



	Experiment title: Ternary blends of diblock copolymers with liquid crystalline semiconductors.	Experiment number: SC1127
Beamline: BM26	Date of experiment: from: 12/02/04 to: 16/02/04	Date of report: 25/02/2004
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Block copolymers of strongly incompatible blocks exhibit a rich variety of morphologies in the melt state, including cubic, hexagonal, lamellar and gyroid structures, according to the volume fraction of the constituents, f_v , and the product, χN , of the interaction parameter and the number of repeat units in the chains^{1,2}. Blends of block copolymers, with either one or two homopolymers with similar chemical structure as the diblock, generate a swelling of the pre-existing morphologies and the formation new microstructures or even macroscopic phase separation, depending on the relative compositions of the blends. At high block copolymer content and low molecular weight homopolymers, it has been reported that the morphologies of the blends are essentially that of the neat diblock, whereas the addition of a large amount of homopolymers results in the formation new and complex microstructures, such as the bicontinuous microemulsion.

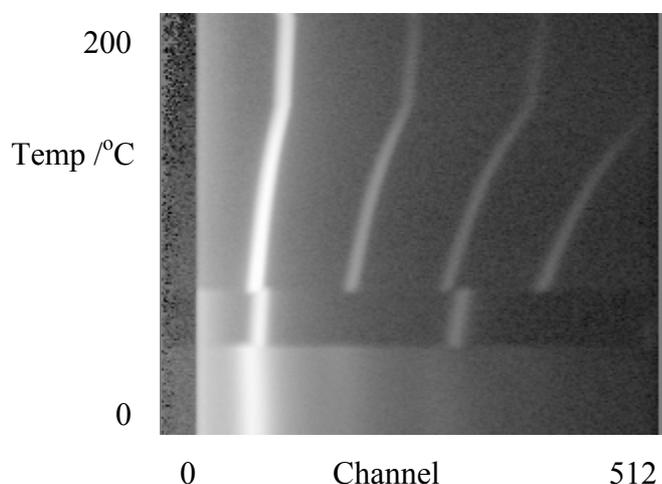


Figure 1.

A series of ternary blends containing a symmetric diblock (A-B) and various amounts of semiconducting liquid crystalline homopolymers (C/D) have been investigated at CRG DUBBLE beamline BM26 of the ESRF, using time-resolved simultaneous SAXS/WAXS/DSC experiments, in order to observe the phase transition of the swollen lamellar structures into the bicontinuous microemulsion, and then macroscopic phase separation at very low diblock content.

For blends containing >30% block copolymer, the microstructures observed are essentially the same as that of the neat diblock, with no significant increase in the d-spacing of the stacks as the homopolymer content is increased. Also, on cooling below the crystal-liquid crystal transition temperature of the homopolymers, the lamellar layers become symmetrical (shown by the absence of the second and fourth order peaks), before the block copolymer itself crystallises (**Figure 1**, SAXS of 60% A-B:40%C/D).

Mean-field theory predicts an isotropic tri-critical point between the lamellar phase of the diblock with low homopolymer content, the macrophase separated mixture with high homopolymer content and the homogeneous melt above the order-disorder transition temperature of the system. However, it has been shown experimentally that the critical point is suppressed by fluctuations in the polymer chains and a thermodynamically stable bicontinuous microemulsion channel is observed^{3,4}. As the microemulsion channel is approached, a sharp increase in the d-spacing of the lamellar layer spacing is expected.

Figure 2 shows the change in the d-spacing of the lamellar layers observed on increasing the homopolymer content at various temperatures. At high temperatures the layers appear to collapse due to the thermal energy of the system overcoming the unfavourable interactions between the incompatible polymer chains, however on cooling, a sharp increase in the spacing is observed at >70% homopolymer content indicating the microemulsion channel is being approached. Unfortunately, blends with less than 10% diblock showed very weak/no small angle scattering and therefore the phases obtained at these compositions cannot be determined at present.

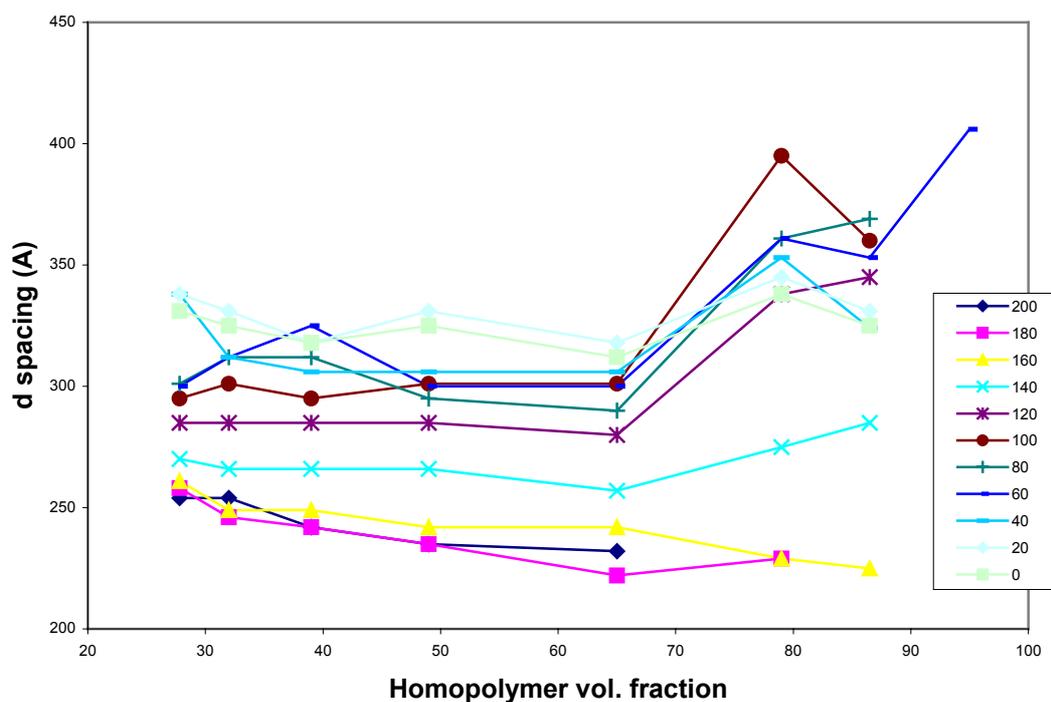


Figure 2.

References

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