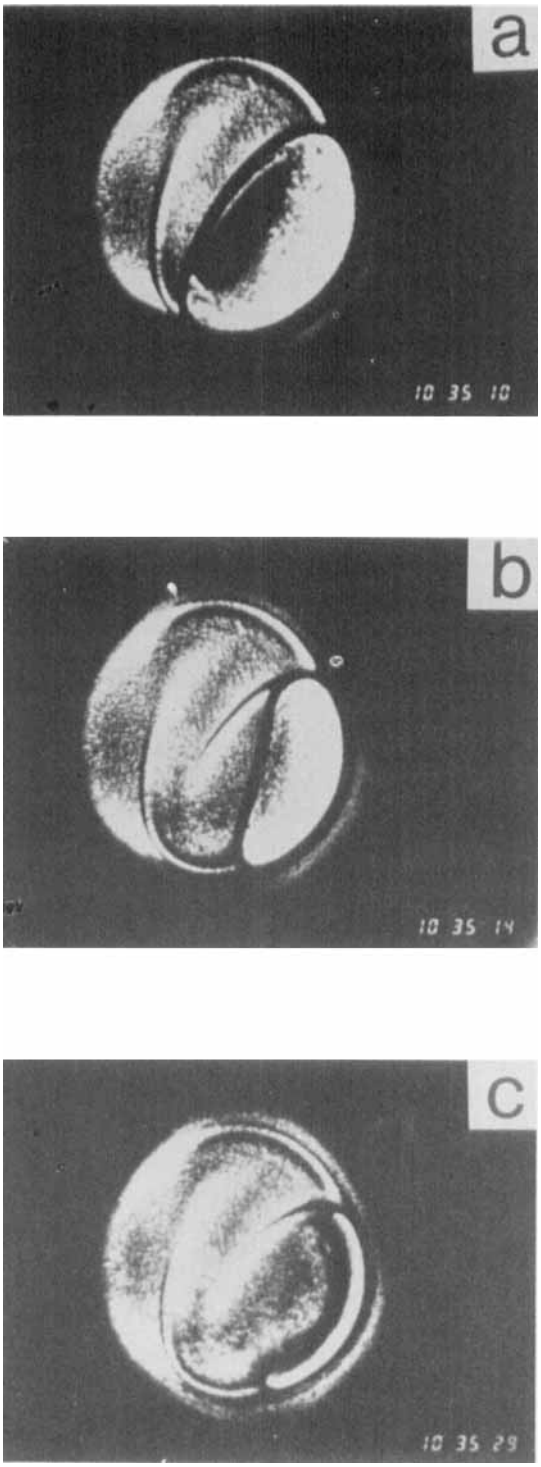


Figure 8. Contraction of the isotropic pool in a 10 per cent specimen on heating with and without crossed polars held at 102°C for (*a*) 12, (*b*) 17 and (*c*) 25 min.

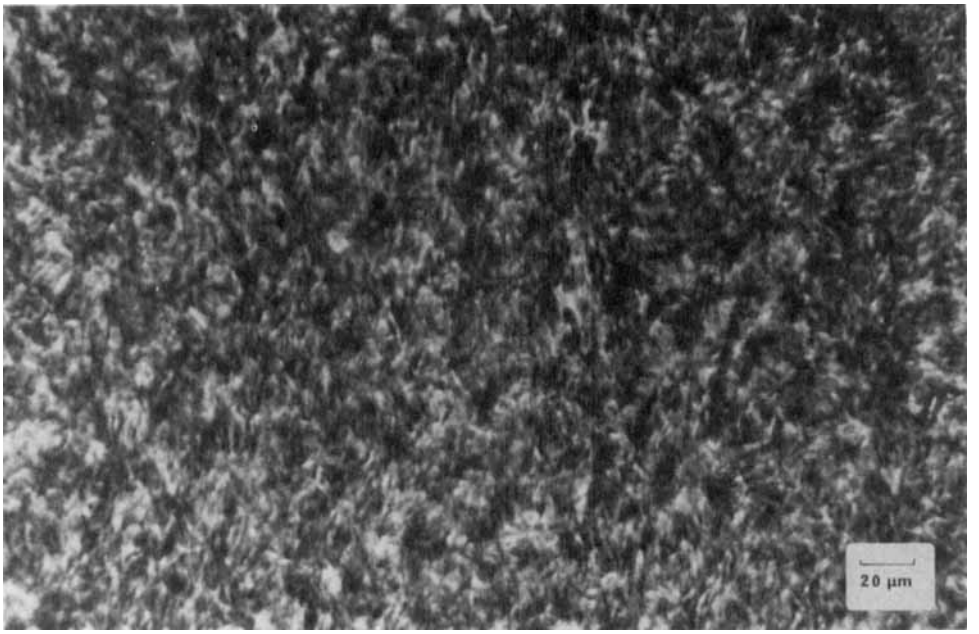


Figure 9. Typical appearance of a 15 per cent gel under crossed polars before heating.

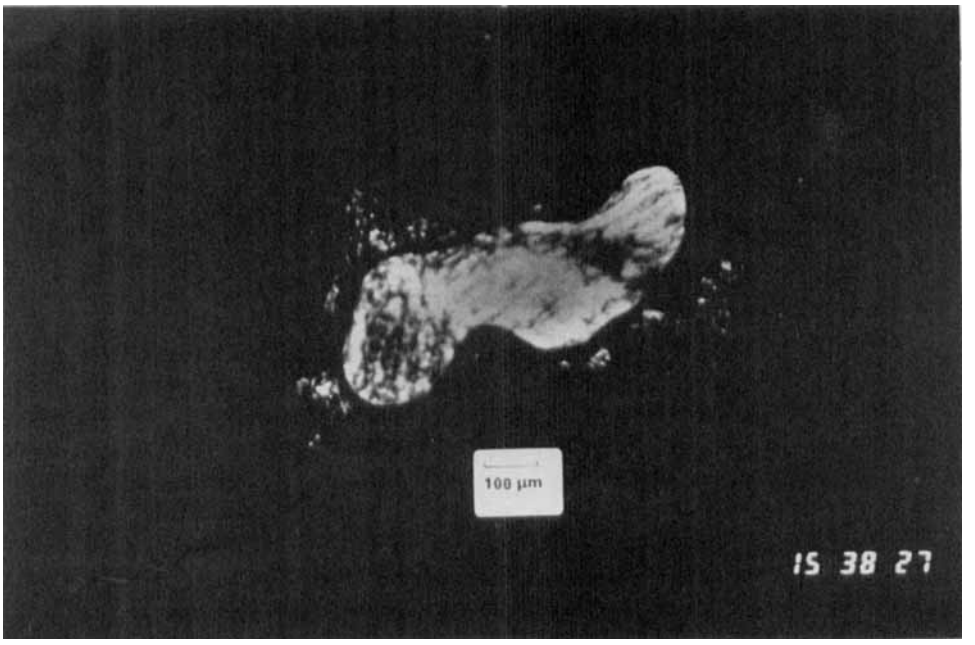


Figure 10. Coexisting anisotropic and cholesteric phases in a 15 per cent gel at 62°C under crossed polars.

phase liquid and gel persisted up to 53°C when the isotropic liquid began to spread over the gel. Held at 56°C the specimen appears as a black bordered anisotropic region, LC2, with a small amount of anisotropic material outside, LC1. At 62°C the black border contracts (see figure 10) and a fingerprint texture is observed in LC2, the spacing being of the order of a micron (see figure 11). Held at 62°C for several hours the black border contracts further but appears to have reached an equilibrium state after about three hours, some dark areas still being visible inside the black perimeter. On increasing the temperature above 62°C the perimeter was seen to contract further at 76°C, leaving the coloured LC2 surrounded by the black and white LC1.

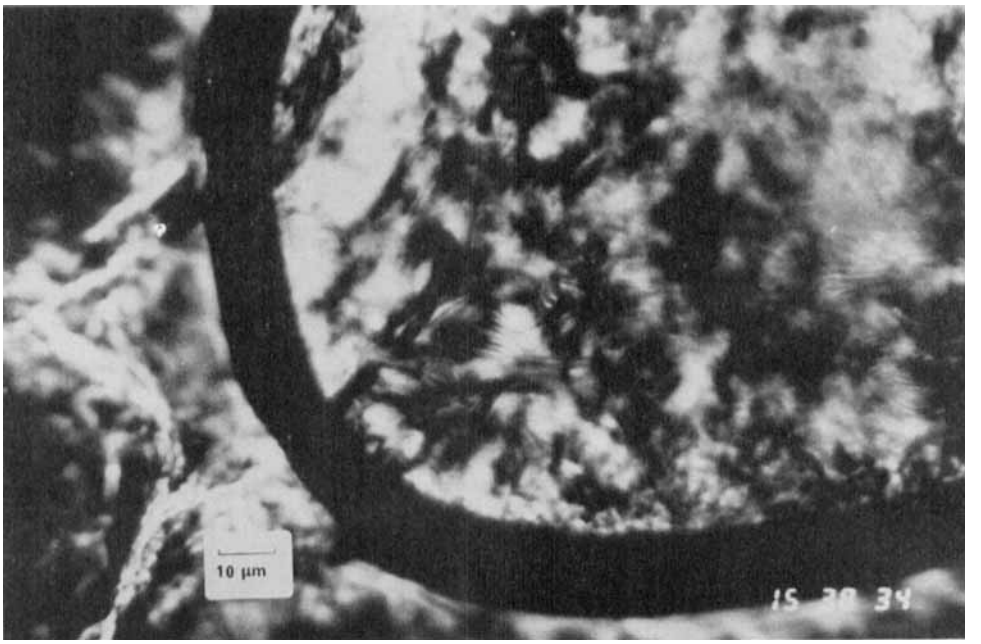


Figure 11. Fingerprint texture of a 15 per cent specimen at 62°C under crossed polars.

All of these results were obtained from small amounts of gel which were surrounded by air when sealed onto the slide. To check that solvent evaporation was not playing a significant role in the phase transitions observed, large volumes completely filling the cell were also used (Isotropic droplets were not visible in these large volume specimens). Morphologically similar results were obtained, but transitions occurred at higher temperatures. It is as if the physical constraints impede the transformation to LC1, as well as problems resulting from thermal lag. At 60°C the boundary of the specimen becomes smoother and the isotropic region is reduced in size. The anisotropic region continues to darken as the temperature is raised. Figure 12 is a representative series of photographs taken of a large sample of 15 per cent gel while held at 110°C. After 25 minutes a granular anisotropic region, LC1, appears and fingerprinting develops in the non-granular region, LC2; the isotropic volume continues to be reduced. On cooling LC2 grows but without the appearance of fresh fingerprinting; there are remnants of the high temperature fingerprinting at room temperature although much reduced, see figure 12 (*d*).

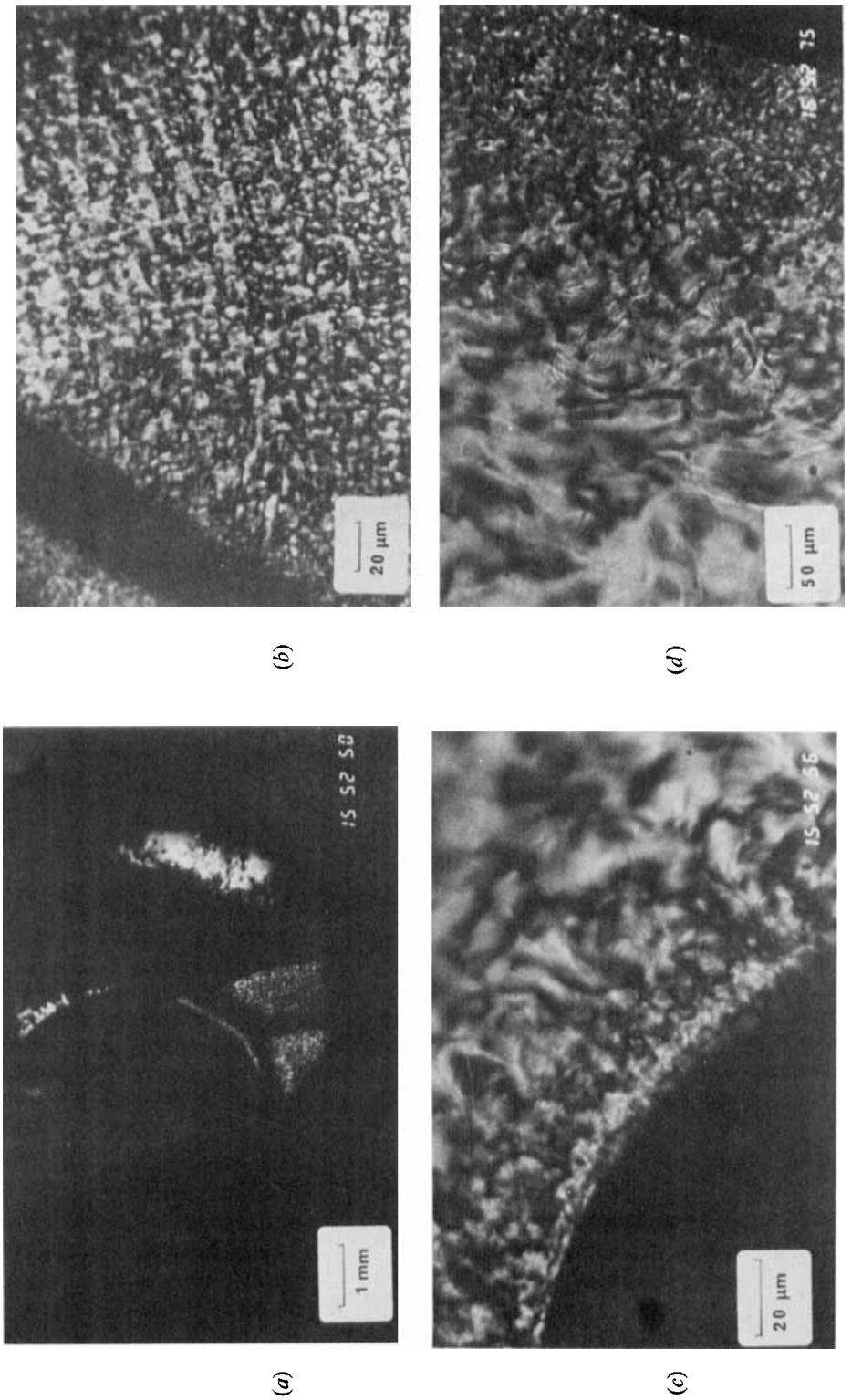


Figure 12. Sequence of events in a 15 per cent gel (*a*) 110°C held for 10 min; (*b*) 110°C held for 25 min, texture in the granular region LC1; (*c*) 110°C held for 37 min, texture in the fingerprinted region of LC2; (*d*) 47°C.

4. Discussion

All concentrations discussed here are mechanically self-supporting gels and do not flow at room temperature; shear modulus measurements show them all to have gel-transition temperatures well above room temperature [7]. According to Miller *et al.* [8], gels of PBLG (MW 310000) in DMF form only below room temperature. When DMF gels do form their appearance is significantly different from the gels described here: all DMF gels whether isotropic, biphasic or ordered solution at higher temperatures appear as a uniform pale yellow field under crossed polars, whereas the higher concentration BA gels show a distinctly anisotropic mottled phase coexisting with an isotropic liquid. The 5 per cent BA gel resembles the DMF gels, being homogeneous (although anisotropic). These differences in microstructure could be due to the mode of preparation of the gels. The BA gels were made at high temperature (70–80°C) and allowed to cool slowly (< 1°C/min). The DMF gels were prepared by quenching from the isotropic state. Miller *et al.* [8] suggest that the network structure of the DMF gels may be formed as the result of the formation of bicontinuous phases, which cannot ripen into two bulk phases by viscous flow in each phase (as shown in other studies of bicontinuous polymer phases [9]) because the polymer-continuous phase will be fibre-like. Alternatively, the difference in appearance may reflect some fundamental difference in the gels.

Assuming that at 25°C all of the gels are in the wide biphasic region of the Flory phase diagram the volume percent of the anisotropic material in the 5 per cent gel must be small ($\leqslant 5$ per cent). Thus, it must be very finely dispersed indeed in order to give the uniform anisotropic appearance under crossed polars. If a true biphasic exists it is beyond the resolving power of the microscope, otherwise this particular concentration appears to be very similar to the bicontinuous gels observed by Miller. If the gel is indeed biphasic we should expect to observe a gradual clearing (darkening under crossed polars) on heating as the amount of anisotropic material decreases. This behaviour is observed in all specimens of the 5 per cent gels, as also with a lower heating rate of 1°C/min. A new equilibrium could be achieved quite rapidly by holding the temperature at any point below the clearing temperature, which was estimated to be between 60°C and 68°C. Reducing the temperature from above the clearing temperature causes anisotropic material to reappear, but probably due to kinetic effects the original texture is not achieved, the final state normally being composed of islands of isotropic and anisotropic phases. Anisotropy first reappears at a temperature much lower than the clearing temperature at between about 30°C and 45°C.

The 8, 10 and 15 per cent solutions resemble each other in their behaviour, but are quite different from the 15 per cent solution. On heating the 10 per cent gel, the amount of isotropic material is seen to increase at the expense of anisotropic material. This behaviour is less marked in the 15 per cent solution which contains a smaller amount of isotropic material, initially. They both, however, eventually develop two anisotropic regions, the region which decreases in volume as the temperature is raised (LC2) exhibiting a fingerprint texture. This is first noticeable at about 75°C in the 10 per cent and approximately 56°C in the 15 per cent solution. (The experiments were performed under carefully controlled conditions, but it is not proposed that the temperatures cited are identically the phase transition temperatures. Temperatures at which changes in the specimen are observed are probably dependent on the thermal history of each specimen.)

Qualitatively the results suggest that there must be three distinct regions in the phase diagram at these higher concentrations. The low temperature region is biphasic, corresponding to the coexistence of isotropic and anisotropic material, as predicted by Flory. The low temperature anisotropic material does not exhibit a fingerprint texture and cannot definitively be assigned a cholesteric nature. It may, however, be or contain a crystal solvate as suggested by Ginzburg *et al.* [6], which might also explain the appearance of the exudate; this possibility is considered further subsequently.

Raising the temperature causes an increase in volume of the isotropic material at the expense of the anisotropic material, in accord with the Flory phase diagram, until a temperature is reached at which a second anisotropic component is apparent. Above this temperature there appear to be three coexisting components, isotropic, and two anisotropic phases, LC1 and LC2. Over some part of the temperature range LC2 can definitely be identified as a cholesteric by the appearance of the fingerprint texture. The small spacing of the lines (of the order of several microns) suggests that this is a highly concentrated phase [4]. The periodicity of PBLG in DMF has been shown to increase with temperature and decrease with concentration [4, 6]. Sasaki *et al.* [9] have shown that for PBLG in BA the periodicity is much lower than in DMF and also increases with temperature (until at about 100°C the sense of twist reverses, so that the pitch becomes infinite). Raising the temperature further now causes a reduction in volume of the isotropic phase and an increase in volume of LC1 until (for the 10 and 15 per cent gels) the isotropic phase completely disappears and LC1 and LC2 alone remain. A further increase in temperature causes LC2 to decrease in volume while LC1 increases.

The coexistence of two anisotropic phases at high temperature might be identified with the upper region of the wide biphasic in the Flory phase diagram where two liquid crystal phases are thought to coexist. (Current work is aimed at looking for gross phase separation in macroscopic samples.) Such coexistence of two liquid-crystalline phases was predicted by Flory, and indirectly has been inferred by Russo and Miller [4], but this appears to be the first direct evidence. It should be noted that once LC1 has appeared it does not subsequently disappear on reducing the temperature again. This anomaly may be due to the long time scales that would be required for molecular rearrangement, or connected in some way with the expected fractionation by molecular weight [15, 16].

The increase in volume of LC1 and corresponding decrease in LC2 with increasing temperature is entirely in accord with the Flory phase diagram if LC2 is identified as the high concentration and LC1 as the low concentration phase. At first sight it seems strange that LC1 does not exhibit a cholesteric texture. However, it should be noted that Sasaki *et al.* [9] observed a cholesteric texture only for high concentrations in the gel state (> 20 wt %; molecular weight 130 000). If PBLG is cholesteric only at high concentrations in BA this would explain the lack of fingerprint texture in the low concentration LC1 phase, although it must be noted that since the PBLG used in this study is of much higher molecular weight than in [9], a direct comparison cannot be made.

The complexity of the behaviour of these gels might appear to indicate a region of triple phase coexistence, with the additional possibility of underlying crystallites (see later). This would appear to contravene the phase rule. Two possible explanations can be put forward. Firstly, the kinetics of the phase transformations observed here are relatively slow. It is quite possible that the LC2 + LC1 + I triple phase

coexistence is not a true equilibrium. This view is supported by the lack of reversibility during heating and cooling, and the fact that LC2 may continue to grow in extent at the expense of the isotropic regions upon cooling. Secondly, the polydispersity of the PBLG is unknown. Thus the system is not a true binary and some of the effects observed may be associated with fractionation by molecular weight. Such fractionation is known to occur in the distribution of polymer molecules in the simple biphasic region of the Flory phase diagram [15, 16] although it has not been studied explicitly for a PBLG based system. If such fractionation does occur, it would be expected to lead to the longer rods preferentially moving to the anisotropic phase(s). This effect will tend to make the viscosity of the anisotropic regions increase, and this will slow the kinetics down even further. It is noticeable that LC1, which physically is not in contact with isotropic regions but remains always separated by a well-defined perimeter, never reduces in volume. This effect is also likely to be kinetic in origin.

These optical microscopy observations are seen to support a phase diagram in general agreement with the Flory model. The very fact, however, that the samples are gels at room temperature suggests that some form of crystals may be present as well: gelation as a consequence of crystallization is a well-known phenomenon [12] and has been observed in many polymer-solvent systems. The rigidity of a gel in such a case is supplied by the crystallites, which interconnect non-crystalline regions.

One observation from this study does support indirectly the presence of some crystallinity. In these samples all of the gels at ambient temperature were observed to exude an isotropic liquid. This effect is similar to the syneresis observed in crystalline gels due to the thickening of crystals after their initial formation [13, 14]. The production of the exudate in these PBLG-BA gels has not been reported previously. The exudate appears only if the solution is kept in the gel state: furthermore if a portion of the gel is removed to a new container further exudate appears. The increasing turbidity of the gels with time is also suggestive of the formation of crystals or a crystal-solvate complex. However other reasons for the appearance of the exudate may be put forward. For instance, it is possible that the exudate may be connected with fractionation by molecular weight, low molecular weight material being preferentially distributed in an isotropic liquid phase, higher molecular weight material remaining in the gel. We believe that the isotropic exudate droplets are distinct from the isotropic (polymer-containing) pool, the former being pure solvent (strongly suggested by the fact that it can coat even the lid of the container).

More substantial evidence supporting the view that crystals, thought to be a crystal-solvent complex, are present and are the source of the gel rigidity are presented elsewhere [7]. Because the crystals are likely to be far below the resolution of the light microscope it is not surprising that direct evidence for their existence is not forthcoming from this study. As a result it is also clear that this study cannot demonstrate the relation if any, between the type of phase diagram drawn by Flory and the gelation process. Indeed, as a comparison of the transitions observed by optical microscopy, presented here, and those revealed by D.S.C. and modulus measurements [7] shows, there is no immediate correlation. That these anisotropic PBLG-BA systems are gels at room temperature is, as it were, coincidental. If the gelation process is associated with crystallization then it is the crystal melting that determines the gel-sol transition, and not the type of optically observed transitions observed here. In the context of this study the melting can probably be associated only with the temperature at which the edges of the specimen become smoother and the sample ceases to be self-supporting.

If such crystallites are present, an alternative explanation for the loss of fingerprinting at room temperature in the LC2 phase is possible: fingerprinting will only appear if long range correlations of the helical twist of the director exist. Such correlations are likely to be disrupted by the presence of crystallites. Thus, locally, the phase may remain cholesteric, yet not possess a macroscopically identifiable pitch. (It should also be noted that fingerprinting can take a long time to reach equilibrium [4], and particularly at low temperatures the large regions of uniform orientation required for clear visibility of the periodicity lines may be hard to develop.) It is also necessary to address the loss of fingerprinting at temperatures near 100°C. Again only a tentative suggestion can be offered at the moment. It has been shown by Sasaki *et al.* [16] that the pitch of PBLG in BA increases as the temperature is raised, and becomes infinite between 95°C and 100°C as the sense of the helical pitch changes from right to left handed. As the pitch increases to a value comparable to or larger than the thickness of the samples in this study ($\sim 25\,\mu$m) the fingerprinting may be expected to disappear, as surface anchoring forces dominate. (Changes in the nature of the anchoring around the dark perimeter at the LC1/LC2 boundary could also affect the appearance of fingerprinting). Thus it seems likely in this study that the presence or absence of fingerprinting cannot be used as a definitive means of identifying a cholesteric phase.

The idea that crystallites (either of a crystallosolvate or pure polymer) are present agrees with the findings of Sasaki *et al.* [10, 17]. It also fits in with the predictions of Ciferri and Krigbaum [18] and Papkvov [11]. For this system there is insufficient data to provide a full phase diagram. We believe, however, that we have evidence to support the curvature of the original phase diagram of Flory which leads to the coexistence of two LC phases, but in addition line(s) relating to the melting of the crystals present must be included.

5. Conclusions

The model that this optical microscopy study supports is as follows: at ambient temperatures the samples consist of a cholesteric LC2 phase and an isotropic phase. The volume of isotropic material increases, for all concentrations studied, as the temperature is raised. A second anisotropic phase, LC1 is then encountered (the simultaneous appearance of three phases probably being a non-equilibrium effect, brought about by sluggish kinetics). LC1 is of lower concentration than LC2 and does not exhibit a fingerprint texture. In the 10 and 15 per cent samples further heating leads to the disappearance of the isotropic phase leaving the LC1 and LC2 phases. Additionally we believe that crystallites are present at room temperature which melt at the gel-sol transition, this melting occurs independently of the other transitions and cannot be simply related to the original Flory phase diagram.

We are grateful to Professor Muthukumar and Dr. Murthy for a fruitful discussion. We would like to thank the AFRC and SERC for financial support.

References

[1] Flory, P. F., 1956, *Proc. R. Soc.* A, **234**, 73.
[2] Wee, E. L., and Miller, W. G., 1971, *J. Phys. Chem.*, **75**, 1446.
[3] Chakrabarti, S., and Miller, W. G., 1984, *Biopolymers*, **23**, 719.
[4] Russo, P. S., and Miller, W. G., 1983, *Macromolecules*, **16**, 1690.

[5] Russo, P. S., and Miller, W. G., 1984, *Macromolecules*, **17**, 1324.
[6] Ginzburg, B., Siromyatnikova, T., and Frenkel, 1985, *Polymer Bulletin*, **13**, 139.
[7] Hill, A., and Donald, A. M., 1988, *Polymer*, **29**, 1426.
[8] Miller, W. G., Kou, L., Tohyama, K., and Voltaggio, V., 1978, *J. Polymer Science: Polymer Sym.*, **65**, 91.
[9] McMaster, L. P., 1975, in *Copolymers, Polyblends and Composites*, edited by N. A. J. Platzer (Adv. Chem. Ser., Vol. 142) (American Chemical Society).
[10] Sasaki, S., Tokuma, K., and Uematsu, I., 1983, *Polymer Bull.*, **10**, 539.
[11] Papkov, S. P., 1984, *Advances in Polymer Science*, edited by M. E. Gordon (Springer-Verlag), 75.
[12] Mandelkern, L., 1964, *Crystallization of Polymers* (McGraw-Hill), p. 112.
[13] Pines, E., and Prins, W., 1973, *Macromolecules*, **6**, 888.
[14] Stainsby, G., 1977, *The Science and Technology of Gelatin*, edited by A. G. Ward and A. Courts (Academic Press), p. 203.
[15] Aharoni, S. M., 1983, *Polymer*, **9**, 186.
[16] Conio, G., Bianchi, E., and Tealdi, A., 1981, *Macromolecules*, **14**, 1084.
[17] Sasaki, S., Hikata, M., Shiraki, C., and Uematsu, I., 1982, *Polymer J.*, **14**, 205.
[18] Ciferri, A., and Krigbaum, W. R., 1981, *Molec. Crystals liq. Crystals*, **69**, 273.