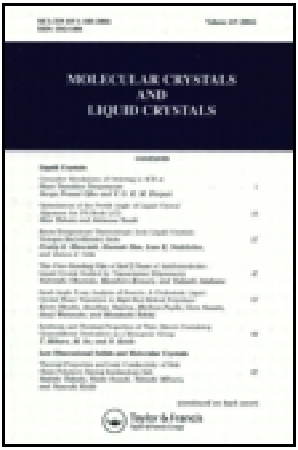

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Solubilization of Immiscible Liquids Into Mesophases Formed from Amphiphilic Block Copolymers

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Version of record first published: 20 Apr 2011.

To cite this article: F. Ballet , Y. S. Leong , J. C. Wittmann & F. Candau (1981): Solubilization of Immiscible Liquids Into Mesophases Formed from Amphiphilic Block Copolymers, Molecular Crystals and Liquid Crystals, 64:9-10, 305-311

To link to this article: http://dx.doi.org/10.1080/01406568108072016

Mol. Cryst. Liq. Cryst. Vol. 64 (Letters), pp. 305-311
0140-6566/81/6409-0305$06.50/0

SOLUBILIZATION OF IMMISCIBLE LIQUIDS INTO MESOPHASES FORMED FROM AMPHIPHILIC BLOCK COPOLYMERS

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(submitted for publication April 13, 1981)

ABSTRACT : Optical microscopy and X-ray diffraction studies reveal the presence of highly swollen mesophases in four-component systems containing amphiphilic triblock copolymers. According to the composition of the system,lamellar phases or hexagonal structures are produced. The polymeric mesophases exhibit textures very similar to those encountered in low molecular weight liquid crystalline phases.

Amphiphilic block copolymers in bulk or dissolved in a selective solvent of one sequence are known to give rise to mesomorphic structures(1) . Recently a study performed on systems formed of polystyrene-polyethyleneoxide graft copolymers dissolved in water-toluene mixtures in the presence of 2-propanol (systems analogous to microemulsions) has given evidence of mesophases occuring at rather high solvent contents (∿70-80%)(2,3) . These homogeneous mesophases, mainly located in the toluene-rich area of the diagram and close to the transition curve between transparent and milky emulsions, are characteristic of inverse hexagonal structures or lamellar phases. An interesting feature is that these relatively fluid systems display most of the textures encountered in low molecular weight liquid crystalline phases.

Similar "hyperswollen" organized four-component systems were also observed in the phase diagrams of microemulsions containing polyoxyethylated C_{16} non ionic surfactants(4).

In this letter, we report an investigation of the structure of the mesophases formed from amphiphilic triblock copolymers. The results obtained by means of optical microscopy and low-angle X-ray diffraction illustrate the influence of the molecular architecture of the polymeric surfactant on the structural characteristics of the swollen mesophases. Some optical textures not yet observed in systems containing block copolymers are described.

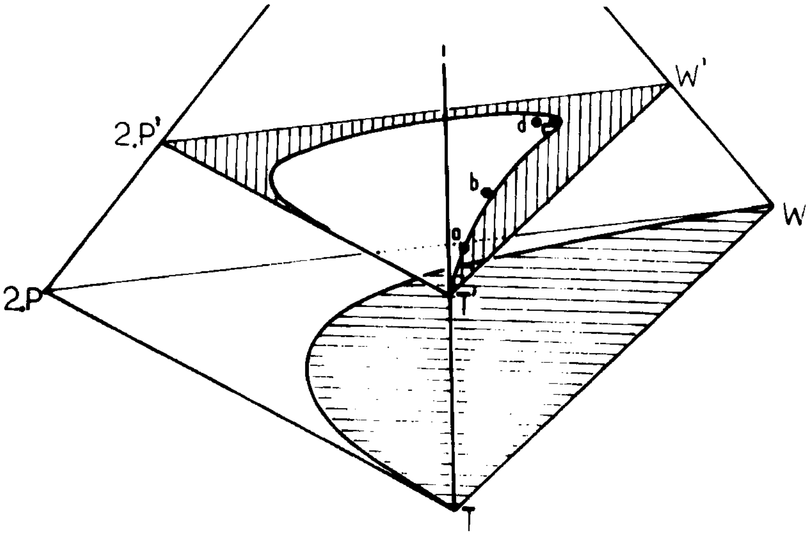

FIGURE 1 : Parallel spatial sections of the phases tetrahedron (wt %) in the four-component systems. Triangle 2P-T-W : phase diagram of the ternary solvent mixture. Triangle 2P'-T'-W' : pseudo-ternary phase diagram with an overall copolymer concentration around 30%. Hatched areas : inhomogeneous phases

The triblock polystyrene-polyethyleneoxide copolymer has been prepared via anionic polymerization according to a procedure described elsewhere(5) and has the following characteristics:

$\overline{M}_n$.cop	$\overline{M}_n$.PS	$\overline{M}_n$.PEO (one block)	wt % PS
5350	2510	1420	47

The different systems that we investigated are located in the vicinity of the transition domain between macro- and microemulsions. We have mainly considered the influence of the toluene-water ratio, the overall copolymer concentration being kept constant. The compositions of the systems are reported in Table I and Figure 1.

The results may be summarized as follows :

1) <u>TOLUENE TO WATER RATIO = 5</u> (system a)

Contrary to the results relative to PS-PEO graft copolymers(2,3), systems containing block copolymers do not exhibit in the same range of concentration spontaneous birefringence. However, if the titration procedure of the copolymer-

Syst.	Composition (wt %)				T/W	Bragg spacing d(Å)	Description of system
	T	W	2.P	Cop.			
a	51.7	10.3	7.0	31.0	5.02	-	hazy mixture
b	33.4	24.7	13.0	28.9	1.35	160	clear, viscous fluid
c	9.4	46.8	15.8	28.0	0.20	157	clear, stiff gel-like substance
d	8.9	44.6	20.0	26.5	0.20	168	elastic clear gel

TABLE I : Effect of the toluene-water ratio on the formation of mesophases.

toluene-water emulsion with 2-propanol is not completely achieved (just before clearing), the opalescent metastable system rapidly separates (1-2 hours) in a birefringent phase in equilibrium with a large excess of toluene and alcohol. Observations, under the polarizing microscope, of the system before phase separation show characteristic bâtonnets, figures which often appear in thermotropic or lyotropic systems, at amorphous-to-smectic phase transitions. An example is given in figure 2 where one can distinctly see enlargements along the axis of revolution of the elongated objects. These protrusions, which have been described in detail by Friedel$^{(6)}$, correspond to focal conic domains, with the lamellae lying normal to the axis of the bâtonnets.

2) TOLUENE TO WATER RATIO = 1.35 (System b)

An increase of the water content in the system requires a larger amount of 2-propanol in order to obtain a homogeneous phase (see the compositions given in table I). For this toluene-water ratio, the stable systems are viscous fluids, birefringent and exhibit textures characteristic of lamellar phases. Figure 3 shows homeotropic regions (block areas) separated by longitudinal defect lines (oily streaks) with confocal domains visible inside. Figure 4 corresponds to an association of focal domains, each of which has a shape of a four-leaved clover. This defect structure often observed in lyotropic systems is refered to as the mosaic texture$^{(7)}$.

The X-ray pattern exhibits one single sharp diffraction line, the periodicity d being equal to 160 Å. Since optical microscopy shows unambiguously a lamellar like-structure, this distance corresponds to the interlamellar spacing. In this structure, each sheet represents the superposition of two layers; one contains the PS sequences swollen by toluene, the other the PEO blocks solvated by water, the alcohol being shared between both layers.

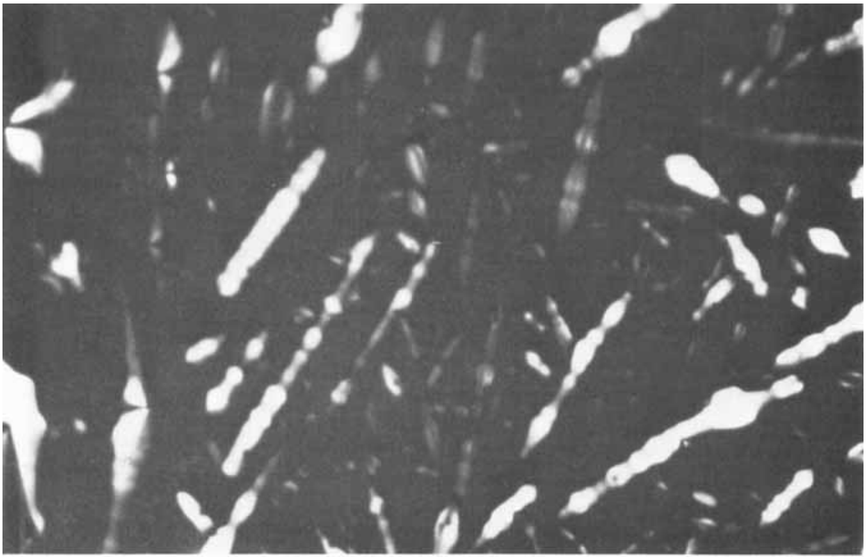

FIGURE 2 : Formation of bâtonnets occuring in the system a prior to phase separation ; crossed polarizers (Gx280)

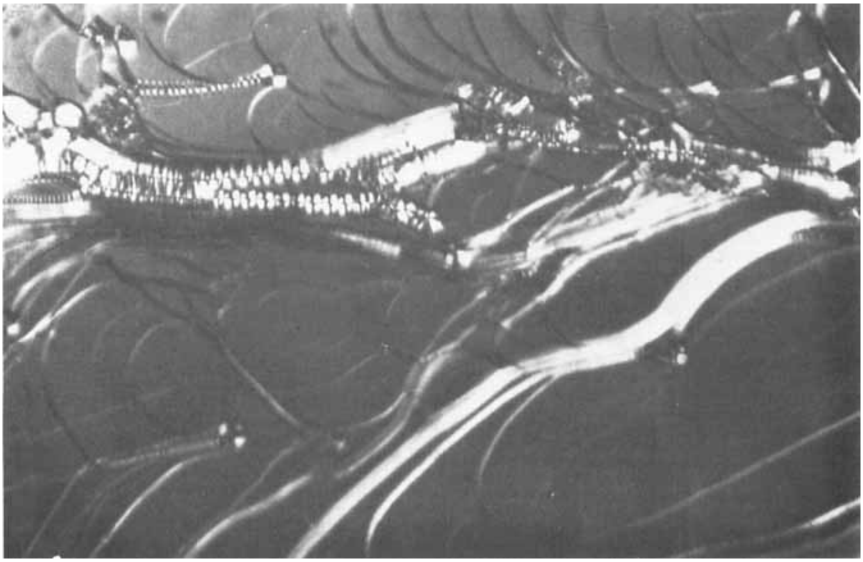

FIGURE 3 : Oily streaks separating homeotropic regions in the lamellar system b ; crossed polarizers (Gx280)

FIGURE 4 : Mosaic texture in a lamellar phase (system b) ; crossed polarizers (Gx580)

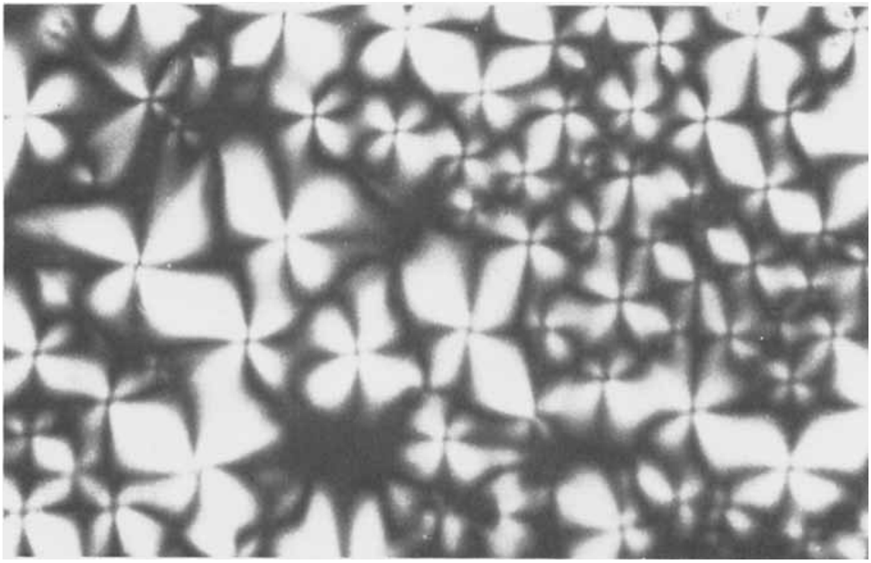

FIGURE 5 : Striated texture adjoining cloudy regions in an hexagonal phase (system c) ; crossed polarizers (Gx525)

3) TOLUENE TO WATER RATIO = 0.20 (systems c and d)

In this water-rich region, the system c appears as a transparent and homogeneous gel, although the copolymer concentration is equal to that of the preceding systems. Observations between crossed polarizers show large cloudy domains bounded by black areas with sometimes appearance of parallel striations as shown in figure 5 and discussed by Rogers and Winsor(8). These textures are representative of a two-dimensional arrangement in which the PS blocks, solvated by toluene are located in the interior of the cylinders, surrounded by the PEO chains solvated by water.

This normal hexagonal structure is confirmed by the corresponding X-ray pattern where two bands related by a $\sqrt{3}$ factor are observed. It is of interest to note that the difference in consistency of the lamellar (fluid) and hexagonal (stiff) phases is very reminiscent of what is observed between the neat and the middle phases of systems containing soaps.

By further addition of alcohol, the system c transforms into an elastic and isotropic gel (system d) which also shows analogies with swollen gels described for oil-water-oleic alcohol systems(9). The X-ray pattern contains one single sharp diffraction line. The absence of additional lines does not allow to determine the nature of the molecular arrangement.

The results reported in this letter show that triblock copolymers dispersed in water-toluene-2-propanol mixtures are able to form highly swollen mesophases (70% solvent mixture). The block structure of the amphiphilic copolymer favors the formation of mesophases in the water-rich area. The opposite trend has been observed for graft PS-PEO copolymers of same ponderal composition, which exhibit mesophases in the toluene-rich area(3). The larger solubility of triblock copolymers in water is presumably at the origin of this behavior.

ACKNOWLEDGEMENTS : The authors are very grateful to the research group of A.J. Kovacs for making available the X-ray apparatus.

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