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EXPERIMENTAL EVIDENCE OF MESOMORPHIC PHASES IN QUATERNARY SYSTEMS CONTAINING AMPHIPHILIC MACROMOLECULES

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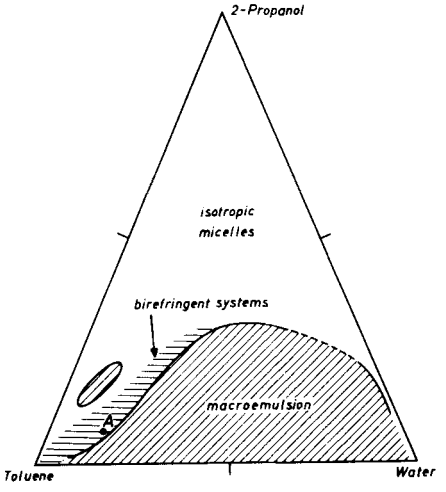
ABSTRACT : Lamellar phases have been evidenced in homogeneous water-toluene mixtures stabilized by amphiphilic graft copolymers. The lamellae have been observed directly using electron microscopy after freeze-fracturing as well as interference contrast optical microscopy.

In this letter, we report preliminary microscopic observations of mesomorphic phases of the lamellar type obtained from toluene-water dispersions stabilized by amphiphilic graft copolymers. In a previous series of papers[1-3], we have demonstrated the ability of poly(ethylene-oxide)-polystyrene (PEO-PS) graft copolymers to solubilize a water-toluene mixture in the presence of a cosurfactant (2-propanol). Figure 1 shows a typical phase diagram corresponding to a copolymer with the following characteristics :

sample: % Polystyrene	$Mw_{backbone}$ (PS)	Mw_{graft} (PEO)	Average number of grafts	$Mw_{copolymer}$
26	18 200	7 800	6.5	75 000

The transparent systems, located in the upper part of the diagram i.e. with high 2-propanol contents (> 40 %) were shown to consist of isotropic copolymer micellar particles[1-3]. In the present work, we investigate the birefringent transparent systems located in the vicinity of the transition line between macro- and micro-emulsions. Such systems appear only for sufficiently high copolymer concentrations (> 12 %/system). Their formation is also favoured by a low 2-propanol content and by decreasing temperature.

Optical and electron microscopic evidences indicate that we are dealing with a lamellar structure.



T = 25°C

FIGURE 1. Triangular section of the tetrahedron corresponding to the quaternary system water/toluene/copolymer PS-PEO/2-propanol ; the ratio of the copolymer mass to the sum of the (water + toluene) masses is kept constant (0.32) in this pseudo-ternary phase diagram.

point A : the ratio of the copolymer mass to the total mass of the quaternary system is 0.24

I - OPTICAL MICROSCOPY

- *Polarized light microscopy*. Figures 3a,b show two examples of birefringent textures often observed between crossed polarizers for a system whose composition corresponds to point A in the diagram (Figure 1). Such textures are reminiscent of those frequently observed with classical liquid crystals, although less well defined ; they are nevertheless better defined than the textures usually encountered in low molecular weight micro-emulsions and in concentrated solutions or melts of block copolymers which are often cloudy and diffuse[4].

- *Interference and phase contrast microscopy*. From the previous observations alone, it is difficult to deduce the particular type of structure that is present. Further information was gained from observations of the very thin films which can be formed between air bubbles and the cover slip or glass slide supporting the sample (Figure 2).

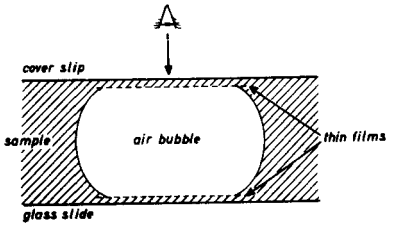


Figure 2

The interference contrast photomicrograph in Figure 4a shows very distinctly stacks or single lamellae lying parallel to the glass surfaces. Dust particles or other heterogeneities (appearing as bright dots in Figure 4a) act as anchoring points for the lamellae which flow like a liquid when disturbed by moving the bubble.

II- ELECTRON MICROSCOPY

Electron micrographs obtained after freeze-fracturing - a technique already used in studies of corresponding micellar solutions[1] - corroborate the above observations.* Figure 4b shows again clear evidence of the existence of lamellar structures. Although a precise determination of the lamellar thickness is precluded by fractures in non-specific directions , one can make a rough estimate of 300 Å.

Lamellar structures have already been observed in mesomorphic phases of polystyrene-poly(ethylene-oxide) block copolymers dissolved in a selective solvent of one sequence at high copolymer concentrations (c > 50 %) ; in these systems, however, the PEO sequences are generally in the crystalline state[5,6]. In the present quaternary systems formed from graft PS-PEO copolymers,on the contrary, lamellar structures exist in far more dilute solutions and the PEO grafts are in a liquid-like or disordered state.

On the other hand, the behavior of such polymeric systems presents some analogies with that of low molecular weight micro-emulsions. In the latter, it is now widely accepted that the surface-active substances (soaps or non-ionic detergents) associate into normal or reverse micelles with a transition to liquid-crystalline phases during the phase inversion[7,8].

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* It should be kept in mind that the cooling prior to freeze-fracturing may introduce artefacts. Thus, solutions which are isotropic at room temperature could well partly or totally transform to a lamellar system by cooling.

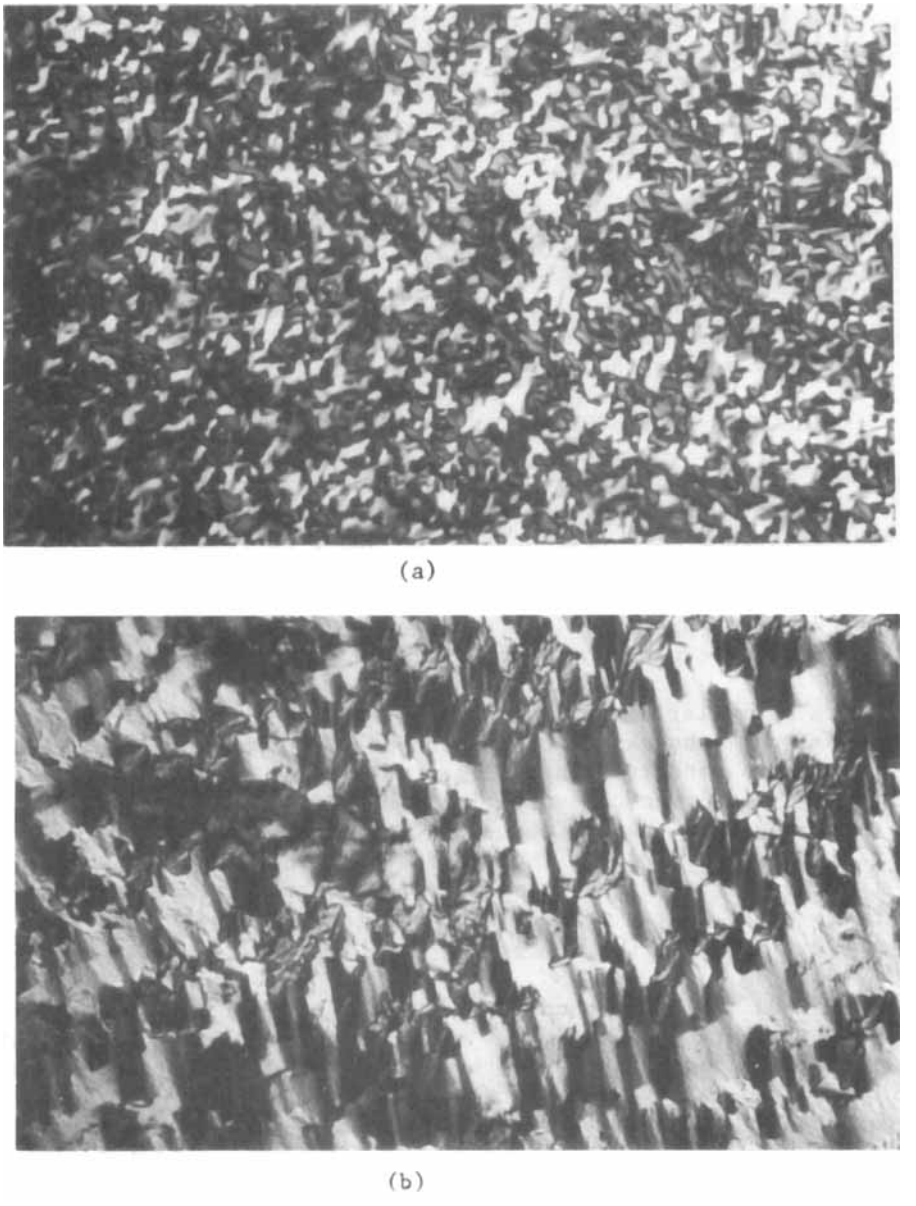
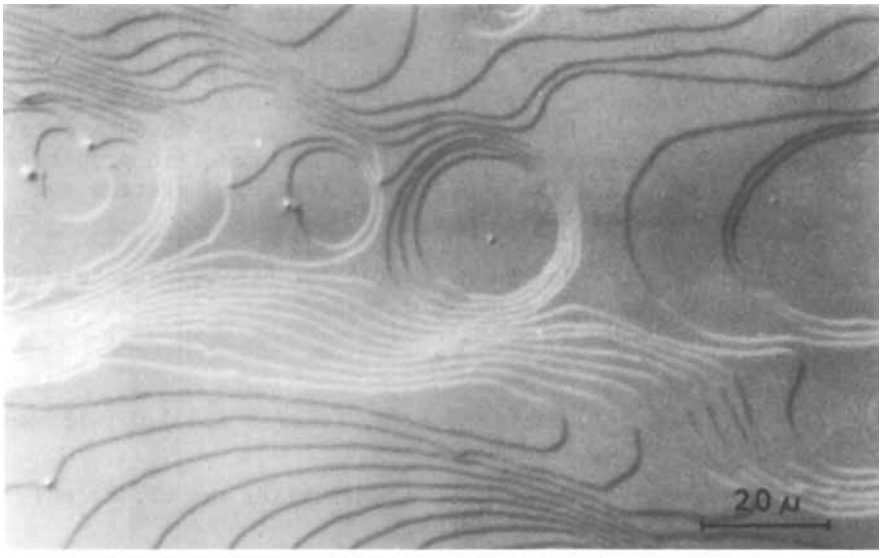
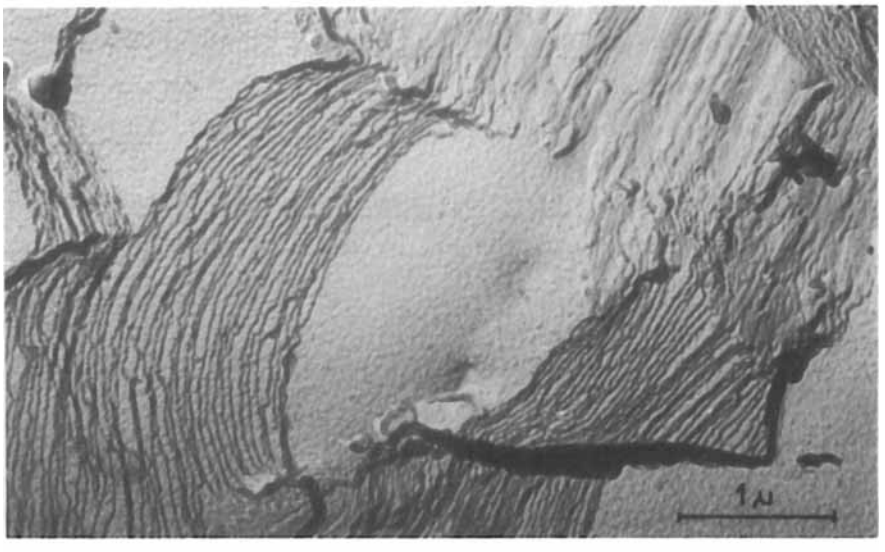


Figure 3 : Textures of quaternary systems observed between crossed polarizers (G = 260)



(a)



(b)

Figure 4 : Lamellar structures of quaternary systems.
(a) Interference contrast optical microscopy. The composition of the system is given in the text (point A, Fig.1).
(b) Electron microscopy after freeze-fracturing. The microphotograph corresponds to a system prepared from a graft copolymer containing 47 % PS in each macromolecule. The ratio of the copolymer mass to the total mass of the quaternary system is 0.17

As both block copolymers and classical micro-emulsions lead to the formation of lamellar structures, it is not surprising a priori to find similar structures in the present systems which can be considered as intermediate between the two preceding ones. However, these systems, of which a detailed study is in progress may exhibit some specific properties since they associate the fluidity of lyotropic systems and large dimensions of lamellae.

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REFERENCES

1. F. Candau, J. Boutillier, F. Tripier and J.C. Wittmann Polymer, 20, 1221 (1979).
2. F. Candau, J.M. Guenet, J. Boutillier and Cl. Picot, Polymer, 20, 1227 (1979).
3. S. Candau, J. Boutillier and F. Candau, Polymer, 20, 1237 (1979).
4. A. Skoulios, Adv. in Liq. Cryst., 1, 169 (1975).
5. A. Skoulios and G. Finaz, J. de Chim. Phys., 473 (1962)
6. A . Skoulios, G. Tsouladze et E. Franta, J. Pol. Sci. C, 4, 507 (1964).
7. S. Friberg, J. Am. Oil Chem. Soc., 48, 578 (1971).
8. J.W. Falco, R.D. Walker, Jr and D.O. Shah, Amer. Inst. Chem. Eng. J., 20, 510 (1974).