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Polymerization in Lyotropic Liquid Crystals. 1. Phase Behavior of Photo-Cross-Linkable Ethylene Oxide (PEO)–Dimethylsiloxane (PDMS) Triblock Copolymers PEO–PDMS–PEO in Aqueous Solution

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ABSTRACT: Binary phase diagrams of water and a linear ethylene oxide–dimethylsiloxane PEO–PDMS–PEO triblock copolymer ($\overline{DP}_n$ of PEO = 19; $\overline{DP}_n$ of PDMS = 16) and of a corresponding photo-cross-linkable PEO–PDMS–PEO triblock copolymer ($\overline{DP}_n$ of PEO = 16; $\overline{DP}_n$ of PDMS = 16) with cinnamate side groups located at the positions where the blocks had been joined are reported. Both systems form liquid–crystalline phases which were investigated by optical microscopy, differential scanning calorimetry, and small-angle X-ray scattering. Distinct changes in the lyotropic mesophase behavior of the amphiphilic triblock copolymer are observed when cinnamoyl moieties are introduced at the linkages between the hydrophilic and the hydrophobic parts of the triblock copolymer. The mesophases are destabilized with respect to temperature and concentration.

Introduction

Amphiphilic compounds capable of undergoing controlled polymerization or oligomerization for which low molar mass amphiphiles such as the esters of oligooxyethylene monoalkyl ethers with acrylic acid are examples have been described recently.[1,2] It has been shown that these monomers and the corresponding polymers display liquid-crystalline phases in aqueous solution. The most obvious effect observed comparing monomers with the corresponding polymers is an extension of the range of the liquid-crystalline state with respect to temperature and concentration. While most work was performed with either the monomer or the polymer considering their lyotropic behavior little work has been carried out to study the polymerization in situ of a mesophase. Polymerization in lyotropic mesophases appears to have been reported in the open literature first by Sadron.[3,4] He described the in-situ photopolymerization of a lyotropic liquid-crystalline system based on polystyrene–poly(ethylene oxide) block copolymer and acrylic acid. After the photopolymerization of the acrylic acid, heterogeneous gels with organized structures were obtained. Also Friberg and coworkers reported the polymerization in a lyotropic liquid crystal of sodium undecenoate and water. They observed a change of structure from hexagonal to lamellar during photopolymerization.[5]

Linear ethylene oxide–dimethylsiloxane PEO–PDMS–PEO triblock copolymers exhibit lyotropic liquid-crystalline phases in concentrated aqueous solution.[6] This paper describes the phase behavior of such a copolymer (I) and a functional copolymer PEO–PDMS–PEO–cinnamate (II) in aqueous medium. II contains two photoactive cinnamoyl moieties located between the hydrophilic PEO and the hydrophobic PDMS parts. We will focus on the influence of the photoactive moieties on the lyotropic mesophase behavior. The following paper in this issue describes the synthesis and the photo-cross-linking as well as the structure of the cross-linked mesophases.

Experimental Section

Materials. Synthesis and characterization of PEO–PDMS–PEO and PEO–PDMS–PEO–cinnamate triblock copolymers by hydrosilylation of α,ω-dihydropoly(dimethylsiloxane) with functional poly(ethylene oxide) will be described in the following paper in this issue.

Sample Preparation and Determination of Phase Diagrams. Freshly boiled, reagent-grade water produced by a Milli-Q filtration system was used to prepare stock samples. Mixtures of water and copolymer were prepared in polypropylene vessels. To obtain homogeneous samples, the mixtures were gently heated above the upper phase-separation temperature where the turbid mixtures exhibit a rather low viscosity and were vigorously shaken. The binary phase diagrams of the triblock copolymers I and II in water were investigated using polarizing microscopy, differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS).

Optical Microscopy. A small amount of the sample was deposited between a glass plate and cover slide sealed with epoxy resin. Observations were made between crossed polarizers with a Zeiss photomicroscope III equipped with a hot-stage unit of Linkam Scientific Instruments.

Differential Scanning Calorimetry. About 10 mg of the samples was weighed in an aluminum ampule shortly before the measurements were made. The ampules were hermetically sealed. DSC measurements were made with a Mettler DSC 30 calorimeter (TA 3000 system) using a heating rate of 5 K/min. Water and indium were used for the temperature and enthalpy calibration.

Small-Angle X-ray Scattering. A small amount of the sample was drawn into a fine-glass capillary tube (0.7-mm diameter). This was then hermetically sealed and allowed to equilibrate for at least another 24 h before measurements are made. X-ray data were obtained using a Kratky compact camera with proportional counter detection operated in continuous scan mode. Nickel-filtered Cu Kα radiation was used. The sample temperature was controlled to ±1 °C. The scattering curves were corrected for slit-smearing effects by a computational desmearing procedure.[7]

Results and Discussion

Phase Behavior of the PEO–PDMS–PEO (I)/Water System. The phase diagram of the triblock copolymer (I) (Figure 1) with water is typical for this type of amphiphilic PEO–PDMS–PEO triblock copolymers, exhibiting a miscibility gap at high temperature and a broad mesophase regime.[6]

The crystallization behavior at low temperatures is that of a eutectic system without formation of mixed crystals. The eutectic point is found at −22 ± 1 °C and about 75% by weight of the triblock copolymer. The region of the two-phase melt is located between the liquidus line and

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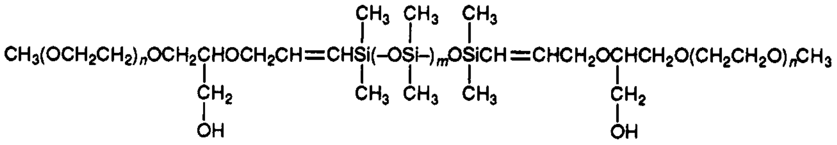
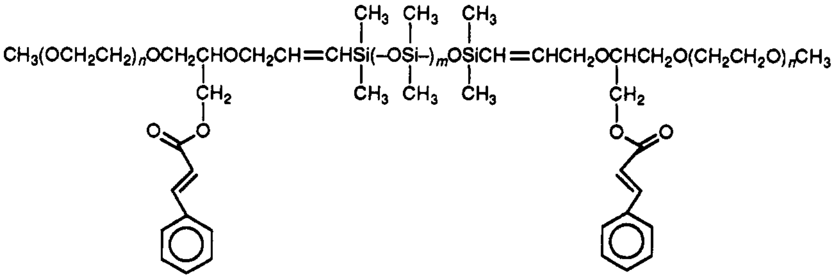


$CH_3(OCH_2CH_2)_nOCH_2CH(CH_2OH)OCH_2CH{=}CHSi(CH_3)_2(-OSi(CH_3)_2-)_mOSi(CH_3)_2CH{=}CHCH_2OCH(CH_2OH)CH_2O(CH_2CH_2O)_nCH_3$

I ($\bar{n}$ = 19, $\bar{m}$ = 16)



II ($\bar{n}$ = 16 $\bar{m}$ = 16)

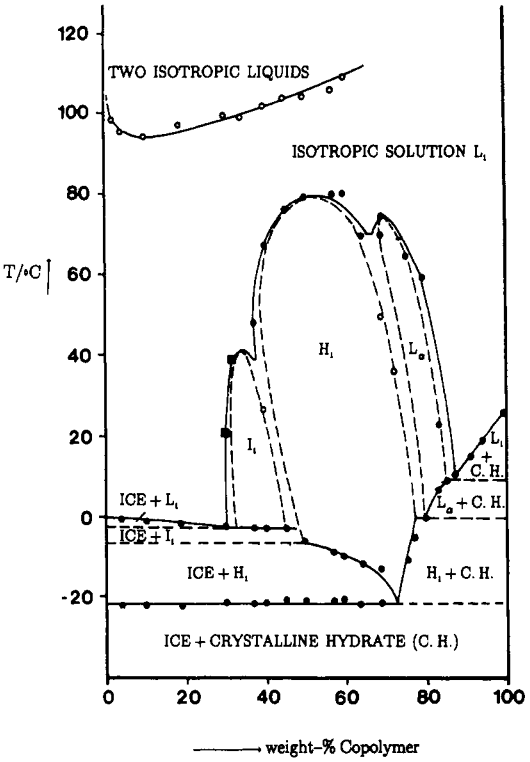


Figure 1. Binary phase diagram of the PEO-PDMS-PEO triblock copolymer (I)/water system. Methods of measurements: (○) optical microscope; (●) DSC and optical microscope with crossed polarizers; (■) SAXS.

the eutectic line, to the water-deficient side and to the water-rich side of the eutectic point. Ice coexists in the area on the left side of the eutectic point with the hexagonal phase H_1, the cubic phase I_1, and the isotropic micellar solution L_1 depending on the temperature. On the right side, hydrated copolymer coexists with the hexagonal phase H_1, the lamellar phase L_α, and the isotropic solution L_1.

All the transitions were located by DSC measurements. Figure 2 represents typical DSC curves as a function of the copolymer content in the aqueous samples. Upon addition of water, the DSC endotherms of the triblock copolymer change remarkably. The decrease of the DSC peak temperature and area related to the copolymer with increasing water content until its disappearance at about 75% copolymer is attributed to the formation of partially hydrated nonfreezing, nonmelting PEO segments.[8] Two new peaks in the temperature range −25 to 0 °C were observed with further increase of the water content. The low-temperature transition (−22 ± 1 °C) is attributed to the melting of the eutectic mixture of water and hydrated copolymer. The peak at higher temperature whose transition temperature varied with the water content is attributed to the melting of free water. These interpretations agree with those reported on PEO/water and PEO–PDMS/water mixtures in the literature.[8,9]

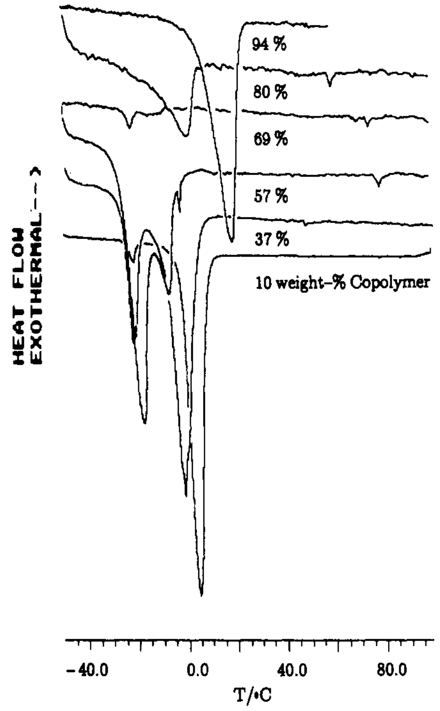


Figure 2. Typical DSC curves of the triblock copolymer (I)/water system as a function of the copolymer content.

In agreement with the polarizing microscopic investigations, we found further DSC peaks at higher temperatures for the concentration range from 37% to 85% of copolymer. These are attributed to the transitions of the liquid-crystalline mesophases (I_1, H_1, L_α) to the isotropic solution. The transitions are accompanied by very small endothermic enthalpy changes of 0.2–0.7 J/(g of sample) according to composition.

The phase diagram of the triblock copolymer (I)/water system exhibits three lyotropic mesophases. There are the cubic phase I_1, the hexagonal phase H_1, and the lamellar phase L_α. The optically anisotropic H_1 and L_α phases were identified by comparison of the observed textures under a polarizing microscope with textures described in the literature.[10–12] Two typical textures of the H_1 phase

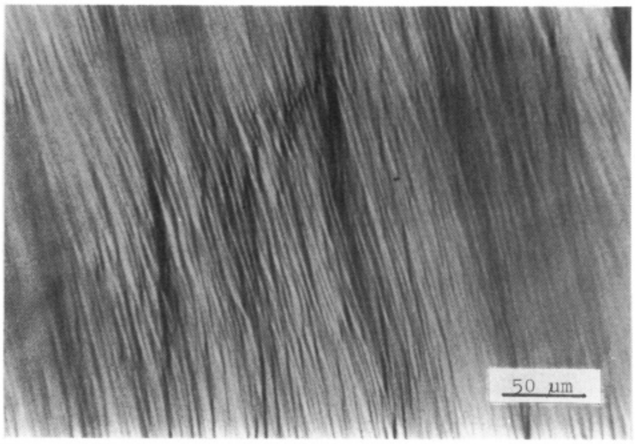


Figure 3. Typical texture with parallel striations of a hexagonal phase (crossed polarizers).

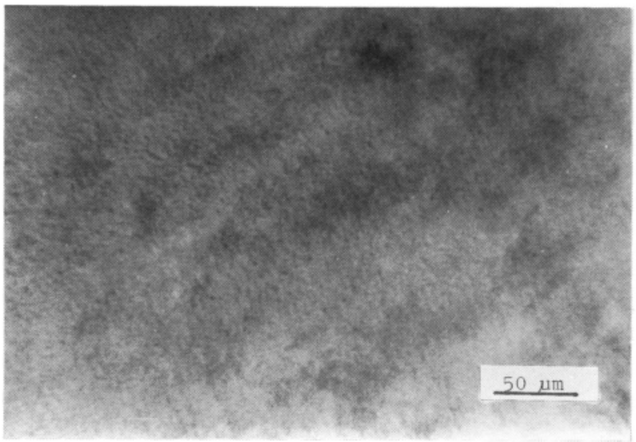


Figure 4. Typical "nongeometric" texture of a hexagonal phase (crossed polarizers).

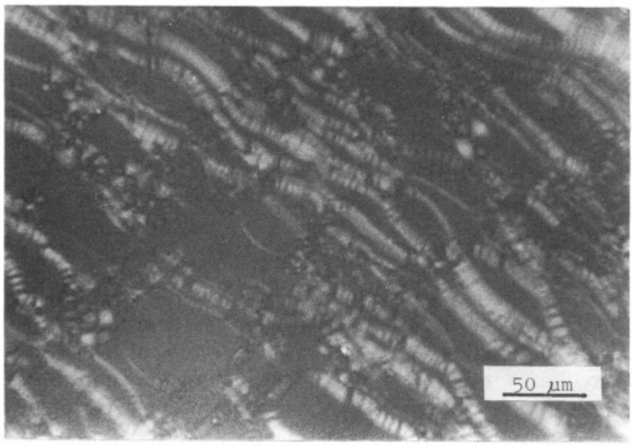


Figure 5. Oily streaks in a homeotropic region of a lamellar phase (crossed polarizers).

are shown in Figures 3 and 4.

The presence of parallel striations (Figure 3) could be ascribed to the defects of curvature of the cylindrical aggregates lying with their long axis parallel to the plane of the preparation.[13] Also the "nongeometric" texture (Figure 4) was observed for the H_1 phase. The most characteristic and commonly observed textures associated with the L_α phase are the oily streaks, appearing as birefringent bands of varying widths in a homeotropic field (Figure 5). In the homeotropic regions (black), the optical axis of the preparation is normal to the glass surface, while the oily streaks are connected with structural defects where lamellae may consist of bundles of line dislocations.[14,15]

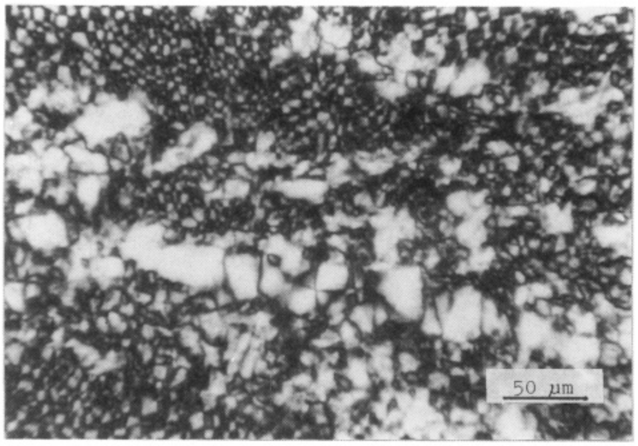


Figure 6. Different type of polygonal arrays in a lamellar phase (crossed polarizers).

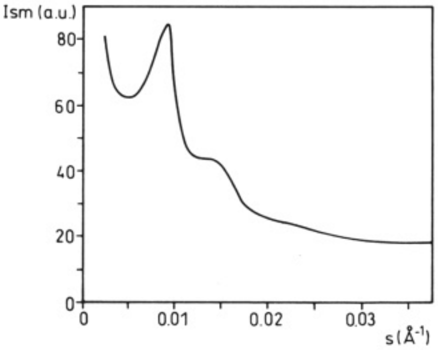


Figure 7. SAXS diagram of the cubic phase of the triblock copolymer (I)/water system (c = 36 wt % copolymer, T = 20 °C).

At high copolymer contents, it is frequently observed that the oily streaks transform spontaneously into polygonal arrays (Figure 6), which have been often described in the neat phase of lyotropic systems and were referred to as mosaic textures.[10] But, the SAXS investigations show that at least for our systems the textures of polygonal arrays belong to the lamellar phase.

The unequivocal identification of the mesophases requires X-ray investigation.[16] SAXS experiments usually supply X-ray patterns which contain two or three peaks corresponding to Bragg spacing in a ratio $1:1/\sqrt{3}:1/2$ typical of a hexagonal lattice or in a ratio 1:1/2:1/3 typical of a lamellar structure. Since the cubic phase (I_1) is optically isotropic, birefringent textures cannot be associated with it because of the cubic symmetry of the micellar arrangement. The existence of the cubic phase can, however, be identified by X-ray scattering experiments. Three orders of a reflection have been resolved in the diffraction experiment, and it was clear from the derived Bragg spacings, $1:1/\sqrt{2}:1/\sqrt{3}$, that the structure was cubic. Figures 7 and 8 show a comparison of the measured SAXS diagram and desmeared SAXS diagram for the cubic phase of the triblock copolymer (I)/water system at room temperature where $s^{-1} = 2 \sin(\theta/\lambda)$, θ is half the scattering angle, and λ is the X-ray wavelength.

The two-phase regions between the mesophases, or between the mesophases and the isotropic micellar solution, were very difficult to determine. The experiments did not supply a clear indication for such a feature. There may be very narrow two-phase ranges, and so, in order to follow equilibrium theory, these coexistence ranges were thus represented in the phase diagrams by dashed lines. In Figure 9, the spacings are plotted versus the concentrations of the triblock copolymer (I) in water.

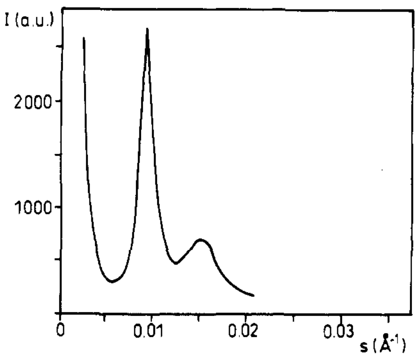


Figure 8. Desmeared SAXS diagramm of the triblock copolymer (I)/water system (c = 36 wt % copolymer, T = 20 °C).

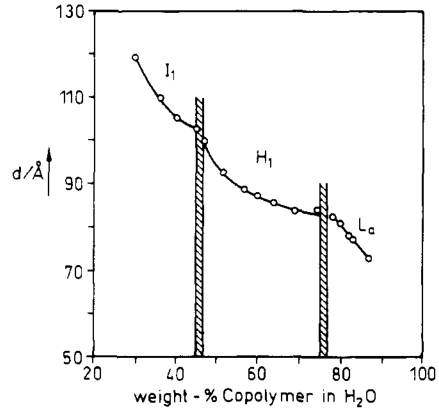


Figure 9. Bragg spacing values (d) versus the concentrations of the triblock copolymer (I) in water. I_1, cubic phase; H_1, hexagonal phase; L_α, lamellar phase. Hatched areas show the two-phase regions.

In analogy to other nonionic PEO-containing surfactants the amphiphilic triblock copolymer (I) shows a miscibility gap at higher temperatures. A lower critical consolute point was found at 94 °C at about 8% copolymer by weight. The temperature at which the separation of the isotropic homogeneous liquid into two isotropic liquids starts is recognized by clouding. This is explained by a partial dehydration of the ethylene oxide units when the temperature increases.[17]

Phase Behavior of the PEO-PDMS-PEO-Cinnamate (II)/Water System. The phase diagram of the functional triblock copolymer (II)/water system differs considerably from the triblock copolymer (I)/water system because the hydroxy groups of the copolymer I are replaced by cinnamoyl groups (Figure 10). In addition, the distribution of molecular weight of the copolymer I changed remarkably after the chemical modification. Thus, the corresponding copolymer II has not exactly the same average chain lengths. Details will be discussed in the following paper. We focus on the influence of the introduction of the cinnamoyl moieties into the copolymer on the lyotropic mesophase behavior, and so the crystallization behavior at low temperatures is disregarded.

Only two types of mesophases were identified as a hexagonal phase and a lamellar phase by their birefringent texture patterns. The thermal stabilities of the mesophases are decreased in comparison to the system composed of copolymer I and water. One possible explanation for the destabilization of the mesophases is to assume a disturbed balance between the hydrophilic and hydrophobic parts of the triblock copolymer. The introduction of cinnamoyl moieties into the copolymer causes an augmentation of the hydrophobic part of the amphiphilic copolymer and, therefore, might be responsible for the disturbance of hydrophilic–hydrophobic balance. However, the association behavior of amphiphilic block copolymers is changed strongly as well. The formation of a hexagonal and a lamellar phase seems to be favored. Furthermore, this results in a shift of the miscibility gap toward lower temperature in comparison to the triblock copolymer (I). Analogous phenomena for oligooxyethylene alkyl ether/water systems have been discussed in the literature.[18,19]

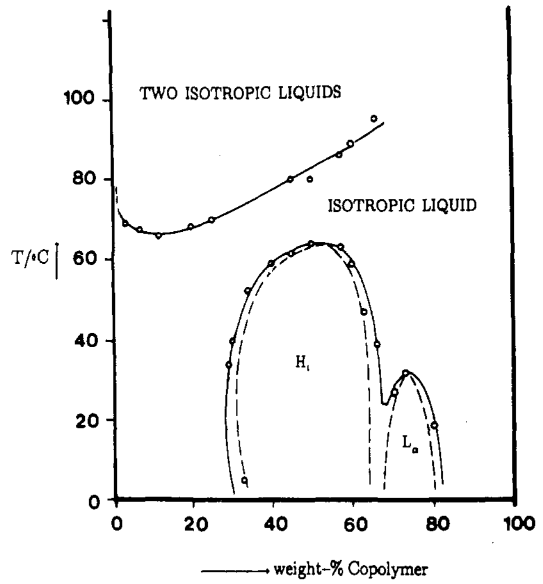


Figure 10. Binary phase diagram of the photo-cross-linkable PEO–PDMS–PEO–cinnamate triblock copolymer (II)/water system.

Conclusions

The phase diagrams of PEO–PDMS–PEO triblock copolymer (I) and its corresponding photo-cross-linkable PEO–PDMS–PEO–cinnamate triblock copolymer (II) with water depend strongly on the structure of the copolymer. Optical microscopic, X-ray, and DSC investigations reported in the present study give clear evidence of the existence of liquid-crystalline phases in both systems. Depending on its compositions, the triblock copolymer (I)/water system may form cubic I_1, hexagonal H_1, and lamellar L_α phases. Going from the triblock copolymer (I) to the corresponding functional triblock copolymer (II), the cubic phase vanishes and the thermal stability of the remaining H_1 and L_α phases is reduced; i.e., the introduction of the cinnamoyl moieties to the copolymer causes a destabilization of the liquid-crystalline phases. However, a change of the phase sequence is never observed. The present phase diagrams of the triblock copolymer and its corresponding photo-cross-linkable triblock copolymer offer a good base for the further investigation of the photopolymerization behavior in the mesophases.

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