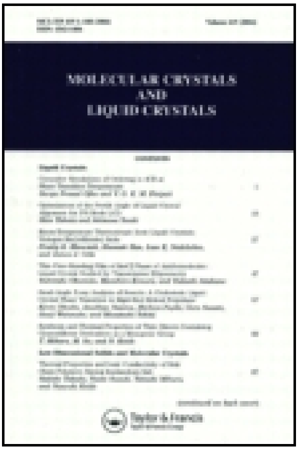

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Alyson Hill [a] & Athene M. Donald [a]

[a] Cavendish Laboratory, Madingley Road, Cambridge, CB3 OHE, England

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GELATION IN THE POLY(γ-BENZYL-L-GLUTAMATE) - BENZYL ALCOHOL SYSTEM

ALYSON HILL AND ATHENE M. DONALD
Cavendish Laboratory, Madingley Road, Cambridge
CB3 0HE, England

Abstract Gels formed from liquid crystalline solutions of poly (γ-benzyl-L-glutamate) in benzyl alcohol have been studied by a variety of techniques. It seems that the junction points in the gels are crystalline in nature, possibly from a crystallosolvate phase. These crystallites are so small that they are well below the resolving power of the optical microscope. Hence observation under the polarising microscope shows behaviour in broad accord with the Flory predictions, and with no correlation betweeen the optical transitions and the gel-sol transition. Additionally, at high temperatures, coexistence of two anisotropic phases is seen.

INTRODUCTION

The problem of the nature of the network in flexible polymeric gels has had a long history. Recently attention has also been focussed on gels from rigid rod polymers, which can form gels which are optically anisotropic. Much of this work has concentrated on the polymer poly (γ-benzyl-L-glutamate) (PBLG). However a consensus on the structure of the gel has not been reached, both crystallosolvate phases and spinodal decomposition having been proposed[1-4]. In this paper we report on a study of gels of PBLG in benzyl alcohol (BA) using three main techniques: DSC, rigidity modulus measurements and polarised light microscopy. Some preliminary Xray experiments have also been carried out.

EXPERIMENTAL

Solutions of concentrations 5, 8, 10, 15 and 15.7 volume % were made up, using PBLG of MW 345000 from Sigma Chemical, and spectroscopic grade BA. Solutions were stored at 25°C, for a minimum of three weeks to allow equilibration to occur. Rigidity modulus measurements were carried out using the method of Ward and Saunders[5]. The DSC used was a Mettler 2000 operated at a heating or cooling rate of 1°C/minute. Optical microscopy was performed on a Carl Zeiss Jenapol with a Stanton Redcroft heating stage.

RESULTS

When the rigidity modulus is plotted as a function of temperature(e.g. Figure 1), it is found that a sharp drop occurs over a narrow range. The transition temperature is identified as the temperature at which a straight line through the lower temperature points crosses a straight line through the higher.

Measurements of the modulus as a function of temperature were carried out on both heating and cooling for all the gels. For the 5% solution a

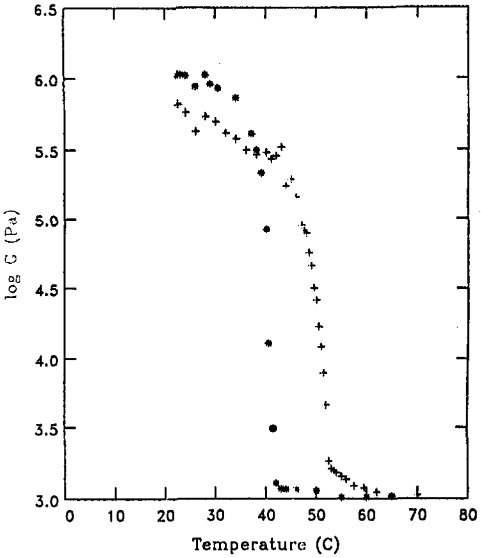

FIGURE 1. Rigidity modulus of 10% gel

single transition was observed both on raising and lowering the temperature, with the latter being some 8°C lower than the former. For the higher concentration solutions, two transitions (i.e. changes in slope) were observed on heating, but again only a single on one on cooling lying a few degrees below the lower of the two heating transitions. The transition temperatures are listed in Table 1.

These results correlate well with the transitions observed by differential scanning calorimetry; here, too, the higher concentrations yield two heating transitions and all solutions show a single cooling transition. The actual

TABLE 1 Transition temperatures

	DSC						rigidity		
conc.	ave.small mass			large mass			modulus		
	T1	T2	T3	T1	T2	T3	T1	T2	T3
5	43.6	-	32.6	54.8	-	30.5	45	-	37
8	-	-	33.9	49.6	56*	35.2	45	53	41
10	50.6	-	41.7	50.8	60.0	39.0	47	54	41.5
15	48.5	57.5	43.1	48.0	57*	46.0	-	-	-
15.7	47.9	57.1	45.8	50.6	59.2	47.4	-	-	50

* ± 2°C

T1 and T2 are the transitions observed on heating; T3 is that seen on cooling.

transition temperatures measured (see Table 1), also agree well. Additionally, using DSC, one is able to explore readily the effect of time on the magnitudes of the endo- (exo-) therms. Preliminary results show the higher (or only, for the 5%) heating transition peak was substantially reduced in magnitude if the experiment was immediately repeated; the cooling transition was not affected.

Optically, the behaviour of the samples is very complex, and it is extremely difficult to be sure that equilibrium is maintained throughout any particular heating cycle. At room temperature, the samples are biphasic - one isotropic and one anisotropic phase being present. It is also found that an isotropic liquid is "exuded" which coats the surfaces of the container. This is thought to be pure solvent. Infrared spectroscopy has failed to identify any polymer present in the liquid; this could mean that a very low concentration was nevertheless contained within the solvent, but in this case one would not expect the liquid to be able to coat the top surface of the container well above the level of the gel, as it does.

Upon heating the 5% gel, the isotropic droplets grow until the whole sample becomes isotropic at a temperature (~65°C) which is well above the transition temperature observed by DSC/modulus measurements. The more concentrated samples never become fully isotropic, as in accord with the theoretical predictions of Flory[6]. For concentrations of 8% and above, the most striking feature in the polarising microscope is the appearance at elevated temperatures of a thick dark boundary separating two anisotropic phases (Figure 2). The "inner" phase (i.e. inside the boundary), designated LC2, is present at all temperatures, and over part of the temperature range exhibits the fingerprint texture (Figure 3). Outside this boundary, which forms at temperatures upward of ~55°C depending on concentration, a second anisotropic phase LC1 forms, which never shows any sign of fingerprinting. Typically LC1 appears to be black and white, while LC2 appears coloured.

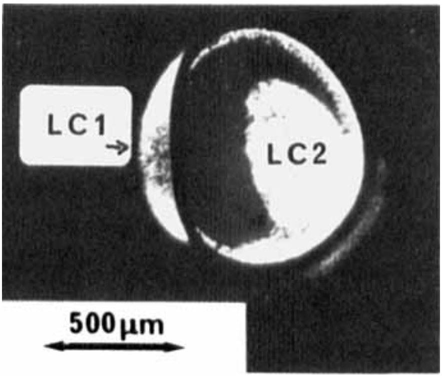

FIGURE 2 Coexisting phases in a 10% sample at 102°C (crossed polars)

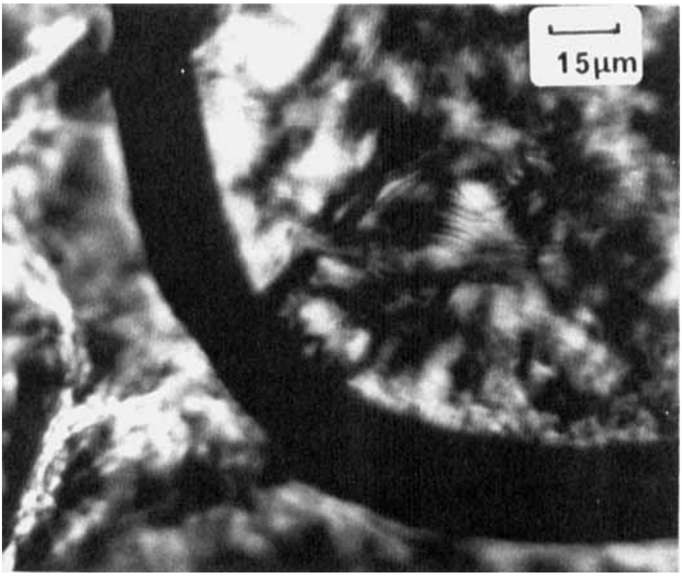

FIGURE 3 LC1 and LC2 in a 15% sample at 62°C

There seems to be a region where three phases coexist - isotropic and two anisotropic - but this may simply reflect the long time required to reach equilibrium.

A microdensitometer scan across Xray photographs of the 5 and 15% gels shows that in the latter a sharp peak is observed superimposed and just inside the diffuse innermost ring (Figure 4). This is indicative of some highly ordered phase in the higher concentration. This view is substantiated by Xray work on oriented 15% gels (Poliks and Samulski, Private Communication).

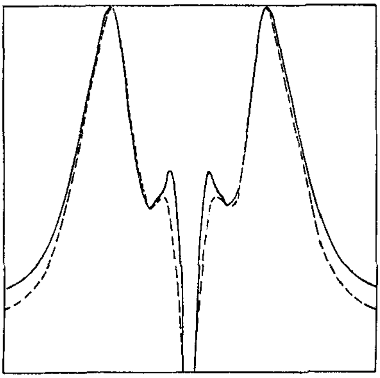

FIGURE 4 Microdensitometer scan of Xray photographs of 5 (---) and 15% (——) gels.

DISCUSSION

The DSC and modulus measurements give transition temperatures in good agreement with one another, but these transitions do not correlate with those seen optically. It seems likely that there are two phenomena being observed, each with its own set of transitions. The polarising microscope is sensitive to the liquid crystal transitions predicted by Flory, and our observations are in accord with the Flory phase diagram, including what seems to be the first direct observation of two coexisting liquid crystalline phases.

On the other hand, the modulus measurements are probing the gel-sol transition. If this transition can be associated with some kind of crystallosolvate phase as suggested by Papkov[7], then the good agreement with the DSC measured transitions is readily explicable: the DSC is monitoring the melting of the crystallites, and it is these junction points that make up the junction points of the gel. However the crystallites (which will be embedded in the liquid crystalline phase) will be far below the resolving power of the light microscope, and hence undetectable by this technique;thus no correlation between the DSC/ modulus and optical transitions is to be expected.

Additional support for this model comes from the preliminary Xray work which also suggests the presence of some kind of crystallite. One might expect all concentrations to show this reflection, but the total volume of crystalline material may be too low to be detectable. These crystallites can probably be identified with the "complex structures" seen by Sasaki et al.[8]. The presence of the exuded liquid is also consistent with this picture, as it could arise from solvent rejection during crystal thickening[9].

However some uncertainties remain. Firstly, both the DSC and modulus measurements show <u>two</u>

transitions on heating in the higher concentration gels. One of these (the higher) is sensitive to kinetics, so that it reduces in magnitude if a second heating run is carried out immediately after the first. One tentative explanation is that this is due to a crystal phase associated with the PBLG molecules alone[3].

Secondly there is the question of identifying the two anisotropic phases. Of particular note is the rather limited temperature range over which we see fingerprinting in LC2. Two possible explanations for this can be put forward. Fingerprinting is only possible if long range xcorrelations of the director exist. These may be sufficiently disrupted by the presence of crystallites to prevent the formation of a macroscopically identifiable pitch, even though locally the phase is cholesteric. Additionally it has been shown for this system that fingerprinting is only seen at rather high concentrations (>20% for a MW of 130000)[8]. This is probably why we never see fingerprinting in LC1, which we believe is the lower concentration of the two anisotropic phases. At high temperatures, the work of Sasaki[8] shows that the pitch increases until the sense of the helix actually reverses near 100°C. As the thickness of the sample (~25μm) becomes comparable with the pitch fingerprinting is also likely to disappear. Thus the limited range of temperatures over which fingerprinting is observed need not imply that LC2 is not everywhere cholesteric.

CONCLUSIONS

The PBLG-BA system forms a gel at room temperatures which appears to be liquid crystalline. However the phase transitions in the liquid crystalline phases, and the sol-gel transition are distinct; the former are in accord with the Flory phase diagram, including the observation of coexisting liquid crystalline phases. It is thought that the gel structure arises from a crystallosolvate phase.

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REFERENCES

1. W.G.Miller, L.Kou, K.Tohyama and V.Voltaggio, J.Poly.Sci. Poly.Symp., 65, 91 (1978).
2. S.Sasaki, M.Hikata, C.Shiraki and I.Uematsu, Rep. Prog.in Poly.Phys.Jap., 21, 557 (1978).
3. S.Sasaki, K.Tokuma and I.Uematsu, Poly.Bull., 13, 539 (1983).
4. G.Ginzburg, T.Soromyatnikova and S.Frenkel, Poly. Bull., 13, 139 (1985).
5. P.R.Saunders and A.G.Ward, Res.Rep. B6, British Gelation and Glue Research Assocn., 1953.
6. P.J.Flory, Proc.Roy.Soc.Lond., A234, 73 (1956).
7. S.P.Papkov, in Contemporary Topics in Polymer Science ed. E.M.Pearce and J.R.Schaefgen Plenum, New York, 1977), 97.
8. S.Sasaki, M.Hikata, C.Shiraki, and I.Uematsu, Poly.J., 14, 205 (1982).
9. L.Mandelkern, in Crystallization of Polymers, (Mcgraw Hill, New York, 1964), Ch.8.