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Gelation

Gelation in the Poly(γ-Benzyl-L-Glutamate) – Dimethylformamide System

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The poly(γ -benzil-L-glutamate)(PBLG)-dimethylformamide (DMF) system was studied in a wide range of concentrations and temperatures. It appears that there are encountered two types of gel in this system. The Ith type is formed at both high temperatures and concentrations, whereas the IIth type is formed at lower temperatures and for all concentrations, from 1 per cent to 76 per cent. Phase diagrams for PBLG with molecular weights of 50,000 and 200,000 contain gel formation curves. The identity period S of the liquid crystalline structure was also measured over the 45°-105°C temperature range for PBLG with molecular weights of 50,000 and 130,000.

The liquid crystalline solutions of poly(γ-benzil-L-glutamate)(PBLG) were aboundantly studied, but only few papers are concerned with the gelation phenomena (MILLER et al. 1978; SASAKI et al. 1982). In the present paper an attempt is made to characterize the gelation phenomena in dimethylformamide (DMF) solutions and describe the changes in the structure of the liquid crystalline phase over the temperature range 45°-105°C for PBLG with molecular weights of $M = 50{,}000$ and $M = 130{,}000$ respectively. The identity period S was determined from the "finger-print" texture ($P = 2S$, where P is the pitch of the cholesteric helix).

Before use DMF was dried over calcinated zeolite and then distilled under vacuum. The amount of residual water in DMF did not exceed 0.01 per cent.

The solutions were prepared in ampoules with an internal diameter 3mm filled with argon and sealed. As a measure of concentrations the weight per cent or weight fractions were used. The cloud points were determined either visually, using a step by step heating (at each temperature solutions were kept not less than 6 hours) or by photoelectric recording of the intensity of non-polarized light transmitted through the solution in the temperature-scanning regime. The occurence of liquid crystalline state was determined with a polarized light microscope.

RESULTS

Examination of PBLG solutions of different concentrations in DMF in a wide temperature range indicated the presence of two types of gel in this system. The type I is a rather transparent anisotropic gel (the region IV in FIG.1b), and the type II is a turbid white gel (the region V in FIG.1b)

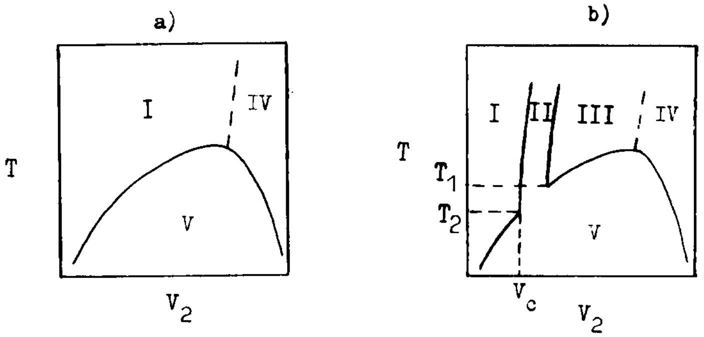

FIG.1 Temperature-composition phase diagrams for a) an amorphous polymer; b) a polymer with mesogenic properties.

I - isotropic solution
II - isotropic solution plus liquid crystal
III - liquid crystal
IV - gel of I type
V - gel of II type

FIG.1 shows the general type of the phase diagram for polymer-solvent systems. FIG.1a corresponds to the case of an ordinary amorphous polymer (de GENNES 1979) and FIG.1b corresponds to a polymer with mesogenic properties. In both figures the broken line represents the gel formation curve.

When the temperature decreases the solutions in the investigated concentration range (0.01-0.76) become turbid, thus indicating a phase separation, and the system developes into a two-phase region (range V in FIG.1). This thermoreversible gelation phenomenon is a result of microphase separation. It should be noted that for systems with low polymer content (up to 0.05) the gelation process takes place more smoothly than for concentrated systems. Thus, at first, the solution at V_2 = 0.02 loses the fluidity, i.e. a transparent gel is formed, in which the size of junctions of the network is small as compared to the wavelengths of visible light. As the temperature decreases the gel gradually becomes turbid. In contrast, in concentrated systems a very turbid gel is formed at rather high rate.

At relatively high temperatures concentration dependent phase transitions also occur.

Thus, at low polymer concentration (range I in FIG.1b) the system is an isotropic solution whereas in range III it is a lyotropic liquid crystal. Between range I and range III is situated the so-called "chimney region" (region II in FIG.1b), where two phases isotropic and anisotropic coexist.

FIG.2 shows the phase diagrams for two PBLG samples with M = 50,000 and M = 200,000. As molecular weight decreases, the phase diagram shifts downwards along the temperature axis, and the "chimney region" becomes wider and shifts towards higher concentrations. These general relationships are in accord with the results of both theoretical and experimental studies. However, in the corresponding papers the phase diagrams show no gelation curve. To our opinion, its existence in the phase diagram is peculiar to the polymeric type of the liquid crystalline system and shows that the gelation process is a regular phenomenon in a wide two-phases region (range V in FIG.1b).

Observations showed that for the PBLG with M = 50,000 the two-phase systems undergo a separation into the isotropic and anisotropic macrophases with a distinct interphase. This is possible because the "chimney region" for low molecular weight PBLG is relatively wide and the system is separated into phases of very different compositions and hence of different densities.

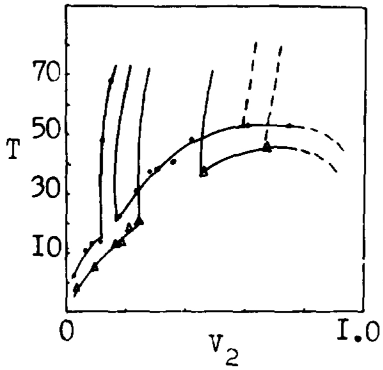

FIG.2 Temperature-composition phase diagram for PBLG in DMF; circles - M = 200,000; triangles - - M = 50,000.

Both phases coexisting in the "chimney region" are fluid systems. Upon cooling to T_1 (FIG.1b) the liquid crystalline phase becomes turbid and loses fluidity, whereas the isotropic phase remains both fluid and transparent. Upon further cooling to T_2 this phase also becomes turbid and nonfluid. Hence, in the case of PBLG with M = 50,000 the coexisting phases behave independently during gelation.

In the case of the two-phase systems of PBLG of M = = 200,000 the separation into macrophases does not occur or is incomplete. Upon cooling this system becomes gradually turbid in starting from the bottom to the meniscus over a wider temperature range than single-phase systems of similar concentrations. However, this is not the only specific feature of behaviour during cooling of PBLG solutions with M =200,000.

Over a relatively narrow concentration range $0.085 \le V_2 \le 0.13$, close to the critical weight fraction $V_c = 0.12$ (FIG. 1b) anomalous dependences of light transmission intensity of solutions were observed during cyclic cooling (FIG.3). The intensity of transmitted light were measured in crossed polaroids. In the first cycle the turbid gel was formed at approximately 10°C. But in the second cycle it did not become turbid at 10°C. In contrast, in the range near 0°C was observed a maximum of light transmission intensity in crossed

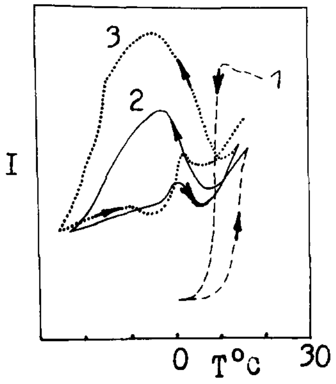

FIG.3 Light transmission intensity in crossed polaroids of PBLG (200,000) in DMF (V_2 = 0.127). Three cycles are represented.

polaroids. Hence, a new "low temperature" liquid-crystalline order has grown from the nuclei appearing during cooling in the first cycle. This ordering displaces formation of turbid gel towards lower temperatures. According to the principle of the "kinetic memory" (FRENKEL 1968) the birefringence maximum is situated upon heating approximately at the same place as upon cooling. Therefore, the "low-temperature" liquid-crystalline order corresponds to an average temperature of the cycle at which the birefringence maximum was observed. As can be seen from FIG.3, this effect increases in the third cycle.

FIG.4 represents dependences of the identity period S of the cholesteric helix on concentration at various temperatures for two samples of PBLG. Three features must be stressed.

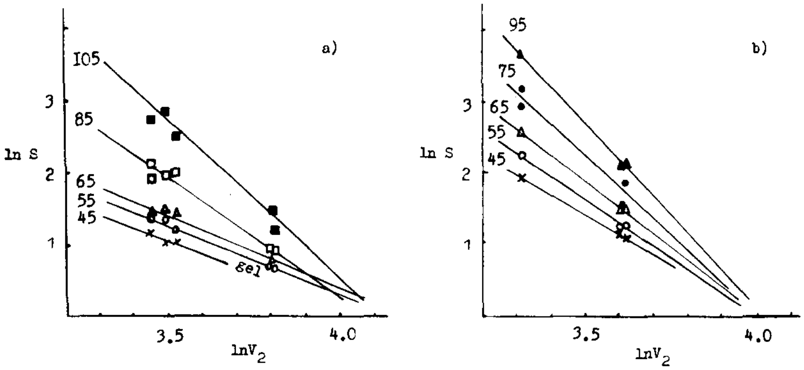

FIG.4 Dependences of the identity period S on concentration at different temperatures in DMF: a) for PBLG (50,000); b) for PBLG (130,000). Number represents the corresponding temperature.

First, at the same concentration and temperature the value of S for PBLG sample with M = 50,000 is lower than for that one with M = 130,000.

Secondly, deviations are observed from the empirical law $P \sim V_2^2$ obtained for PBLG in dioxane at room temperature (ROBINSON 1958). Moreover the exponent "a" in the relation $S \sim V_2^a$ increases with the temperature.

Third, it is note worthy that at relatively high polymer content (V_2= 0.5 - 0.6; ln V_2= 4.0 - 4.1) all dependences exhibit a trend to intersect in the same region. At $V_2 > 0.5$ the "finger-print" texture was not more observed.

DISCUSSION

It is of interest that the values of V_2 above which the "finger-print" texture was not more observed are correlated with those V_2 at which the system passed from the liquid crystalline state into the gel state (range IV in FIG.1b). The introduction of the region of a type I gel in the phase diagram leads to narrowing of the range of liquid crystalline state. Therefore the question arises, what is the structure of this type I gel (range IV in FIG.1b) and what is the difference between this structure and that one of the type II gel existing at lower temperatures (range V in FIG.1b).

It should be noted that PBLG is a crystallizable polymer, and the polymer concentration V_2 = 1 corresponds to the crystalline state in the phase diagram.

According to modern conceptions (PARKOV and DIBROVA 1983) any gels (with the exceptions of the gels with chemical crosslinking) should be considered as at least two-phase systems. Moreover one of the phases is composed of the gel junctions. Since PBLG is a crystallizable polymer, probably these junctions are of crystalline nature. If the structure of the transparent anisotropic gel is considered from this standpoint, it should be assumed that it is a two-phase system in which the liquid-crystalline and the crystalline phases coexist. The junctions are very small crystallites which can appear during local crystallization of PBLG molecules.

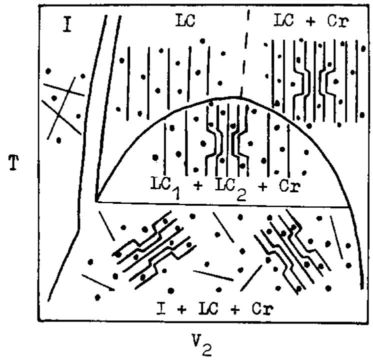

FIG.5 Scheme of the phase diagram with corresponding models of possible structures.
I - isotropic solution; LC - liquid crystal; Cr - crystallites.

Further, developing this approach it should be concluded that in the upper part of range V (FIG.5) three phases coexist: the liquid crystal and the anisotropic gel which in its turn is a two-phase system. Hence, three phases coexist: two liquid-crystalline phases with different compositions and the crystalline phase. In the lower part of range V (FIG.5) three phases also coexist: the isotropic, the liquid-crystalline and the crystalline phases. The models for these structures are shown in FIG.5. The problem whether the suggested models correspond to the structure of real gels requires additional structural investigations.

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