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Morphology of diacrylate copolymer networks formed in liquid crystalline media

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The morphology of polymer networks in polymer-stabilized liquid crystals (PSLC) can be controlled by copolymerization of different monomers at isothermal conditions. Copolymerization of 4,4′-bis(acryloyloxy) biphenyl (BAB) and 4,4′-bis(6-(acryloyloxy)hexyloxy)biphenyl (BAB6—a monomer similar to BAB, but with a hexamethylene flexible spacer between the mesogen and the polymerizable acrylate moiety) produces a polymer network of intermediate flexibility, leading to a morphology intermediate between the bead-like morphology of BAB and the smooth fibrous morphology of BAB6. However, copolymerization of BAB6 and BABB6, a monomer with a longer mesogen, can produce a single morphology characteristic of BABB6 alone. Furthermore, at very high polymerization temperatures, when differences in monomer reactivity may be exaggerated, copolymerization yields neither uniform composition nor morphology. Instead, morphologies characteristic of each homopolymer coexist. These studies emphasize the significance of monomer structure and reactivity for the polymer network morphology formed in liquid crystal media. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Low-molar-mass liquid crystal–polymer composites containing very low concentrations of polymer are a new class of materials for device applications such as flat-panel displays, high-intensity light-shutter valves, privacy windows etc. These composites, called polymer-stabilized liquid crystals (PSLCs), typically have polymer concentrations below 5 wt%[1–8]. The composites are prepared by thoroughly mixing low-molar-mass liquid crystals with a suitable monomer and photoinitiator, followed by photopolymerization, resulting in a polymer network formed in non-reactive low-molar-mass liquid crystal solvent. The addition of polymer networks in small amounts improved the electro-optic properties of the twisted-nematic (TN) and supertwised-nematic (STN) cells in terms of the steepness of electro-optic response, a decrease in the threshold voltage, and elimination of undesirable light-scattering stripe formation[9]. Also the display devices made of polymer-stabilized liquid crystals possess bistability, increased viewing angle, faster response or switching time[10]. Preliminary work on understanding the switching behaviour of these (liquid crystal/polymer) composite systems both theoretically and experimentally have been reported[11,12].

The processes controlling the morphology of polymer networks formed in dilute solution is therefore of scientific and industrial interest. Recent investigation, to be reported elsewhere[13], has shown that in cases in which the solubility of monomer and polymer is low, polymerization leads first to precipitation of tiny microgel polymer particles. The final network structure is the result of the aggregation of these relatively rigid, but reactive particles. Phase separation has

been demonstrated clearly by phase contrast optical microscopy (OM), which is sensitive to differences in index of refraction, and provides contrast between the polymer-rich and solvent-rich domains. The phase separation is irreversible, because it is produced by a reaction which results in both an increase in molecular weight and the formation of a microgel. As reaction proceeds, the aggregation of particles can be seen by OM. When the concentration of radical species is low, aggregates can become quite large and easily observable by OM, before the eventual formation of an infinite network. Other investigations have focused on characteristic lengths of the final network as controlled by aggregation kinetics[12,13].

At the smallest length scales, the final morphology is either fibrous, beaded or plate-like, depending apparently on the structure of the monomers and their order in the LC medium[8,12]. The focus of the current work is to explore how the morphology of the polymer network could also be manipulated by blending different monomers of nearly equal reactivity and copolymerizing them in appropriate conditions. In this way, the morphology of polymer networks in PSLCs can be controlled at isothermal conditions.

EXPERIMENTAL METHODS

Sample preparation

Samples were prepared by dissolving the diacrylate monomers in varying proportions (25:75, 50:50, 75:25) maintaining the overall concentration of the monomers in the low-molar-mass liquid crystal solvent at 3 wt%. The diacrylate monomers used in this study are 4,4′-bis (acryloyloxy) biphenyl (BAB), 4,4′-bis(6-(acryloyloxy)-hexyloxy)biphenyl (BAB6) and 4,4′-bis{4-[6-

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(acryloyloxy)hexyloxy]benzoate}biphenylene (BABB6). BAB and BAB6 have similar mesogens, whereas BAB6 and BABB6 have the same spacers between the mesogen and the polymerizable acrylate moiety. These monomers differ from one another in that BAB has no flexible spacer and that BABB6 has a longer mesogen when compared to BAB6. The low-molar-mass liquid crystal solvent and the photoinitiator used in this study are E48, a nematic liquid crystal mixture with a broad temperature range, and benzoin methyl ether (BME), respectively. The synthesis of the monomers and photoinitiator has been described previously[1,14]. The liquid crystal solution (monomer dissolved in appropriate solvent) was then sandwiched between properly treated glass slides. The glass slides had been spin-coated with polyimide precursor solution (Oligomeric polyimide DuPont PI 2555 mixed with a thinner), cured for an hour at 250°C then buffed unidirectionally to obtain a homogenous boundary condition. Mylar spacers of approximately 12.5 μm thickness were used to control the thickness of the cell, which was filled with the monomer solution. Uniform, homogeneous, alignment of the LC director before polymerization was confirmed by cross-polarized light microscopy. The samples were irradiated for 20 min with UV light of 365 nm wavelength and intensity of 1.75 mW/cm^2, assuring complete photopolymerization[15]. The temperature of the sample was controlled using a Mettler hot stage. The nematic to isotropic phase transition temperature of E48 is 87.2°C, and that of the monomer solutions is 2–3°C less.

Morphology examination

Phase contrast OM is an *in situ* technique that is sensitive to differences in index of refraction, so that, after polymerization and phase separation, regions which are rich or poor in polymer may be distinguished. The sample cell before polymerization appears uniform if examined in the isotropic state, and a dynamic and very low contrast fine-scale speckle pattern arising from thermal director fluctuations is seen in the nematic state. After polymerization, a static speckle pattern having greater image contrast is formed, which persists and remains static if the specimen is heated to the isotropic state. The length scale characteristic of this pattern depends on composition and polymerization conditions[13].

To prepare the specimen for SEM examination, the liquid crystal solvent was first replaced with hexane by soaking the cell in the solvent for 2 days. No change in the static speckle pattern was observed by optical microscopy after solvent exchange. Hexane was allowed to evaporate, and the cell was delicately split open when dry. Distortions of the network caused by evaporation have been prevented in other experiments in which the cells were soaked in ethanol and dried in supercritical CO_2. However, comparison of the preparation methods reveals that distortions caused by normal evaporation do not affect the fine-scale morphology as presented in this report, but only the larger-scale organization of the polymer aggregates, observed at lower magnification. The dry network was coated with 90 angstroms of gold using the Biorad-Polaron divisions' SEM sputtering system. The morphology of these samples was then observed using the JEOL JSM 840 scanning electron microscope operated at 25 KV in secondary electron imaging mode. The comparison of SEM and OM micrographs demonstrates that the speckle pattern observed by OM corresponds to variations in the network density observed by SEM[13].

RESULTS AND DISCUSSION

Since this investigation makes use of the similar reactivity of the three monomers, the results of kinetic studies will be summarized first. The rate of photopolymerization at 28°C of a 3 wt% solution of BAB, BABB6 and BAB6 in E48 are 130, 85 and 68 min^{-1}, respectively, and the dependence of the rate of photopolymerization with temperature is weak. These rates are similar in magnitude to each other, decreasing slightly with increasing flexibility of the monomer. This is in contrast to the bulk polymerization of
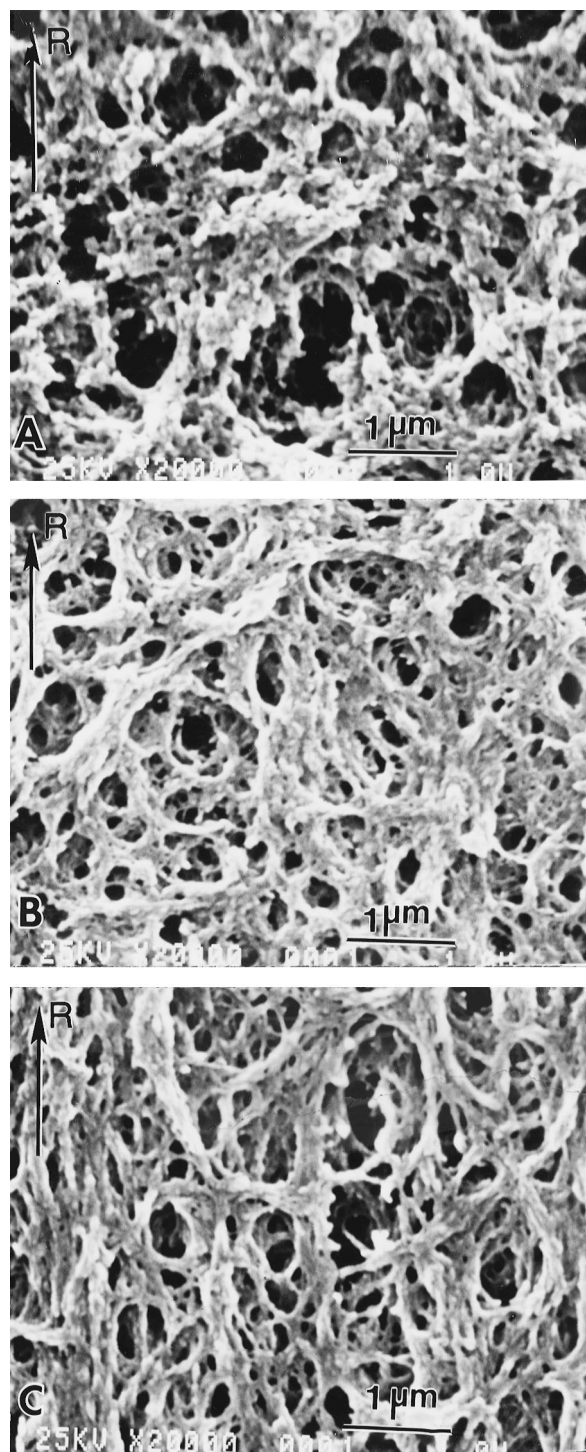

Figure 1 SEM micrographs of the copolymer network of **BAB6** and **BAB** polymerized in **E48** under nematic conditions. The comonomer weight ratio is (A) 25:75, (B) 50:50, (C) 75:25, and *R* denotes the direction of rubbing of the polyimide to get a homogenous alignment of the liquid crystalline monomer solution

acrylates where increasing the flexibility of the monomers increases the rate of polymerization because the reaction is influenced by the mobility of the reactive moiety[16–18]. In dilute solution, however, differences in mobility are less, so that other factors such as the electronic structure of the monomers are more important.

Morphology of copolymers of BAB and BAB6

Our previous work suggests that the fibre-like morphology of BAB6 and the bead-like morphology of BAB are related directly to the presence and absence of flexible spacers between their mesogen and the polymerizable acrylate moiety, respectively[8]. Since the polymer flexibility can be controlled by copolymerization of these monomers, the control of their morphology is also expected. When the monomers BAB6 and BAB, are blended at the ratio of 25:75, respectively, and photopolymerized at nematic condition (35°C), the morphology is similar to that previously obtained from pure BAB (*Figure 1A*). The network is porous, comprising interconnected nodular beads approximately $0.2 \pm 0.1 \mu m$ in size. Although the flexibility at this composition is insufficient to form fibrils, fibrillar morphology is obtained when the relative concentration of the flexible monomer is increased to 50% (*Figure 1B*). The average fibre diameter, $0.2 \pm 0.1 \mu m$, is equal to the bead diameter in the previous structure. Thicker strands are also present. The fibres are aligned along the rubbing direction. As the fraction of BAB6 is increased further to 75% (*Figure 1C*), the polymer fibres become smoother, smaller in diameter ($0.1 \mu m$), and more highly aligned.

Therefore, as the relative concentration of BAB6 is increased, the morphology of the copolymer network changes from an initial beaded network morphology to a fine, relatively smooth fibrillar morphology. The fibre alignment and the pore anisotropy increase with BAB6 content. The uniformity of the morphology throughout the specimen at a given composition suggests that the network is indeed a random copolymer, as expected.

Our previous work suggests that the formation processes for both BAB and BAB6 polymer networks are similar and that fibrillar alignment results from the anisotropic shrinkage of more flexible and anisotropic network elements[8]. A similar process for the development of a fibrillar morphology has been reported recently for another diacrylate polymer network[19]. Copolymer networks also are expected to form by the same process, when the reactivities of the monomers are similar to one another. By increasing the relative concentration of flexible spacers (BAB6), the decoupling of the mesogen and copolymer backbone conformations is increased, and an oriented fibrous morphology is possible only for a sufficient fraction of flexible units in the copolymer.

In the isotropic state, there is no long-range order in the system. After polymerization at 110°C, an isotropic packing persists and the morphology for either BAB, BAB6 or their copolymers is bead-like. As the BAB6 content is increased, the bead size increases from $0.1 \mu m$, at a relative concentration of 25% BAB6, to about $0.3 \mu m$ at 75%. Although the reason for this difference in bead size is not certain, our recent model[12] suggests that the lower reactivity and increased solubility of BAB6 may be factors. A similar difference in size was found for isotropic polymerizations at lower temperatures, using 5CB as the solvent.

Morphology of copolymers of BAB and BABB6

BABB6, like BAB6, is a monomer that at lower temperatures forms a fibrous morphology. Not surprisingly

then, the morphology of BAB and BABB6 copolymers formed in nematic conditions (58°C) resemble those of BAB and BAB6 (*Figure 1*). Again, as the relative concentration of BABB6 is increased, the morphology gradually changes from bead-like to fibrillar. Also, the roughness of the network strands decreases, the pores in the network become elongated in the rubbing direction, and the fibres become more aligned along the rubbing direction. As before, blending the monomers BAB and BABB6 produces a single morphology intermediate to the bead-like and the fibrous homopolymer morphologies, again suggesting that the blending of these monomers yields a copolymer network due to their similar reactivity.

At higher temperatures, BABB6 forms a plate-like morphology and copolymers with BAB result in some interesting morphologies. The morphology of the copolymer derived from the monomers BAB and BABB6 in the ratio 75:25 polymerized at isotropic condition (110°C) is bead-like, with nodular beads about $0.1 \mu m$ in size (*Figure 2A*). Some of these have aggregated into large irregular structures. The bead-like network appears to be dense with mostly small round pores. The morphology of the 50:50 copolymer (*Figure 2B*) is a bead-like network, yet with plates in the interstices. The beads are of similar size ($0.1 \mu m$) and nodular, and the plates are smooth and found in varying size, shape and orientation. These range from less than one to several μm in size. Large pores are also present in the network. The morphology of the 25:75 copolymer (BAB: BABB6) (*Figure 2C*) is a mixture of bead-like and plate-like networks. While the beads are slightly larger ($0.3 \pm 0.1 \mu m$ in size), the plates are now much larger (several μm). The increased amount of plates in this system is consistent with the higher concentration of copolymer rich in BABB6.

At low relative concentrations (25%) of BABB6, there is a single beaded morphology, again suggesting that a copolymer has been formed. At higher concentrations of BABB6, two morphologies coexist. This result suggests that at least one of the monomer reactivity ratios, under these conditions, is greater than unity. Some of the copolymer product is rich in BABB6, and vice versa. The resulting distribution of copolymer composition is sufficiently large, so that the structures that nucleate upon separation are distinct, some forming beads, some forming plates. Although inherent values of monomer reactivity ratios could cause such behaviour, the effective values of these ratios also can be influenced strongly by phase separation[20]. One of the monomers may be more soluble in one or the other of the polymer-rich phases, thus increasing locally the apparent reactivity of that monomer.

Morphology of copolymers of BAB6 and BABB6

The morphology of blends of BAB6 and BABB6, both of which have flexible spacers, was also investigated. Our previous work shows that the morphology of BABB6 is similar to that for BAB6 but with a large fibre diameter and increased roughness at the same temperature[12]. The most significant difference between these two monomers is in the plate formation at elevated temperatures. BABB6 forms large plates over a broad temperature range while BAB6 shows plate-forming tendency only near the nematic to isotropic phase transition temperature.

The morphology of copolymers of BAB6 and BABB6 photopolymerized at 58°C, regardless of their monomer ratio, is fibrillar (similar to *Figure 1C*, yet having smoother fibres). It is not surprising to find the morphology of the

copolymer networks to be fibrillar, since both homopolymers form fibres under these polymerization conditions. The fibres are oriented along the rubbing direction with anisotropic pores and about 0.2 ± 0.1 μm in size, some of which have aggregated into thick strands. As the relative concentration of BABB6 is increased the fibres become more rough. The copolymer having the least amount (i.e. 25%) of BABB6 has much smoother fibres that are highly oriented along the rubbing direction, while the copolymer containing the most BABB6 (75%), has rough, thicker fibres and less orientation. The presence of fibrous morphology and the thickness of those fibres between that of the fibres of the two homopolymers suggests a high degree of copolymerization.

In the isotropic state, the effect of copolymerization is most profound. At all relative concentrations of BAB6 and BABB6, the plate-like morphology of BABB6 is formed (*Figure 3*). Each plate is 0.1 μm in thickness and averages approximately 1 μm in breadth. The plates are irregular in shape, smooth, and of varying orientation and have aggregated into a dense network with large pores. Because copolymerization of BAB6 and BABB6 monomers in isotropic solution forms a plate-like morphology at all the
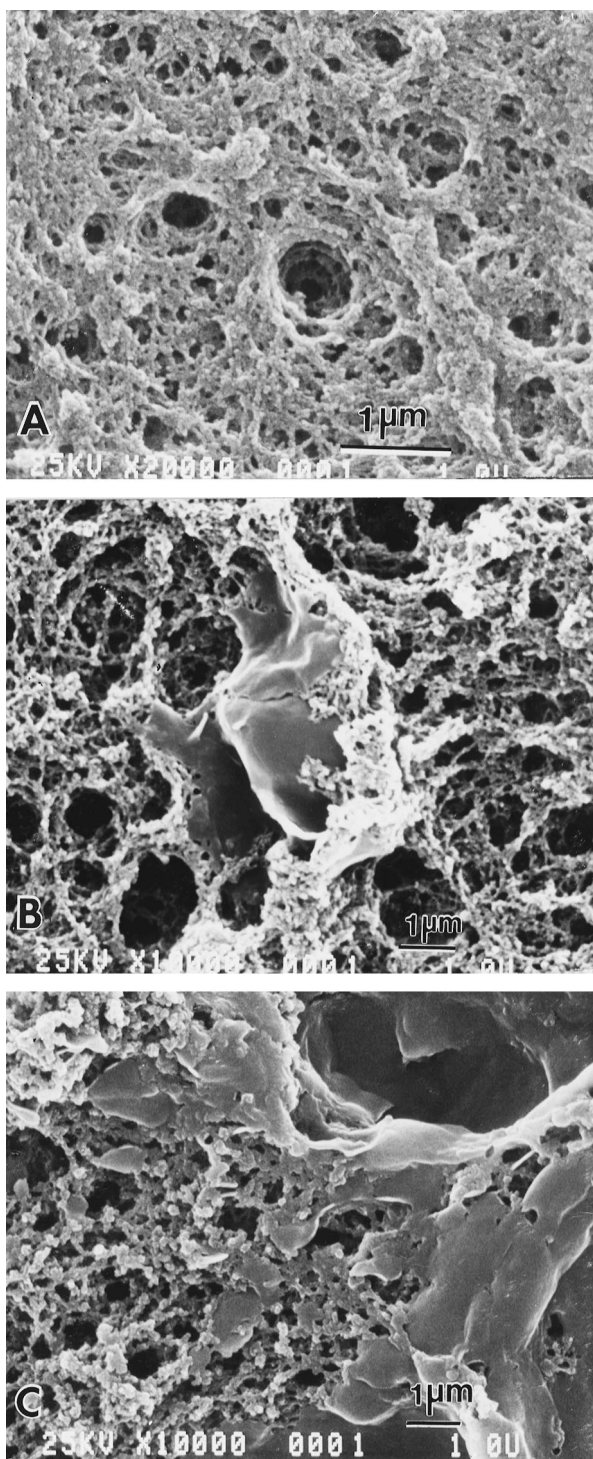

Figure 2 SEM micrographs of the copolymer network of **BABB6** and **BAB** polymerized in **E48** under isotropic conditions; the comonomer ratio is (A) 25:75, (B) 50:50 and (C) 75:25
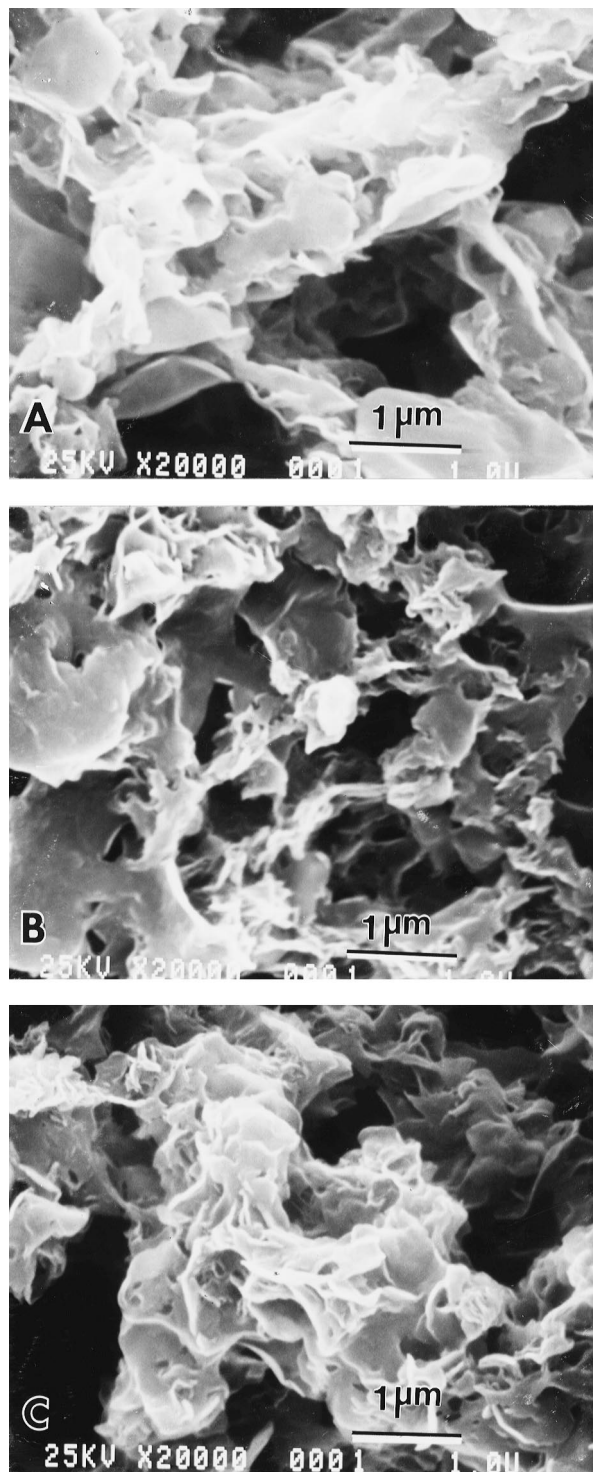

Figure 3 SEM micrographs of the copolymer network of **BAB6** and **BABB6** polymerized in **E48** under isotropic conditions (at 110°C); the comonomer ratio is (A) 25:75, (B) 50:50 and (C) 75:25

relative concentrations of BAB6 and BABB6, it suggests that a small amount of BABB6 in predominantly BAB6 polymer network can nucleate layered structures leading to a plate-like morphology (*Figure 3c*). This is possible because both BABB6 and BAB6 have identical flexible spacers which are attached similarly in the 4, 4′ position of the mesogen, making it possible for them to accommodate and pack together into layered structures. The smoothness of the plates is also consistent with phase separation of the copolymer networks initially as plates, and not as beads which only subsequently transform to plates. The subsequent aggregation process is similar as for other morphologies.

CONCLUSION

The morphology of polymer networks in polymer-stabilized liquid crystals could be manipulated at isothermal conditions by copolymerizing different monomers, which on homopolymerization form different morphologies. The effect of the relative concentration of flexible spacers is observed for the copolymers of BAB and (BAB6 or BABB6), which as homopolymers form bead-like and fibrillar morphologies, respectively. When polymerized in the nematic state, these copolymers form morphologies intermediate between their homopolymer extremes, depending on the relative monomer proportions. That is, the morphology of these copolymers is generally fibrous, with increasing roughness as the content of flexible spacers is decreased. BAB6 and BABB6, when copolymerized in the nematic state, also form intermediate morphologies. Increasing the relative concentration of BABB6 increases the roughness of the fibres and decreases the orientation of the fibres. Formation of intermediate morphologies suggests that the copolymer is readily formed.

Nevertheless, copolymerization in the isotropic state does not always produce an intermediate morphology, suggesting variation in copolymer composition and in the relative influence of each monomer on the phase-separated structure. The effective monomer reactivity ratios are sufficiently different for BAB and BABB6 that two different structures, both plates and beads, coexist. On the other hand, copolymerization of BAB6 and BABB6 yields only the plate-like morphology characteristic of BABB6 alone, at all relative concentrations of these monomers.

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