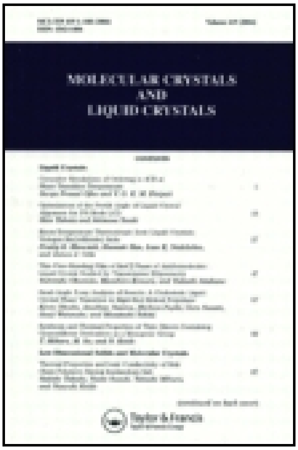

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Phase Behavior in a Ternary Rod/Coil/Solvant System: Poly (γ-Benzyl-α, L-glutamate)/Nylon-6/m- cresol

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Abstract Ternary phase diagrams for the system, Poly(γ–benzyl–α,L–glutamate)/Nylon–6/m–cresol, were determined by optical microscopy at room temperature, for several different molecular weights. The phase diagrams do not closely resemble those predicted from the athermal theory for rod/random coil/diluent mixtures, as set forth by Flory. The appearance of a biphasic system occurs at lower concentrations than predicted. It is proposed that this phenomenon might be caused by the different hydrogen bonding characteristics of the two polymers. The utility of epifluorescence microscopy as a supplement to the usual crossed–polars technique for structural determinations is discussed.

INTRODUCTION

Interest in lyotropic properties of rigid rodlike polymers dates at least to the 1930's, when it was discovered that tobacco mosaic virus could form structured solutions[1]. In the 1950's the pioneering work of Robinson established the nature of twisted nematic solutions of chiral rodlike polymers[2–4]. The phase transition from the anisotropic to the liquid crystalline state occurred at concentrations similar to the Flory theory of biphasic rodlike solutions[5]. These classic works, and others of the same genre, convey justifiable fascination with the strange morphological aspects of liquids bearing anisometric particles. Interest in practical applications soon followed, and in the 1970's it became widely known that the liquid crystal state could be exploited—for example, in the production of ultrahigh–modulus fibers[6–8].

Today, there is great interest in the production of practical rigid rod molecular composites (R2MC's), in which the orientable rodlike polymer serves to reinforce another macromolecular component, typically a thermoprocessible random coil[9–18]. In some cases the "host" random coil is mixed with the rodlike polymer in the presence of a mutual solvent, which is later removed[9–12]. In others, the random coil is formed "in situ" by polymerization of a solvent, usually a vinyl monomer, which can dissolve the rodlike polymer at concentrations favorable to mesophase formation[13–17]. After the liquid crystalline structures have reached equilibrium, bulk polymerization of the solvent is initiated to produce the composite. Of course, even in the final stages of polymerization, some unreacted monomer persists, so the "in situ" preparations, like the simple mixtures, are properly treated as ternary systems. A clever new approach is the mixture of two random coil polymers, one of which is designed to thermally isomerize "in situ" to a rodlike conformation[18].

Perhaps no aspect of mixtures and composites containing rodlike components has received more attention than phase behavior[19]. In the case of rodlike/random coil/solvent mixtures, the theory of phase behavior was worked out by Flory[20] , in the athermal limit. Phase behavior of such systems is clearly important for the production of R2MC's from pre–formed polymers. Phase behavior is also relevant to the "in situ" method, because polymerization may proceed slowly enough that phase separation can occur before the system solidifies. In this article, we consider the phase behavior and morphology of a polypeptide, poly(γ–benzyl–α,L–glutamate), PBLG, dispersed together with poly(iminocarbonylpentamethylene), Nylon–6, in m–cresol. The selection of PBLG as the rodlike component imparts to these studies some of the same features which were helpful in earlier explorations of binary solutions[21,22]. More rigid[23] and more monodisperse[24,25] than most other synthetic rodlike polymers, PBLG can be dispersed in simple solvents without aggregation or ionization. These characteristics allow one to focus on the effects of geometric asymmetry. Additionally, the chiral nature of the polymer has proven valuable. For example, the long–standing question of whether coexistent liquid crystalline phases really occur in binary solution, as Flory tenuously postulated[5] in 1956, was resolved by monitoring the temperature dependence of the cholesteric pitch[22]. A non–chiral polymer could not have provided the same information.

EXPERIMENTAL

Polymer will be designated by the common name or acronym followed by molecular weight: e.g., PBLG–28,000 for a 28 kdalton sample of PBLG. The PBLG molecular weights are those supplied by the vendor, Sigma. In the course of our other studies, we have found these molecular weights to be reasonably accurate. For example, diffusion coefficients measured from photon correlation light scattering in dilute solution agree closely with those expected for a rod of the Sigma–reported molecular weight, assuming a pitch of 1.5 A per monomer repeat unit as expected for the α–helix, and hydrodynamic diameter of 2 nm. The polydispersity parameter M_w/M_n is typically less than 1.4 for the as–supplied PBLG[25]; similar or lower values are reported for PBLG from other sources[24]. The Nylon samples, Nylon–64,000 and Nylon–22,000, were the generous gift of Allied Signal Corporation. Intrinsic viscosity data for Nylon in m–cresol was supplied and converted to weight average molecular weight using the relationship of Tusar et al.[26]. Aldrich Gold Label 99% m–cresol was used without further purification.

The sample preparation scheme was designed to conserve the expensive PBLG for experiments involving the dynamics of rodlike polymers in various "complex" solutions. These include isotropic solutions in the semidilute regime (both binary and ternary[25]), structured solutions (biphasic and otherwise), as well as rodlike polymer gels[27],[28]. A second concern was the hygroscopic nature of m–cresol, since the influence of very small degrees of nonsolvent on phase behavior of rodlike polymers is dramatic[29]. The basic scheme was to prepare solutions with different polymer ratios, then vary the amount of solvent, thus sampling the phase behavior along straight lines radiating from the solvent apex on the triangular phase diagram. Initial attempts to progress from dilute solution to concentrated by partially evaporating the solvent in a vacuum oven were not particularly successful, because m–cresol evaporated very slowly at the moderate temperatures required to prevent solvent and/or polymer decomposition with attendant solution discoloration. Thus, we worked from higher to lower concentrations. Polymers were weighed into glass machine vials, which could be tightly sealed with a Teflon–faced rubber septum, similar to those supplied with water–sensitive HPLC–grade solvents. Total polymer at a given polymer ratio was typically 0.1 gm or less. A small Teflon–coated magnetic stirbar was included to aid in mixing. Metered aliquots of m–cresol were added and weighed, taking great care to hasten these operations and minimize surface area, in order to reduce water vapor contamination. As the equilibration times were very long, the largest threat of water contamination came from slow leaks. Testing with several moisture–sensitive samples has shown the Teflon–capped vials to be essentially moisture–proof for periods exceeding two–three weeks at a minimum, and sometimes more than a year. Even so, the samples in their tightly–sealed vials were placed inside a desiccator and removed from light (to retard photodecomposition of the m–cresol). The m–cresol itself was stored tightly capped and refrigerated in a separate desiccator, which was always warmed to room temperature carefully prior to use. The samples were periodically observed under a polarizing microscope (Olympus BHA) to determine whether morphological equilibrium had been achieved. When such was the case, the appearance was recorded, either by written description or microphotographs. Then more m–cresol was rapidly added to proceed to the next composition. The equilibration times following dilution ranged from several months to a few days. Equilibration was much faster at low overall polymer concentration. All observations were made at room temperature.

RESULTS AND DISCUSSION

Phase diagrams for various molecular weight combinations are shown in Figures 1 – 3. The polymer–conserving "dilution" approach to preparing the samples has advantages and disadvantages relative to the methods of other studies, in which larger amounts of polymer seem to have been used[30–35]. A disadvantage: it is difficult to centrifuge such small samples to isolate the individual phases and determine their compositions. On the other hand, information about the solution morphology under conditions which are more typical of actual composite processing becomes available. This is important, because the structure in the polymer dopes affects final strength of the composite.

The solutions were either uniphase isotropic or biphasic. In the biphasic systems, one phase was always birefringent, the other isotropic. Often, the birefringent regions had irregular shapes: "birefringent chunks". Small, nonspherical birefringent structures, sometimes called "islands" [10,11], have a long history in liquid crystal studies[1]. This morphology was more common at low solvent content. As the solvent content was raised, these birefringent regimes took on the characteristics of well–formed spherulites. Both the number and average size of the spherulites decreased with added solvent, until they disappeared into the isotropic phase. In the system with highest molecular weights, a denser brightly–colored (under crossed polars) phase was found in equilibrium with a lighter

Figure 1

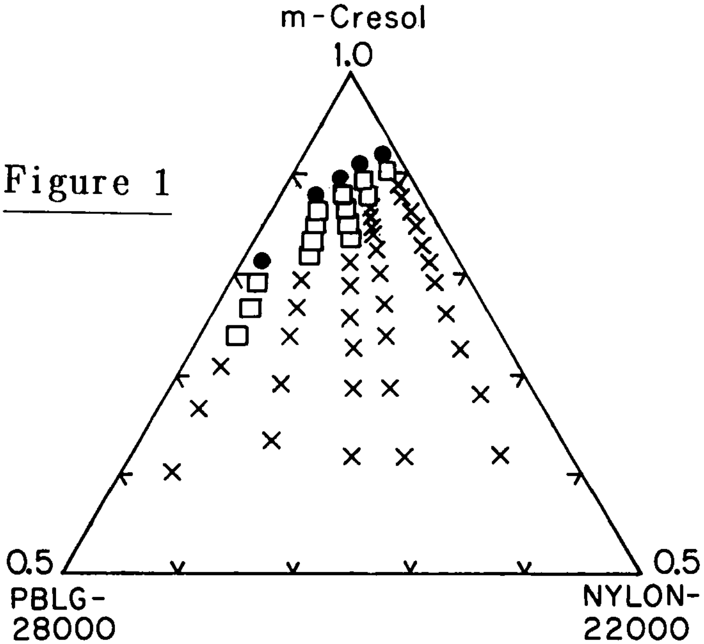


Figure 2

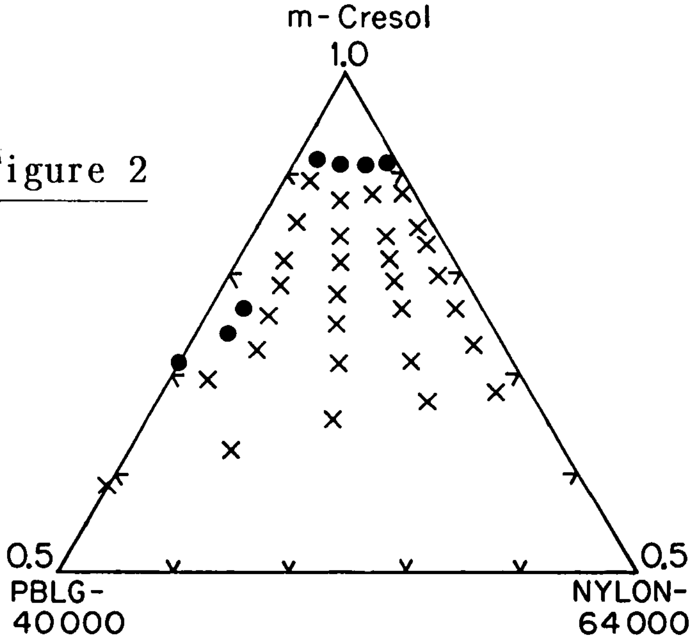
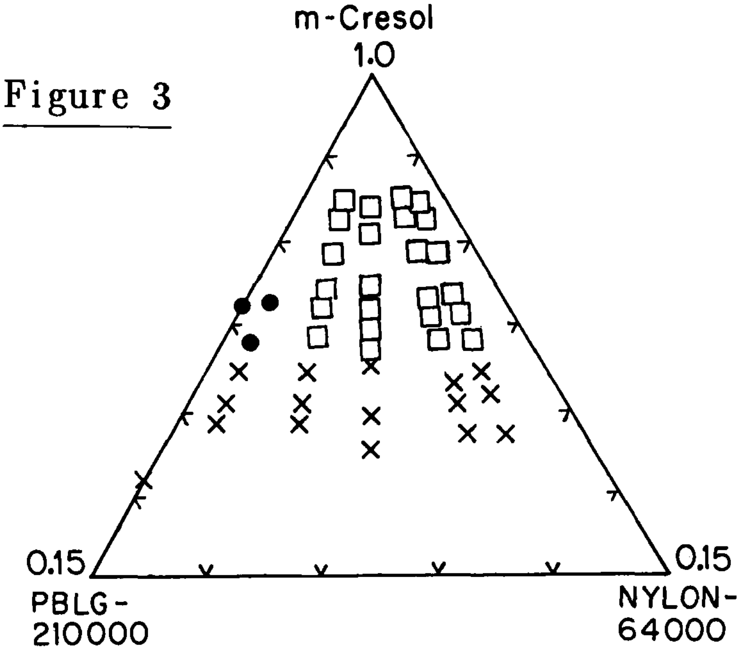


Figure 3



Figures 1 – 3. Weight fraction phase diagrams for PBLG/Nylon/m–cresol mixtures, with molecular weights indicated. Key to structure:

× = birefringent + isotropic
□ = well–formed spherulites + isotropic
● = isotropic

In Figures 1 and 2, symbol × indicates birefringent "chunks" in equilibrium with isotropic. In Figure 3, symbol × incidates compositions where the birefringent phase was a well–separated, easily identifiable fluid. Dilution in Figure 3 was terminated before achieving complete conversion to single isotropic phases at some polymer ratios. If it exists at all for these ratios, the isotropic phase lies at less than 3% total polymer.

isotropic phase; at the interface between these two were found spherulites, possibly "droplets" of the former dispersed in the latter.

In general, the overall polymer concentration required for formation of a liquid crystal phase decreased with increasing molecular weight of either polymeric component. Thus, for the PBLG–28,000/Nylon–22,000/m–cresol system, the transition to biphasic systems occurred at between 10% and 20% total polymer content for the samples measured. These numbers are not much changed for the PBLG–40,000/Nylon–64,000/m–cresol system. For PBLG–210,000/Nylon–64,000/m–cresol, the isotropic regime does not extend much above 6% at any polymer composition, and generally lies below 3%.

A curious finding, evident in all the phase diagrams but most obvious in Figure 1 for low molecular weights, is the slope of the boundary between the isotropic and liquid crystal regimes. It appears that the addition of Nylon actually hastens the onset of biphasic systems containing a liquid crystalline phase. Of course, at zero PBLG content (i.e., along the rightmost leg of the phase diagrams), no liquid crystal or birefringent region should form, and this was confirmed. The solubility limit of Nylon in m–cresol was found to be larger than the concentration one would obtain by drawing a smooth curve from the available data along the isotropic–biphasic interface and then extrapolating to zero PBLG content. For example, for Nylon–22,000, it was simple to prepare a 20 % solution by weight. This implies that the upward sloping boundary must eventually turn sharply downward near the rightmost leg of the triangle diagram. Preliminary studies show that even at very low PBLG contents (e.g., a few mg/ml) two "phases" exist; typically the PBLG is dispersed as almost imperceptibly small aggregates. A similar aggregation is mentioned in a study of rotational diffusion of PBLG through polystyrene solutions[36].

The phase diagrams, Figures 1–3, do not resemble those predicted theoretically by Flory for athermal mixtures of rods and coils[20]. This observation is not changed if the weight fraction diagrams are converted to volume fraction. The principle differences between the measured and calculated phase boundaries are the general location of the anisotropic–isotropic transition very near the solvent apex, and the slope of the line bounding this transition. Figure 4 shows a calculated phase boundary which may be compared to Figure 1 for PBLG–28,000 and Nylon–22,000. The relationship between the calculations and the measured systems is complicated by the fact that PBLG and Nylon do not possess similar

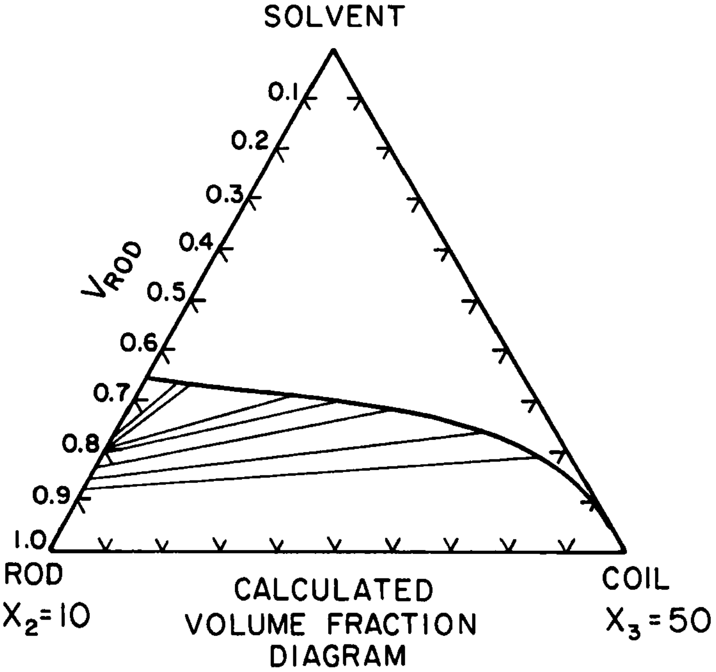


Figure 4. Calculated[20] volume fraction phase diagram in the athermal limit. An axial ratio of 10 is expected for PBLG–28,000.

cross–sections, a major assumption of the Flory theory. The axial ratio of PBLG–28,000 was taken as 10, appropriate to this molecular weight (assuming diameter = 2 nm). The calculation was repeated using several plausible values for the degree of polymerization (X_3) of Nylon, but in no case did the theoretical diagram even remotely resemble the experimental. As shown by the tie lines of Figure 4, the theory predicts that the isotropic phase tolerates substantial amounts of rigid rod polymer, but the liquid crystal phase strongly excludes the random coil polymer. Experimental tie lines are required for complete comparisons to theory, but these are are not available from the present data. However, at overall polymer concentrations that are not extremely high, it is virtually certain that the experimental tie lines have a positive slope (i.e., running from "southwest" (ordered phase) to "northeast" (isotropic), with "north" defined as the solvent apex of the triangle diagram). This is because, given the shape of the isotropic–anisotropic boundary (see especially Figure 1), negative sloping tie lines at moderate overall polymer content would imply an isotropic–isotropic equilibrium, which was not observed. Thus, the isotropic phase appears to be quite intolerant of rodlike polymer. The isotropic phase is also surprisingly dilute.

The present experiments may be compared to several others involving a virtual rod and a second polymer[30–35]. For example, in poly(alkylisocyanate)/polystyrene/tetrachloroethane systems, agreement with the general features of the Flory theory is good[35]. For mixtures of poly(p–phenylenebenzo–bisthiazole) and two different random coils, with methane sulfonic acid as solvent, reasonable agreement with the Flory theory is again found[11]. In the case of poly(p–benzamide) and poly(acrylonitrile) in dimethylacetamide–3% LiCl, the experimental phase relationship was quite like that predicted by Flory; minor deviations were attributed to the role of polymer incompatibility[31]. In the cellulose/cellulose acetate/dimethylacetamide–7.8% LiCl system, there was less agreement with theory[30]. In this system, as overall polymer concentration increased, at first biphasic solutions (isotropic + isotropic) appeared, then biphasic (isotropic + LC). The solvent content at the onset of birefringent phases exceeded the Flory prediction, and the experimentally determined tie lines sloped in a direction opposite to the theoretical prediction. These features were again attributed to polymer–polymer interactions. Rather complex behavior has been observed in those cases where both polymeric components are essentially rigid[32,33] (as evidenced by ability to form mesophases in binary solutions). The deviations from theoretical predictions are once again attributed to polymer–polymer interactions.

One may safely surmise from the foregoing, and the observations of reference 29, that addition of a third component—polymeric or otherwise—to a solution containing rodlike polymers dramatically complicates phase behavior. To gauge the importance of thermal interactions in the present case, one may consider simple solubility parameters, δ.

These may be estimated from the relationship[37,30–33] $\delta = \frac{\rho}{M_0}\sum_i G_i$. In this expression, ρ is the polymer density, and M_0 the molecular weight of the repeat unit. The sum is taken over all chemical groups in the repeat unit; G_i is an interaction parameter for each group. Several tabulations of the interaction parameters are available, leading to slightly different results. Taking the values of Hoy[37] results in $\delta_{PBLG} \approx 11.4\ (cal/cm^3)^{1/2}$, while $\delta_{Nylon} \approx 11.1\ (cal/cm^3)^{1/2}$. For m–cresol, the three–dimensional solubility parameter[37] is 11.1 $(cal/cm^3)^{1/2}$.

Judging from these estimates, the observed dramatic deviations from the athermal Flory theory are surprising. One possibility is that specific differences in the H–bonding interactions between Nylon, PBLG and m–cresol lead to the strange behavior. Hydrogen bonding is not always well accounted for with solubility parameters, because the effects can be "localized" to a given part of the chain. For example, the α–helix of PBLG is stabilized by strong intramolecular H–bonds, but the benzyl rings at the polymer surface will not H–bond to the solvent. Thus, along most of its cylindrical "surface", PBLG will not be H–bonded to the solvent. (H–bonding of solvent to the PBLG probably does occur near the ends of the polymer, accounting for the lack of end–to–end aggregation in m–cresol. Similar H–bonding is probably operative in those few solvents in which PBLG disperses without any aggregation[38]. The role of H–bonding at the ends of PBLG in its molecular dispersion is demonstrated by the observation that end–to–end aggregation of PBLG in toluene can be defeated by addition of a H–bonding solvent, such as methyl–ethyl ketone[39]). In comparison, Nylon should enjoy H–bonded interactions with m–cresol over its entire length. A reasonable explanation for the intolerance of the isotropic phase for rodlike polymer is that the system seeks to maximize its H–bonded interaction with the random coil, and in so doing banishes the rodlike polymer to the liquid crystalline phase where interactions among the sidechains of the rods are favorable.

It needs to be emphasized that these conjectures would be greatly substantiated by true experimental tie lines. An expensive way to measure the tie lines would be to prepare samples sufficiently large that the phases could be separated for composition analysis—for example, by infrared spectroscopy. A different approach would be to fluorescently tag one component, and use fluorescence microscopy to determine the local concentrations within the various phases, which could still be identified by polarized microscopy. For example, if PBLG were labeled (LPBLG), and if it was found that isotropic regions were very deficient in fluorescence, this would be evidence for the exclusion of the rod by the random coil, in contrast to the athermal theory. With video image analysis, such observations can even be quantified, although one must worry about self–quenching, absorbance, and other artifacts. To explore this interesting possibility, LPBLG has been prepared by covalently attaching one fluorescein isothiocyanate group to the amino terminus of the polypeptide. The procedure has appeared in a study of the reversible gel morphology of PBLG[27,28].

At this time, we cannot present any conclusive results from the labelling technique in the LPBLG/Nylon/m–cresol system. However, in order to demonstrate the potential of the method, we present preliminary results from a related ternary system containing LPBLG and a second polypeptide, poly(ϵ–carbobenzoxy–L–lysine), PCBL. The backbone of PCBL is identical to that of PBLG, but the longer sidechain contains an amide link to the carbobenzoxy moiety. Although mesogenic in binary solutions[21], PCBL is slightly less rigid than PBLG[40,41]. It is reported that PCBL undergoes a thermal transition to the coil state in pure m–cresol[42]; preliminary dynamic light scattering measurements in our laboratory substantiate this result. In the very rigid PBLG, such transitions can only be induced in the presence of a solvent which supports the random coil state, such as dichloroacetic acid. Figure 5 shows epifluorescence and crossed–polars photomicrographs of a ternary LPBLG/PCBL/dimethylformamide solution. It is plainly evident from the crossed polars view that birefringent regions exist. The composition of polymers within such regions is not available from the crossed polars view. The epi–fluorescence micrograph of the identical region shows the presence of LPBLG in a region which appears dark under crossed polars. Thus, the specific locations of one polymer in a heterogeneous mixture are quickly located by fluorescence microscopy. The epifluorescence method, which coexists easily with ordinary polarizing equipment on most microscopes, should be of special interest in systems containing highly conjugated polymers, such as poly(p–phenylenebenzo–bisthiazole)[10,11], which are strongly fluorescent, even without labelling[43].

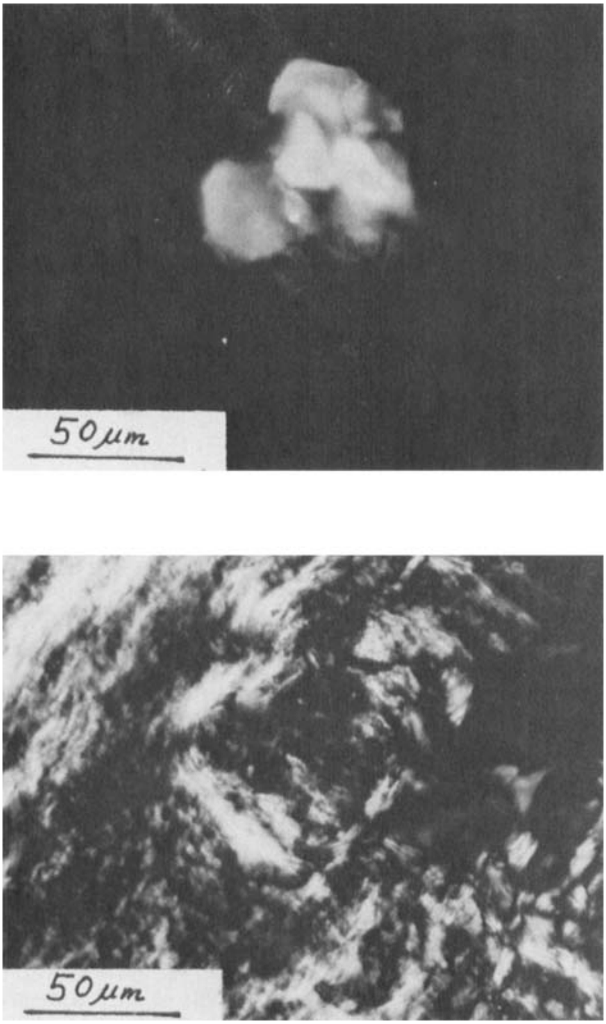


Figure 5. Ternary mixture containing LPBLG–≈150,000 (15 wt%)/PCBL–480,000 (14 wt%)/dimethylformamide (71 wt%). Top: epi–fluorescence micrograph, showing location of LPBLG. Bottom: identical region viewed between crossed polars.

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