Morphology of Polymer-Stabilized Liquid Crystals

C. V. Rajaram and S. D. Hudson*

Department of Macromolecular Science, Case Western Reserve University,
Cleveland, Ohio 44106

L. C. Chien

Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

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The morphology of liquid crystal/polymer composite systems developed for potential applications in flat-panel displays has been studied in detail. Composites were prepared by free-radical polymerization of a dilute solution of a tetrafunctional monomer in a liquid-crystal solvent. The growth mechanism for the morphology was observed and the effect of flexible spacers in the mesogenic monomers on the morphology has been studied. The initial polymer micronetwork formed by these tetrafunctional cross-linkable monomers grows to a critical molecular weight and/or branch content and phase separates from its low-molar-mass liquid-crystal solvent. The internal structure of these beadlike structures depends strongly on the flexible spacers and the temperature of polymerization. As the reaction proceeds, the beads aggregate initially by a reaction limited mechanism, and they continue to expel the liquid-crystal solvent as the cross-link density increases. The final diffusion-limited morphology ranges from a disorderly collection of nearly isotropic beads to a highly oriented fibrillar network. The interaction between the final polymer network and the liquid-crystal solvent is also markedly different.

Introduction

Dispersions containing polymers and liquid crystals have grown into a broad class of materials with the weight concentration of liquid crystals varying anywhere between a few percent to nearly 100% depending upon the type of polymer material and the targeted application. These dispersions are usually prepared by mixing the low-molar-mass liquid-crystal solvent and the polymer (well above the glass transition temperature or melting point) into a uniform mixture. The low-molar-mass liquid-crystal solvent phase separates from the polymer as the polymer solidifies. Another method is to dissolve both the polymer and the low-molar-mass liquid crystal in a suitable solvent followed by the evaporation of solvent causing a solvent induced phase separation of the low-molar-mass liquid-crystal solvent from the polymer. These dispersions present unique electrooptical properties which are well suited for applications such as privacy windows, large-area flexible displays, high-intensity displays, light shutters for optical signal processing, etc. The systems which are currently studied extensively are the polymer dispersed liquid crystals (PDLC). In these materials, low molar mass liquid crystals (typically 50 wt %) are dispersed as droplets in a polymer matrix.[1] These are generally milky white to translucent materials at zero field due to randomly oriented liquid-crystal director in the droplets leading to the mismatch in the refractive indexes of the polymer matrix and the dispersed low-molar-mass liquid crystals. Application of electric field orients the liquid-crystal director along the field leading to refractive index matching with the polymer for the light polarized perpendicular to the nematic director.[2]

On the other end of the spectrum are the dispersions containing liquid crystals and polymers where the concentration of the polymer is typically in the order of 3% or less. In these systems called polymer stabilized liquid crystals (PSLC),[3] a small amount of monomer and photoinitiator are dissolved in a nonreactive low-molar-mass liquid crystal. The monomer is then cross-linked in situ leading to a polymer network in the liquid-crystal solvent. Such polymer networks in liquid-crystal solvent were first used for display applications as light shutters.[4] This was later improved to produce displays having faster switching properties including bistable on and off states and principally haze-free transparent state with large viewing angle.[5] These polymer-stabilized liquid crystals also show a significantly lower threshold switching voltage when compared to the threshold switching voltage of the device made without the polymer network.[6]

The polymer networks formed in such systems containing mesogenic monomers have been studied.[7–12] Typically the monomer was photopolymerized while the

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solution is kept in preferred alignment between two glass plates. The resultant polymer network structure was studied after the extraction of the low-molar-mass liquid crystals. The polymer was found to be as lamellae even at lower concentrations of around 0.5%. When composites formed from a different monomer were studied in situ by neutron scattering, it was suggested that the polymer phase separated into fibrils of 600 Å radius.[13] Optical study of these polymer networks in confined droplets have shown that the optical anisotropy is small.[14] A deuterium nuclear magnetic resonance spectroscopic study shows that the nematic director orientation is fixed by the polymer network without any change in the order parameter.[15] The effect of the polymer network on the alignment and the rotational viscosity of the nematic liquid crystal were studied by rotational and diamagnetic measurements which suggests that the polymer network is anisotropic similar to the liquid-crystal solvent.[13]

Since knowledge of the evolution of the polymer network structure is lacking, we have studied the final polymer morphology and the process of its formation. Specifically in this report, we investigate the influences of temperature (i.e., solvent order) and of monomer structure (i.e., flexible spacer) on the morphology of the polymer network.

Experimental Section

Sample Preparation. Samples were prepared by dissolving varying concentration of diacrylate monomers 4,4′-bis(acryloyloxy)biphenyl (**BAB**) and 4,4′-bis(6-(acryloyloxy)hexyloxy)biphenyl (**BAB6**) into the common low-molar-mass liquid crystal 4′-pentyl-4-cyanobiphenyl (**5CB**) along with a small amount of photoinitiator benzoin methyl ether (**BME**). The monomers and photoinitiator were lab synthesized at Kent State University.[3,5,6] The monomer dissolved in **5CB** was sandwiched between properly treated glass slides. Usually Mylar spacers of approximately 12.5 μm thickness were used to control the thickness of the cell. The cell was then sealed on all sides with epoxy mixture in order to create a near-inert condition for the ensuing photopolymerization. Treatment of glass slides was done to impose desired boundary conditions. For homeotropic conditions, thin layers of lecithin were deposited from a 0.35 wt % solution of lecithin in ethanol. For homogenous alignment, the glass plates were initially spin-coated with a polyimide precursor solution in a thinner (PI 2555 diluted to 25% with a thinner) and then baked in an oven at 250 °C for an hour and then buffed unidirectionally. In some cases, selected areas of the specimen were polymerized by the use of an aperture. The samples were irradiated for different times, temperature, and intensity using a mercury lamp with the UV light of 365 nm wavelength. A lower intensity was used to study **BAB6** because of its higher reactivity. The temperature of the samples were controlled using a Mettler hot stage. The nematic to isotropic transition temperature (the temperature when the nematic phase completely changes to isotropic state, T_{ni}) was measured using a Zeiss optical microscope under cross polarizers.

Morphology Examination. Light microscopy was also used to examine polymer morphology. The samples initially made were checked for their alignment by placing them under cross polarizers. The homeotropic alignment is assured when the cell appears dark under cross polarizers while the homogeneous alignment is ensured when the cell appears alternatively dark and bright under cross polarizers as the stage of the microscope is turned. The schematic representation of a homeotropic cell, a homogeneous cell, and a cell in isotropic state is shown in Figure 1. After the polymerization, the samples were viewed to check for the effect of polymerization on the optical texture of the cell under cross polarizers. Much higher resolution information was obtained by electron microscopy. The specimen preparation for electron microscopy are as follows:

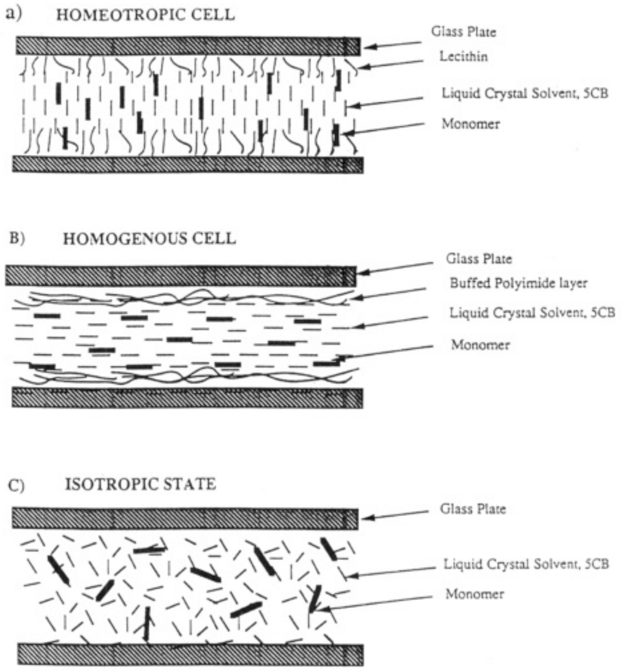

Figure 1. Schematic representation of the (a) homeotropic cell, (b) homogeneous cell, and (c) cell at isotropic state containing the monomer solution in low-molar-mass liquid-crystal solvent, **5CB**.

The cell after exposure to UV light was fractured at the edges and immersed in hexane or acetone for two days. The solvent leaches out the low-molar-mass liquid crystal **5CB** leaving the bare polymer network on the glass slide. The cell is then delicately split open and coated with a 90 Å thick layer of gold using the Biorad-polaron divisions' SEM coating system. The morphology of these samples were then observed using the JEOL JSM 35CF scanning electron microscope operated at 25 kV in secondary electron imaging mode.

Results and Discussion

Preliminary Observations. To understand the phase separation of polymer network, we did a preliminary investigation on a droplet containing 2.8% **BAB** monomer (i.e., without spacer) and 0.3% **BME** photoinitiator in pure low-molar-mass liquid-crystal solvent, **5CB**. The droplet was suspended on a wire (see Figure 2) and held at 42 °C, a temperature above the clearing temperature of the solvent, in inert nitrogen atmosphere. Illuminated with reflected light and using no polarizers, the droplet was clear. Upon exposure to UV light of intensity 8 mW/cm^2 for 3 min; however, the droplet appeared turbid, suggesting phase separation. As a control, the clarity of the droplet in the isotropic state without UV exposure is stable for at least 2 h. To test whether the polymerization had raised the isotropization temperature above the test temperature, the specimen was cooled and observed under cross polarizers. However, the T_{ni}, which after polymerization remain well-defined, was found to decrease with increasing polymerization time. For polymerization times

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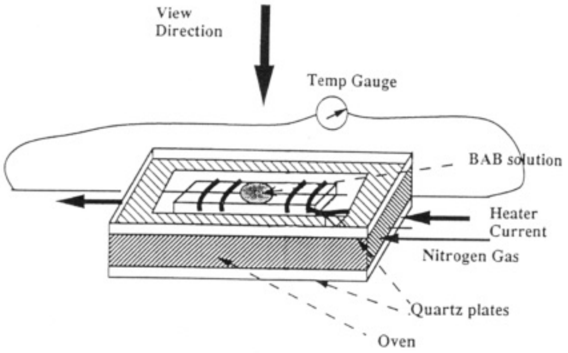

Figure 2. Schematic representation of the experimental setup for the study of phase separation in the droplets of polymer-stabilized liquid crystals.

longer than 10 min, the T_{ni} remained steady ~2 °C below that for an unpolymerized sample. Another result of polymerization was that the isotropic state was very weakly birefringent, suggesting some orientation of the polymer network. Any orientation of the polymer suggests that phase separation has occurred since at 2.8% concentration no anisotropy of conformation is expected. Given the possibility of phase separation, anisotropic polymer conformation may be possible within the more concentrated polymer-rich phase.

We also monitored the droplet shape to learn more about the phase-separation process, since volume transitions in gels are well-known.[16] Although the unconstrained experimental geometry would allow for the polymer network to macroscopically change size and shape during phase separation, none was found in this system. The appearance of cloudiness was not accompanied or followed by shrinkage of the network. Therefore phase separation occurred before gelation. Moreover, this result suggests that the polymer-rich regions after phase separation were sufficiently rigid so as to prevent their collapse during subsequent separation.

Optical Microscopy. The orientational coupling between the polymer and the low-molar-mass liquid crystal was explored using polarized light microscopy of homogenous cells for both the **BAB6** (i.e., with spacer) and **BAB** (i.e., without spacer) monomer mixtures. Initially a homogenous cell was filled with 2.8% **BAB6** solution and observed in light microscope under cross polarizers. The cell appeared black when either the polarizer or the analyzer is aligned along the rubbing direction of the polyimide and bright when they are at 45° to them demonstrating alignment of the director along the rubbing direction in the plane of the glass plate. This cell was polymerized by exposure to UV light for 3 min in isotropic state at 42 °C. The cell was then observed in the microscope under nematic conditions (28 °C). The appearance of the unexposed regions was unchanged from that described above. The exposed region, on the other hand, had a very fine grain texture, whose general appearance was independent of cross polarizer orientation (Figure 3a). The local birefringence of this region remained high but the nematic director is now highly distorted, and memory of the initial polyimide rubbing direction is lost. When this cell was heated to its isotropic state at 42 °C, both the regions that were exposed to UV light and those that were not exposed appeared black, independent of cross polarizers' orientation. Therefore both the **5CB** and the polymer network are isotropic. A fresh cell was again filled with 2.8% **BAB6** (i.e., with spacer) and polymerized by UV exposure for 3 min at nematic state (28 °C). The cell was then observed in the microscope in the nematic state. In this case, the overall brightness of the region which was exposed to UV light, depends on polarizer orientation in much the same way as the unpolymerized material. However, when the specimen is rotated so that the unpolymerized material is black, the polymerized region is not completely dark, but a fine grain texture is apparent. But when viewed with the rubbing direction 45° to the polarizer or the analyzer two regions appeared similar; the fine grain texture of the polymerized region being less, but still apparent. Therefore the nematic director is only slightly disrupted from the uniform alignment in the rubbing direction.

After heating this cell to the isotropic state (42 °C), the polymerized region was found to be uniformly birefringent with molecular orientation along the rubbing direction. When the rubbing direction was aligned parallel to the analyzer, no difference between the polymerized and unexposed regions could be detected; the light intensity was completely extinguished in each case. But when the cell was aligned at 45° to the polarizer and analyzer, the regions which were exposed to UV light showed strong birefringence while the unpolymerized region still appeared black (Figure 3b). The **BAB6** network, polymerized in the nematic state, is therefore aligned.

The magnitude of this network birefringence is considerably less than the aligned nematic **5CB**. This can be easily checked by monitoring the change in birefringence of the polymerized region upon transforming from the nematic to isotropic states. The birefringence in the isotropic states can arise from two factors: the molecular orientation within the polymer network and the low-molar-mass liquid-crystal alignment along the interface of the polymer network.[14] To evaluate the relative contributions qualitatively, we immersed this cell which was polymerized in nematic conditions in an isotropic solvent, acetone, and watched acetone replace the low-molar-mass liquid-crystal solvent. Figure 3c shows the optical micrograph of unpolymerized regions being replaced by the acetone solvent. As the acetone diffuses into and replaces the liquid crystal solvent, the solution becomes isotropic. The boundary between nematic and isotropic can be used to follow this diffusive process. Figure 3d shows an optical micrograph of regions of the cell (**BAB6**) which were exposed to UV light under nematic conditions with the dissolving away of the low-molar-mass liquid-crystal solvent by acetone with polarizers and analyzers aligned at 45° to the rubbing direction. Some of the initial birefringence detected in the isotropic state arose from the low-molar-mass liquid-crystal solvent alignment at the polymer interface, because the birefringence decreased with increasing soaking time in acetone.

To further understand these systems, homogeneous cells made of **BAB** (i.e., without spacer) in low-molar-mass liquid-crystal solvent were studied. These cells were then polymerized in either the nematic or the isotropic state, and were observed at nematic (28 °C)

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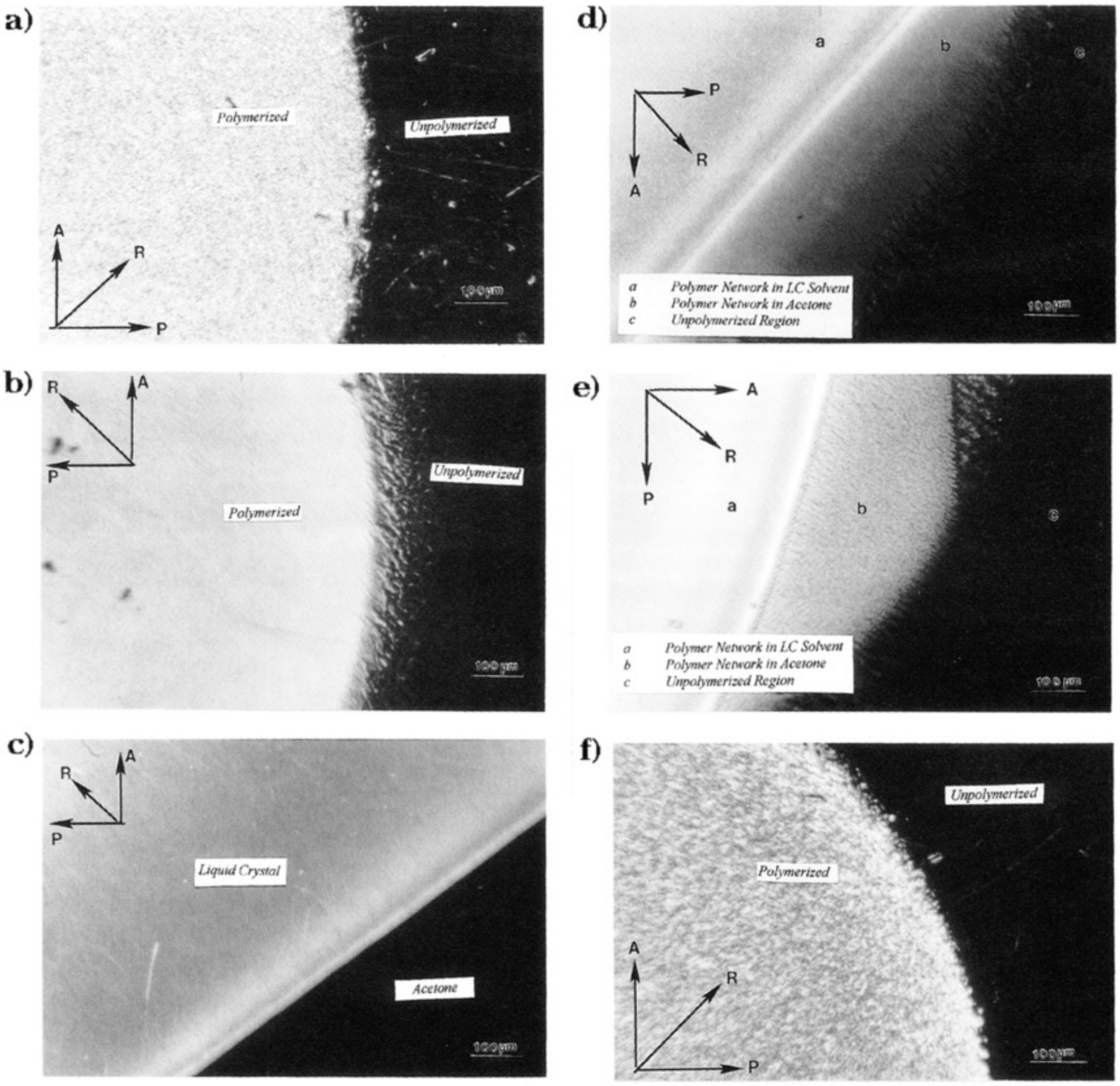

Figure 3. (a) Optical micrograph of a homogeneous cell of 2.8% **BAB6** polymerized in isotropic state (42 °C) and viewed at 28 °C (nematic conditions) under cross polarizers. (b) Optical micrograph of a homogeneous cell of 2.8% **BAB6** polymerized in nematic state (28 °C) and viewed at 42 °C (isotropic conditions) with polarizers and analyzers aligned at 45° to the rubbing direction. (c) Optical micrograph of regions of 2.8% **BAB6** solution not exposed to UV irradiation being replaced by the acetone solvent under cross polarizers. (d) Optical micrograph showing regions of a homogeneous cell of 2.8% **BAB6** which were exposed to UV light under nematic conditions with the dissolving away of the low-molar-mass liquid-crystal solution by acetone with polarizers and analyzers aligned at 45° to the rubbing direction. (e) Optical micrograph showing regions of a homogeneous cell of 2.8% **BAB** which were exposed to UV light under nematic conditions with the dissolving away of the low-molar-mass liquid-crystal solution by acetone with polarizers and analyzers aligned at 45° to the rubbing direction clearly showing the gradient in birefringence from the acetone front (high) to bulk of acetone (low). (f) Optical micrograph of a homogenous cell of 2.8% **BAB** polymerized in nematic state (28 °C) and viewed at 42 °C (isotropic conditions) under cross polarizers.

and isotropic (42 °C) conditions, with either the polarizer or the analyzer aligned along the rubbing direction or 45° to them. These cells showed similarities with the **BAB6** cell but also some striking differences.

When a homogeneous cell of **BAB** in low-molar-mass liquid-crystal solvent was polymerized in isotropic state (42 °C) and observed under nematic conditions (28 °C), bright fine grain texture regardless of cross polarizers' orientation was obtained. This optical texture is very similar to the homogeneous cell of **BAB6** (i.e., with spacer) polymerized in the isotropic state.

When a cell of **BAB** in liquid crystal solvent was polymerized in the nematic state (28 °C), the polymerized regions showed bright fine grain texture regardless of cross polarizers' orientation. When this cell was then heated to isotropic state (42 °C) and observed under cross polarizers, all the regions (polymerized and unpolymerized) of the cell appeared black when the polarizer or the analyzer is aligned along the rubbing direction but when viewed at 45° to the polarizer or analyzer, we could observe some faint birefringence with lots of black specks in the regions that were exposed to UV irradiation (Figure 3f). This indicates that the orientation of the polymer network formed by **BAB** monomer is low.

The order of the polymer network was further examined after replacing the liquid-crystal solvent with acetone solvent. The qualitative similarity of the appearance at isotropic conditions, whether achieved by heating to 42 °C or by replacing the liquid-crystal solvent with isotropic solvent indicates that the washing away of the low-molar-mass liquid-crystal solvent by acetone does not disrupt the network morphology.

On examination of the acetone front (Figure 3e), we can clearly see a gradient in the intensity of birefringence from near the front (high intensity) to the bulk of the acetone (low to zero intensity) which has replaced the liquid-crystal solvent. Since the concentration of the low-molar-mass liquid-crystal solvent decreases, as we move away from the front to the bulk of the acetone, it is clear that the contribution to the birefringence by the induced orientation of the liquid crystal solvent at the interface (of polymer network and the bulk) is much higher than the contribution of the polymer network itself. Thus the birefringence of the polymer network due to the molecular orientation within the network is small compared to the birefringence arising from the induced orientation of the solvent at the interface between the polymer network and the bulk liquid-crystal solvent. We could see that this gradient of the intensity of birefringence is much stronger in the case of **BAB** (i.e., without spacer) than **BAB6** (i.e., with spacer), indicating the relative contribution of the polymer network to the birefringence is much less in the case **BAB** than **BAB6**.

Network Morphology. To investigate the morphology of these polymer-stabilized liquid crystals more thoroughly, electron microscopy was carried out. Figure 4 shows the morphology of the polymer network formed by the monomer **BAB** (i.e., without spacer) in nematic conditions both in homeotropic and homogeneous cell respectively.

The network of p(**BAB**) formed at nematic conditions in homeotropic and homogenous boundary condition consists of fused beads. On closer examination, each of the beads appears to be quite rough and nodular. The beads are about 0.3 ± 0.1 μm in size and are found in varying orientation and shape. These beads have aggregated to a network formation of beads. The pores in this network vary in size (0.5–3 μm), orientation and shape. Figure 4c shows the morphology of p(**BAB**) formed at isotropic conditions.

Although the latter network is more irregular, the overall morphology of p(**BAB**) formed at both nematic and isotropic conditions are similar, i.e., beadlike. As we will demonstrate later, the polymer morphology reflects its molecular orientation. This suggests that the molecular order in the polymer network at nematic conditions is nearly isotropic, consistent with the earliest studies on side-chain liquid-crystalline polymers.[17] The lack of flexible spacer between the mesogen and the polymerizable moiety couples the backbone and mesogen strongly. Disordered polymer conformations lead to mesogen disorder.

Both the molecular order and the morphology may be different when flexible spacers are present. Figure 5 shows the morphology of the polymer network formed by the polymerization of the monomer with spacers (i.e., **BAB6**) under nematic conditions in the homeotropic cell (Figure 5a) and a homogeneous cell (Figure 5b). The network is clearly fibrillar in nature unlike the beadlike morphology of **BAB**. Also, there is a clear difference in the morphology of the p(**BAB6**) polymerized in the homeotropic and homogeneous cell. In the homeotropic cell, we observe the structure to be very porous with pores ranging in size and orientation, with a fairly uniform round shape. The thickness of strands are about 0.1 μm. The fibers are fairly smooth, and some of the fibers are not single strands but have aggregated to form thicker fibers. Tilting the sample demonstrates the predominantly homeotropic orientation of the fibers.

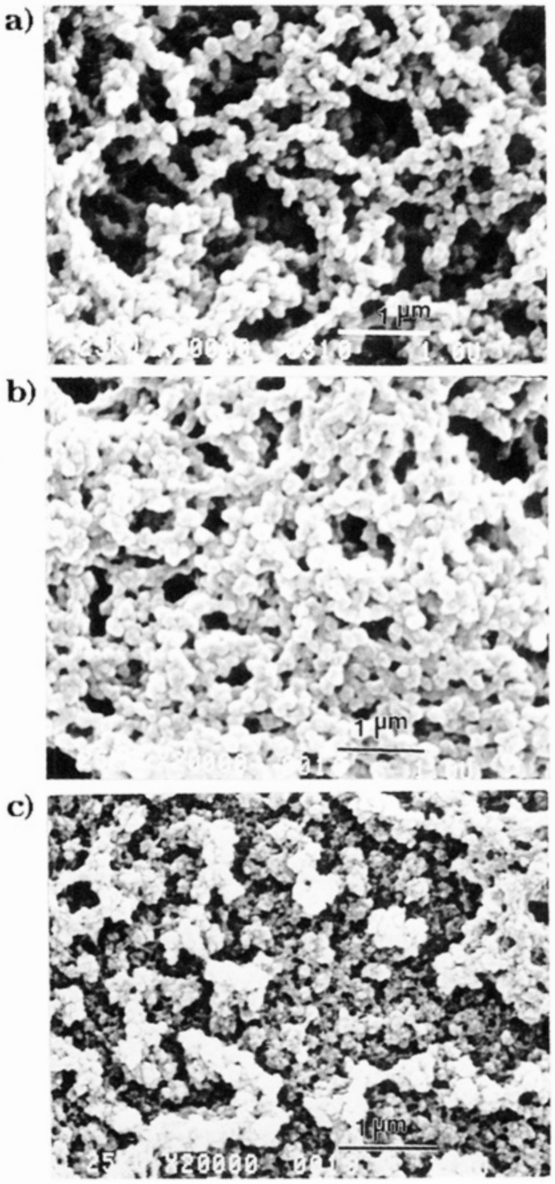

Figure 4. SEM micrograph of a cell containing 2.8% **BAB** solution in **5CB** polymerized at nematic conditions (28 °C) under (a) homeotropic and (b) homogeneous boundary conditions. (Note lower magnification.) (c) SEM micrograph of a cell containing 2.8% **BAB** solution in **5CB** polymerized at isotropic conditions (42 °C).

The morphology of the p(**BAB6**) formed in a homogeneous cell is also fibrillar. The orientation of the fibrils in the rubbing direction is apparent. The pores between fibers are anisotropic along the rubbing direction. The similarity of the homeotropic and homogeneous networks has been confirmed by tilting of the specimens. Figure 5b is a cross section of the structure in Figure 5a.

The morphology of p(**BAB6**) being fibrous suggests that there is higher degree of ordering in this system. In p(**BAB6**), due to the presence of hexamethylene spacers between the mesogen and the polymerizable acrylate moiety, the monomers incorporated into the polymer network have greater conformational freedom

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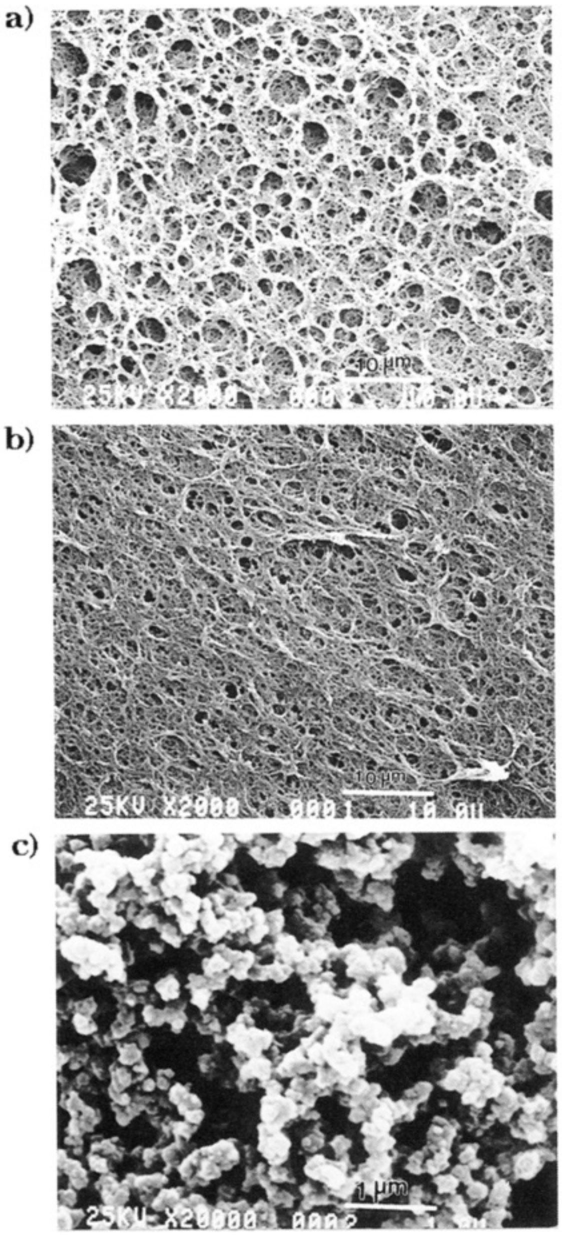

Figure 5. (a) SEM micrograph of a cell containing 2.8% **BAB6** solution in **5CB** polymerized at nematic conditions (28 °C) under homeotropic and (b) homogeneous boundary conditions. (c) SEM micrograph of a cell containing 2.8% **BAB6** solution in **5CB** polymerized at isotropic conditions (42 °C).

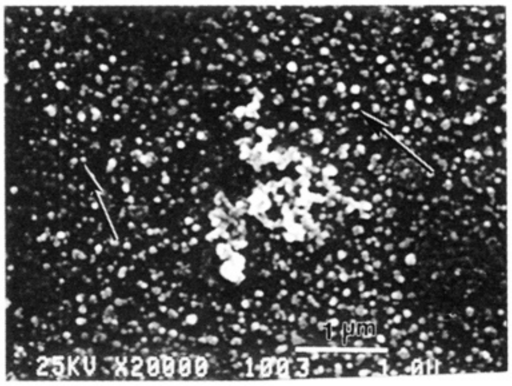

Figure 6. SEM micrograph of the polymer formed by 0.28% **BAB** solution in **5CB** exposed to UV light of intensity about 8 mW/cm^2 for just 6 s in a homeotropic cell.

Table 1. Summary of Morphology of BAB and BAB6 Monomers Polymerized at Nematic and Isotropic State

monomer	liquid-crystal solvent phase	morphology
BAB	nematic (28 °C)	beadlike
	isotropic (42 °C)	beadlike
BAB6	nematic (28 °C)	fibrous
	isotropic (42 °C)	beadlike

(unlike the **BAB** monomers without flexible spacers). As the polymerization proceeds, the overall conformational freedom of the monomers is reduced, due to permanent covalent cross-links, thus disrupting the nematic order of the mesogens. This disruption of nematic order is offset to a certain extent by altering the conformation of the flexible spacers and preserving the orientation of the mesogens. This less perturbance of the mesogens in the monomers away from its nematic order during the polymerization leads to a highly ordered fibrous structure. This is clearly observed from the difference in the morphology of the specimen polymerized in the homeotropic state and in the homogeneous state, in which the mesogens are aligned perpendicular and parallel to the glass plates, respectively. Also this is a clear evidence against any artifacts of the sample preparation technique because if the structure formed is due to washing or drying of the network, the morphology of the polymer network formed both in the homeotropic and homogeneous boundary condition would be very much similar.

Figure 5c shows the morphology of the same solution, but polymerized at isotropic conditions. The morphology of the p(**BAB6**) formed at isotropic conditions is very different and surprisingly similar to the **BAB** (without spacers) networks. These beads are nodular and of 0.3 ± 0.1 μm in size. The pores vary in size, shape and orientation. In the isotropic state, there is no long-range order in the system. The mesogens of the monomers orient itself in all possible orientations. Polymerization of these disordered monomers leads to an isotropic polymer network which is a spherical beadlike structure. Because the polymer network is sufficiently cross-linked, its conformation is frozen-in during polymerization.

Thus the morphology of these monomers **BAB** and **BAB6** change depending upon the phase of the liquid-crystal solvent in which it is polymerized. The various morphologies formed by the monomers **BAB** and **BAB6** at different conditions is briefly summarized in Table 1.

Evolution of Network. To understand the evolution of the network morphology in these systems, we studied the morphology at p(**BAB**) at various extent of reaction. Figure 6 shows the SEM micrograph of the polymer formed by **BAB** at a concentration of 0.28% in a solution of low-molar-mass liquid crystal **5CB**, exposed to UV light of intensity of 8 mW/cm^2 for just 6 s in a homeotropic cell. We can observe nodular beads and single smooth beads. These smooth beads are approximately 0.1 μm in size. This size corresponds to the size of the nodules in the beads of polymer network formed by **BAB** at a concentration of 2.8% in a solution of low-molar-mass liquid crystal which has been exposed to UV light for more 10 min. Because the appearance of the primary particle is unchanged by further polymerization, we conclude that the micronetwork as it initially precipitates is sufficiently rigid that it is not severely affected by the specimen preparation method.

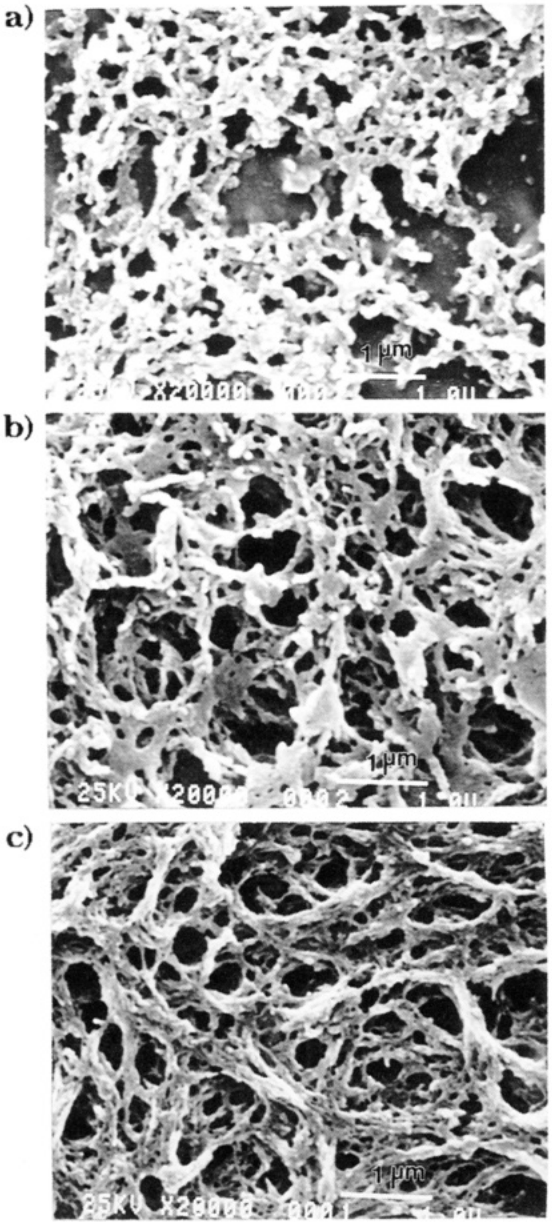

Figure 7. SEM micrograph of p(**BAB6**) polymerized in a homogeneous cell of 2.8% **BAB6** solution in **5CB** and exposed to UV light of intensity 1.75 mW/cm^2 for (a) 30 s, (b) 3 min, and (c) 10 min.

We also observed some areas which are a network of nodular beads.

As we increased the UV exposure time, we observed progressively lesser number of smooth individual beads of about 0.1 μm in size, while there is an increase in the number of nodular beads, and correspondingly, the network structure formed by the nodular beads became more prevalent and well defined. Increasing the conversion of the monomers of **BAB** into polymer does not increase the size of the nodular beads, suggesting that the polymer network after reaching a critical molecular weight/branch content phase separates from the LC solvent and further increase in conversion is accomplished by the diffusion-limited aggregation of beads into a network morphology.

Increasing the concentration of the monomer causes a corresponding increase in the size of the nodular beads. Since an increase in concentration increases the rate of reaction, the increase in nodular bead size suggests that the aggregation of the primary phase-separated beads is initially reaction limited. At larger length scales, the aggregation is diffusion limited, producing a much more open structure. A more detailed investigation will be forthcoming shortly.

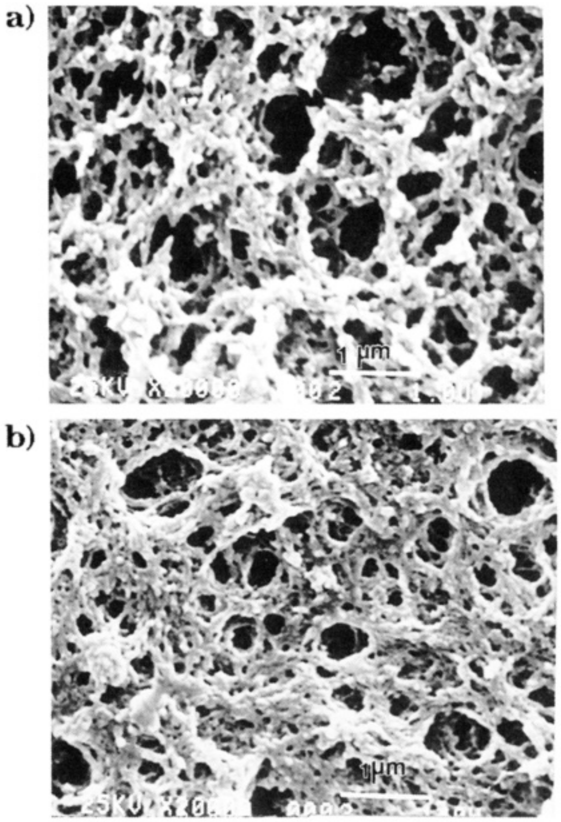

Figure 8. SEM micrograph of p(**BAB6**) polymerized in a homogeneous cell of 2.8% **BAB6** solution in **5CB** and exposed for 3 min to UV light of intensity (a) 26 mW/cm^2 and (b) 72 mW/cm^2.

The more flexible system (**BAB6**) was also studied as a function of cure. Figure 7 shows the morphology of **BAB6** polymerized under nematic conditions in a homeotropic cell.

Figure 7a shows the morphology of p(**BAB6**) which was exposed to UV light of intensity of about 1.75 mW/cm^2 for only 30 s. The morphology is a network of beads. This morphology is similar to the polymer network formed by **BAB** monomers except that these beads are not very nodular. The beads are 0.2 ± 0.1 μm in size. The polymer network formed by **BAB6** at this low conversion has pores of varying sizes, orientation, and shapes.

Figure 7b shows the morphology of p(**BAB6**) which was exposed to UV light of intensity of about 1.75 mW/cm^2 for 3 min. The network appears much smoother and the beads are becoming less noticeable. The pores formed by these network are of varying size, shapes, and orientation. It appears that the average diameter of the strands have reduced with increase in conversion and also the density of the network has increased leading to a corresponding decrease in the average size of the pores. Reduction of fiber diameter suggests that the shrinkage of the polymer-rich phase occurs as polymerization continues. Shrinkage is likely to occur for the **BAB** network as well. However, when the network is locally isotropic, shrinkage will be isotropic and beadlike morphology will be preserved as seen in

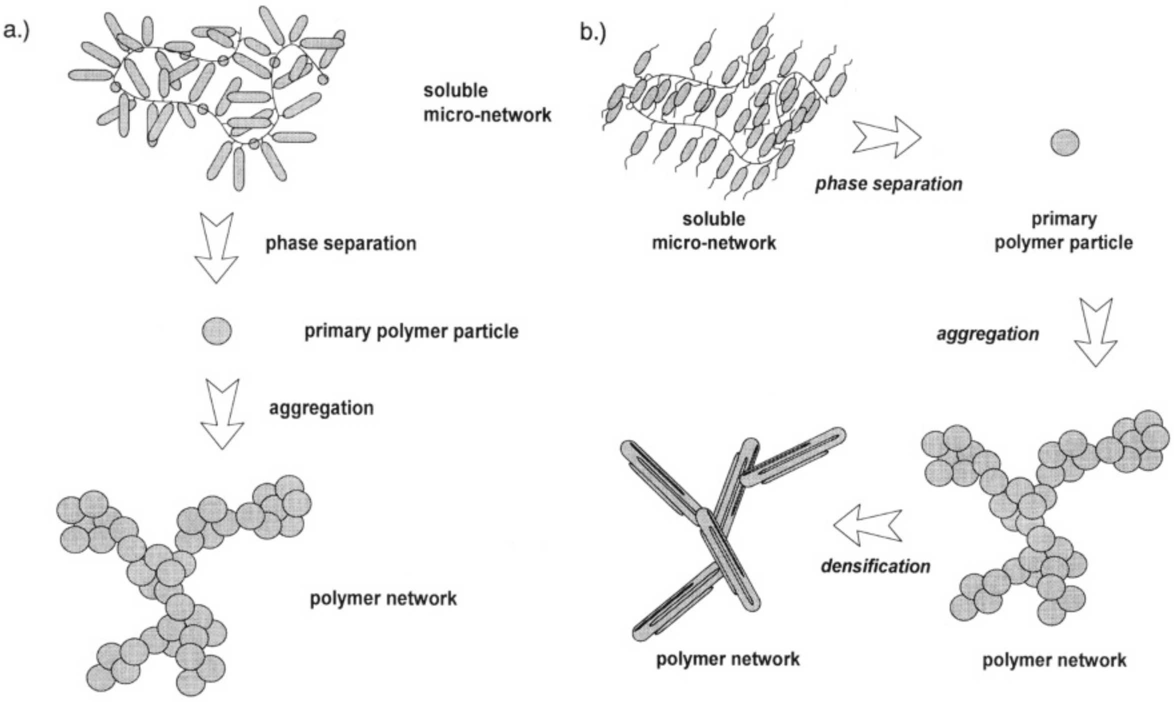

Figure 9. Schematic representation of a proposed model for the evolution of polymer network morphology of (a) p(**BAB**) and (b) p(**BAB6**). Some mesogens are drawn foreshortened, to indicate out-of-plane orientation.

Figure 4. When the network is locally nematic, shrinkage is anisotropic and the morphology becomes increasingly fibrous.

Figure 7c shows the morphology of p(**BAB6**) which was exposed to UV light of intensity of about 1.75 mW/cm^2 for 10 min. The average diameter of the strands have reduced even further to less than 0.1 μm in diameter. The strands are having very little trace of any beadlike structures. These strands form a network with pores of varying size, shape and orientation.

This phenomenon can be further verified from the morphology of these p(**BAB6**) networks as we increase the intensity of UV light. Increase in intensity of UV light increases the number of polymer chains initiated and correspondingly the number of polymer chains being terminated. An increase in the intensity of UV light will lead to corresponding increase in the conversion of the system. Figure 8 shows the morphology of p(**BAB6**) formed on exposure to UV light of higher intensities. Figure 8a shows the morphology of 2.8% BAB6 monomer solution in **5CB** polymerized by exposing to UV light of intensity 26 mW/cm^2 for 3 min. The network is clearly beadlike with pores of varying sizes, shapes, and orientation. The network strands are oriented predominantly along the rubbing direction and the beads forming the network strands are anisotropic along the direction of the strand. Figure 8b shows the morphology of the same system polymerized by exposing to UV light of intensity 72 mW/cm^2 for 3 min. Now the morphology of the network is less beadlike and more fibrous in nature. The network is more dense with pores of varying size, shape, and orientation. The average size of the pores is reduced. The strands are smaller in diameter and are found predominantly oriented along the rubbing direction.

This experiment further confirms the fact that increase in conversion of **BAB6** leads to changing the morphology of network from beady network structure to a fine fibrous structure. Also, the average diameter of the strands decreases with increasing conversion due to anisotropic shrinkage of the polymer network with simultaneous rejection of low molar-mass liquid-crystal solvent from the polymer-rich phase.

Synthesis of the above results leads to the following proposed model for the evolution of network (Figure 9). In the case of polymer-stabilized liquid crystals formed from monomers without spacers, the initially soluble **BAB** monomers polymerize into a polymer network of some critical molecular weight and/or branch content when it phase separates into smooth round particles of approximately 0.1 μm called primary particles. Any anisotropy of these is slight, arising only from anisotropy of the interfacial tension. The reactive functionality on the surface of these particles reacts with other particles, thus coagulating to form nodular beads. This is evident from the size of the nodules being approximately the size of the primary particles. Also these nodular beads in turn react with similar structures leading to the formation of network of beads. This aggregation is similar to the diffusion-limited cluster aggregation found in colloids and other systems.[18] Even while the nodular beads and network of these beads are formed, there is continuous increase in the cross-link density in the primary particles with simultaneous rejection of any low-molar-mass liquid crystal present inside them. Since there is very little order in this **BAB** system there is no change in the shape of the secondary or primary structure thereby leading the polymer structure to remain beadlike even after complete conversion (Figure 9a).

In the case of polymer-stabilized liquid crystals formed by **BAB6** monomers the primary particles are fairly anisotropic due to the ability of the mesogens in the polymer network to maintain their nematic order. As the polymerization continues further, the beads

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[18] Ball, R. C.; Weitz, D. A.; Witten, T. A.; Leyvraz, F. *Phys. Rev. Lett.* **1987**, *58*, 274.

become less evident because the increased cross-link density leads to squeezing out the low-molar-mass liquid crystals from the polymer-rich phase with corresponding shrinkage of the beads (Figure 9b). Also there is increased order in the system leading to anisotropic growth of the polymer network. It is because of these reasons there is an apparent decrease in the average diameter of the strands. As the system approaches very high conversion, we see an even further decrease in the size of the strands thus the morphology of this system continuously changes itself from the initial beadlike morphology to the final fibrous morphology.

Conclusion

In this paper, we have clearly shown the morphology and its evolution in polymer stabilized liquid crystals. In these materials, in situ photopolymerization of the monomers leads to formation of polymer network which after attaining a critical molecular weight and/or branch content phase separates into primary particles. These primary particles compact into small nodular beads due to reaction limited cluster aggregation. These nodular beads in turn aggregate sparsely into a network by a diffusion-limited cluster aggregation process. Flexible spacers have a profound effect on the morphology of these polymer stabilized liquid crystals. Polymer morphology in the case of **BAB** (i.e., without spacers) is beadlike, while **BAB6** (i.e., with spacers) is fibrous. As the polymerization proceeds, there is a continuous rejection of the solvent from the polymer-rich regions leading to continuous change in the shape of the beads and the overall morphology. A continuous change in morphology of the polymer network formed from monomers with spacers (i.e., **BAB6**) from bead-like to fibrous unlike **BAB** (i.e., without spacers) as photopolymerization proceeds, demonstrating the higher molecular order in **BAB6** than **BAB**. The morphology of the polymer network is consistent with the molecular orientation (homeotropic or homogeneous) and order (nematic or isotropic state) in the monomer solution prior to photopolymerization. There is a strong orientational coupling (important for display applications) between the polymer network and the low-molar-mass liquid-crystal solvent. The strength of the orientational coupling depends on the orientational order of the monomer solution prior to photopolymerization and the morphology of the polymer network formed. The polymer morphology, orientational order and the orientational coupling between the polymer network and the low-molar-mass liquid-crystal solvent can be controlled by flexible spacer length and the polymerization conditions.

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