(9) Jontê, J. M.; Dunsing, R.; Kricheldorf, H. R. *J. Macromol. Sci.—Chem.* **1986**, *23*, 495.
(10) Kricheldorf, H. R.; Mang, T.; Jontê, J. M. *Macromolecules* **1984**, *17*, 2173.
(11) Kricheldorf, H. R.; Mang, T.; Jontê, J. M. *Makromol. Chem.* **1985**, *186*, 955.
(12) Schindler, A.; Hibionada, Y. M.; Pitt, C. G. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 319.
(13) Ito, K.; Yamashita, Y. *Macromolecules* **1978**, *11*, 68.
(14) Deffieux, A.; Boileau, S. *Macromolecules* **1976**, *9*, 369.
(15) Kricheldorf, H. R.; Berl, M. *Macromolecules*, in press (part 9 of this series).

Polymerization in Nonaqueous Lyotropic Liquid Crystals with a Polymerizable Solvent

Stig E. Friberg* and Chang Sup Wohn

Chemistry Department, University of Missouri—Rolla, Rolla, Missouri 65401

Frances E. Lockwood

Technology Division, Pennzoil Products, Inc., The Woodlands, Texas 77387.
Received October 31, 1986

ABSTRACT: Lamellar liquid crystals of lecithin and 2-hydroxyethyl methacrylate (HEMA) were polymerized by using UV radiation. Optical microscopy, infrared spectroscopy, and small-angle X-ray diffraction were used to compare the structure prior to and after polymerization. The lamellar structure was retained after polymerization with increased interlayer spacing.

Introduction

The properties of lyotropic liquid crystals based on surfactants have been extensively investigated[1-3] following the pioneering contributions by Ekwall.[4] In parallel with these investigations, a great volume of research has been reported on systems with lecithin and water,[5] an expected consequence of the importance of this combination for the structure of biological membranes.[6] Recently, the structure[6-10] as well as the dynamics[11] have been clarified of nonaqueous liquid crystals with lecithin as the amphiphile and various polar organic compounds as the solvent. These nonaqueous liquid crystals also have an importance for biological systems.[12]

The introduction of polymers into lamellar liquid crystals is a fascinating phenomenon of pronounced importance in understanding biological structures in which polysaccharides and proteins interact with the bimolecular organization of lecithin in the biomembrane.[13-17] Attempts to bring polymers into lamellar liquid crystals have met with limited succes[18] due to the space demands from the conformational freedom requirements of a high molecular weight polymer and the limited dimensions of a lamellar liquid crystal. Poly(ethylene glycol) of medium molecular weight has been included in lamellar liquid crystals.[19-22] Poly(ethylene glycol) of small molecular weight has been used as the sole solvent for lamellar liquid crystals with lecithin,[23] and polyacrylic acid of low molecular weight has been polymerized while retaining a thermodynamically stable lamellar liquid-crystalline structure.[24] Polymeric substances per se form liquid crystals[25-27] and the phase behavior of those with lyotropic side-chain polymers in aqueous solutions has been investigated.[28]

With this background, it appeared reasonable to approach the problem from the opposite angle to the earlier attempts of introducing a polymer into a liquid-crystalline phase based on water as the solvent. We found an approach using a polymerizable polar liquid as the solvent, a logical step in this area against the foundation of known structures of nonaqueous liquid crystals.[6-11] The present publication describes the polymerization of 2-(hydroxyethyl methacrylate) (HEMA) in a lamellar liquid crystal with lecithin.

Experimental Section

Materials. The lecithin, L-α-phosphatidylcholine, was obtained from Sigma Chemical Co., No. P-3644, and hydroxyethyl methacrylate (HEMA) was supplied by Scientific Polymer Product. Disposable chromatographic columns DMR-4 from Scientific Polymer Product were used to remove the inhibitor and any polymer residue.

Determination of the Lamellar Liquid-Crystalline Phase. HEMA (30 wt %) was added to lecithin (70 wt %) by using small glass vials with screw tops. The sample was matured at 35 °C for at least 24 h by using a Blue M transite oven, and a vortex vibromixer was used every 2 h to facilitate vigorous mixing. Finally, the sample was left to equilibrate overnight at room temperature. The lamellar liquid crystals were confirmed by their optical pattern in polarized light in an optical microscope.

Polymerization. The polymerization was accomplished by UV radiation from an Ace Glass, 450-W quartz mercury arc lamp source. One hour was required for polymerization in the absence of initiator.

To remove the exothermic heat caused by polymerization, air was circulated through the reaction chamber covered with aluminum foil to maximize refraction of UV radiation.

Optical Microscopy. A small amount of the sample was deposited between a glass plate and cover slide to form a thin film. Polymerization was performed directly on this sample to compare the structure prior to and after polymerization. An Olympus microscope with crossed polarizers was used.

X-ray Diffraction. A small amount of equilibrated sample was drawn into a fine glass capillary tube, and polymerization was carried out in the tube (0.7-mm diameter). Wide-angle X-ray photographs were taken with GE Model 11, Ni-filtered Cu Kα radiation, with Debye-Scherrer camera.

Infrared Spectroscopy. A small amount of equilibrated sample was deposited between sodium chloride mediums to form a film of between 0.01- and 0.02-mm thickness. Polymerization was made in the sodium chloride cell and the spectra were recorded on a Perkin-Elmer 521 allgrating IR spectrophotometer.

Results

The observed optical microscopic textures of lyotropic mesophases (Figure 1) formed by lecithin and HEMA, prior to an after polymerization, were characteristic of a lamellar liquid crystal. The typical "oily streaks" are present in both photos and the overall pattern is strikingly similar.

0024-9297/87/2220-2057$01.50/0

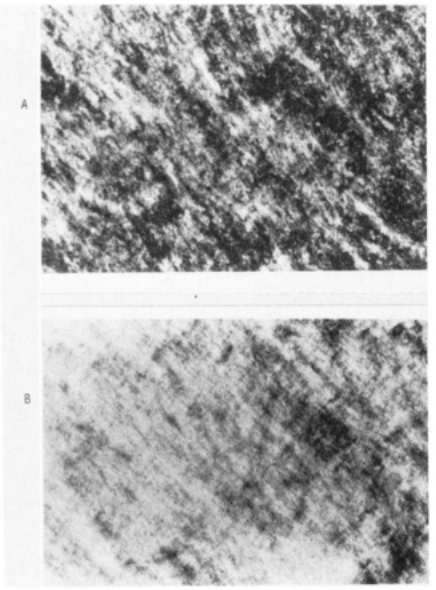

Figure 1. Optical microscopy patterns in polarized light before (A) and after (B) polymerization; both are typical of a lamellar liquid crystal.

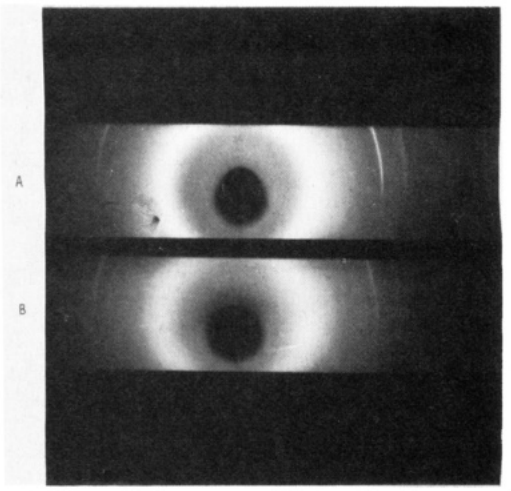

Figure 2. X-ray diffractogram diffuse reflection at 4.5 Å characteristic of a liquid crystal both before (A) and after (B) polymerization. The sharp lines are from the interlayer spacing.

The X-ray diffractograms (Figure 2) showed a wide diffuse reflection with a position corresponding to a spacing 4.5 Å for both samples, which showed the liquid state of the hydrocarbon chains in an amphiphilic liquid crystal.[29]

The interlayer spacing was 38.6 Å before polymerization and 44.6 Å after polymerization. For both cases the low-angle X-ray diffraction patterns gave reflections which enabled the structure to be identified as lamellar.[29]

The IR spectrum, prior to polymerization, of the lamellar liquid crystal (Figure 3) showed the characteristic absorbance of olefinic carbon–carbon double-bond stretching at 1600–1650 cm^{-1} and out of plane bending of terminal vinyl groups at 950–1000 cm^{-1} (Figure 3). After polymerization, those absorbances disappeared and the spectra showed no carbon–carbon double bond (Figure 3).

Discussion

The results revealed facts of importance both for nonaqueous lyotropic liquid crystals and for polymerization in lamellar liquid crystals.

The results show that it is possible to obtain a lamellar liquid crystal from an amphiphile and a polymerizable

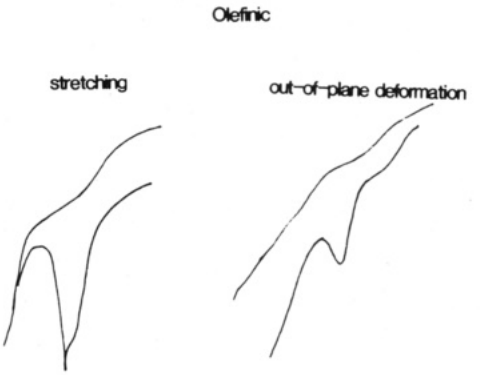

Figure 3. IR spectrum before polymerization showing the absorbancies typical of a terminal ethylene group. After polymerization the absorbance was removed.

solvent and to polymerize this polar solvent while retaining the lamellar structure.

The combination of the present small-angle X-ray diffraction results and those from earlier studies gave information on the location of the HEMA molecules within the lamellar structure. For identical weight fraction of water, ethylene glycol, and HEMA, the interlayer spacings are 52.5, 44.0, and 38.6 Å.[8] These values are for equal weight ratios; corrections for different densities of the polar solvent give a new set of values at 52.4, 44.5, and 39.6 Å, retaining the reduction in interlayer spacing.

The reduction in interlayer spacing is due to a combination of disorder of the lecithin hydrocarbon chains *and* an enhanced penetration of the solvent molecules from the polar group layers into the space between the methylene groups of the lecithin hydrocarbon chains. The first factor is a consequence of the latter one; the penetration of a small solvent molecule causes enhanced disorder.

The influence of disorder may be estimated by using Seelig's expression[30]

$$\langle L \rangle = 1.25n/2 - \sum_{i=1}^{n} S_{cd}{}^{i}$$

in which $\langle L \rangle$ is the effective length of the hydrocarbon chain, n is the number of atoms in the chain, and $S_{cd}{}^{i}$ is the deuterium order parameter.

The correct relation between the deuterium order parameter $S_{cd}{}^{i}$ for the ith carbon and the segmental order parameter $S_{mol}{}^{(i)}$ is[30]

$$S_{mol}{}^{(i)} = -(1/8)(18S_{cd}{}^{i} - {}^{6}P_{90} + 1)$$

in which P_{90} is the probability for the segment being oriented at the angle 90°.

For the present purpose the expression for axially symmetric motion characterized by one order parameter[31] is sufficient

$$S_{mol}{}^{(i)} = -2S_{cd}{}^{i}$$

Hence, the effective chain length becomes

$$\langle L \rangle = 0.625(n + \sum_{i=1}^{n} S_{mol}{}^{i})$$

or with an averaged order parameter S_{av}

$$\langle L \rangle = 0.625n(1 + S_{av})$$

Assuming no penetration the thickness of a single layer of lecithin becomes

$$L = 13.85 \text{ Å}$$

After removal of 2 Å for the polar group and assuming $n = 18$, an averaged order parameter

$$S_{av} = 0.05$$

This value is unrealistically small and identical with the value obtained if the polar group of lecithin is included in the value on n.

The corresponding value for water[7] is at the level of 0.4, which is greater than commonly found for liquid crystals based on ionic surfactants as the amphiphile[32] but at the level of the common L_α phase of lecithin.[33]

The pronounced difference in order parameter between the aqueous and the HEMA system and the extremely low order parameter values in the latter support the assumption of the reduction of interlayer spacing being due both to a significant penetration of HEMA into amphiphilic layer and enhanced disorder as a consequence.

The conditions after polymerization are illustrated by the facts that the wide-angle X-ray diffraction pattern retained the diffuse reflection at 4.5 Å and that the interlayer distance increased to 44.6 Å. The first results show that the hydrocarbon chains remained in the disordered state of a liquid state after the polymerization, e.g., the polymerization did not lead to crystallization.

After polymerization a calculation of the order parameter gives the value $S_{av} = 0.11$. This increase is due to a reduction of penetration by the HEMA and, hence, to an increase of order. The value is still lower than the level of 0.2 found for a lamellar phase of ionic surfactants. Assuming a ratio between S_{mol}^{i} similar to those found in the ionic surfactants the "plateau" values becomes 0.15.

Hence, a reasonable conclusion is that even after polymerization the poly(HEMA) disorders the lecithin layers, probably by penetration. Such a penetration would at first appear less probable due to the incompatibility between the geometric dimensions of a lamellar liquid crystal and the space requirements to sustain the conformational entropy of the polymer,[34] but the recent results by Cabane et al.[22] support the notion that the polymer may enjoy a high entropy content by partial penetration into the amphiphilic parts of the lamellar structure. The large translational diffusion coefficient within each layer of the liquid crystal[35,36] may be the reason for this compatibility.

Acknowledgment. This research was supported by a grant from Office of Naval Research, No. N00014-84-K0509.

Registry No. HEMA, 868-77-9; PHEMA, 25249-16-5.

References and Notes

(1) Tiddy, G. J. T. *Phys. Rep.* **1980**, *57*, 1.
(2) Lindman, B.; Wennerström, H. *Phys. Rep.* **1979**, *52*, 1.
(3) Lindman, B.; Wennerström, H. *Topics in Chemistry No. 87: Micelles*; Springer-Verlag: New York, 1980; p 1.
(4) Ekwall, P. In *Advances in Liquid Crystals*; Brown, G. H., Ed.; Academic: New York, 1975; p 1.
(5) Luzzati, V. In *Biological Membranes*; Chapman, D., Ed.; Academic: London, 1968.
(6) Singer, S. I.; Nicholson, G. L. *Science (Washington, D.C.)* **1962**, *175*, 720.
(7) Larsen, D. W.; Friberg, S. E.; Christenson, H. *J. Am. Chem. Soc.* **1980**, *102*, 6565.
(8) El-Nokaly, M. A.; Ford, L. D.; Friberg, S. E.; Larsen, D. W. *J. Colloid Interface Sci.* **1981**, *84*, 228.
(9) Ganzuo, L.; El-Nokaly, M. A.; Friberg, S. E. *Mol. Cryst. Liq. Cryst.* **1982**, *72*, 183.
(10) Evans, D. F.; Kaler, E. W.; Benton, W. J. *J. Phys. Chem.* **1983**, *87*, 533.
(11) Larsen, D. W.; Friberg, S. E.; Christenson, H. *J. Am. Chem. Soc.* **1980**, *102*, 6565.
(12) McIntosh, T. J.; McDaniel, R. V.; Simon, S. A. *Biochim. Biophys. Acta* **1983**, *731*, 97.
(13) Bermal, J. D. *Discuss. Faraday Soc.* **1958**, *25*, 7.
(14) Fendler, J. H. In *Membrane Miemtic Chemistry*; Wiley-Interscience: New York, 1982.
(15) Naegels, D.; Ringsdorf, H. *Midl. Macromol. Monogr.* **1977**, *3*, 79.
(16) Hoffman, D. S. In *Polymers in Medicine and Surgery*; Kronenthal, R. L., Oser, Z., Martin, E., Eds.; Plenum: New York, 1974; p 33.
(17) Ratner, B. D.; Hoffman, A. S. *ACS Symp. Ser.* **1976**, *No. 31*.
(18) Rand, P. *ACS Symp. Ser.* **1980**, *No. 172*.
(19) Ballet, F.; Leong, Y. S.; Wittmann, J. C.; Candau, F. *Mol. Cryst. Liq. Cryst.* **1981**, *64*, 305.
(20) Candau, F.; Ballet, F.; Debeauvais, F.; Wittmann, J. C. *J. Colloid Interface Sci.* **1982**, *87*, 356.
(21) Candau, F.; Wittmann, J. C. *Mol. Cryst. Liq. Cryst.* **1980**, *56*, 171.
(22) Kekicheff, P.; Cabane, B.; Rawiso, M. *J. Colloid Interface Sci.* **1984**, *102*, 51.
(23) El-Nokaly, M. A.; Friberg, S. E.; Larsen, D. W. *J. Colloid Interface Sci.* **1984**, *98*, 274.
(24) Friberg, S. E.; Wohn, C. S., unpublished results.
(25) Finkelmann, H.; Day, D.; Makromol. *Chem.* **1979**, *180*, 2269.
(26) *Liquid Crystalline Order in Polymers*: Blumstein, A., Ed.; Academic: New York, 1978.
(27) Finkelmann, H.; Rehage, G. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1984; pp 100–149.
(28) Finkelmann, H.; Lühmann, B.; Rehage, G. *Colloid Polym. Sci.* **1982**, *260*, 56.
(29) Fontell, K. In *Liquid Crystals and Plastic Crystals*; Gray, G. W., Winsor, P. A., Eds.; Ellis Harwood: Chichester, 1974; Vol. 2, p 80.
(30) Schindler, H.; Seelig, J. *Biochemistry* **1975**, *14*, 2283.
(31) Seelig, J.; Niederberger, W. *J. Am. Chem. Soc.* **1974**, *96*, 2069.
(32) Persson, N.-O.; Fontell, K.; Lindman, B.; Tiddy, G. J. T. *J. Colloid Interface Sci.* **1975**, *53*, 461.
(33) Charvolin, J. In *Lyotropic Liquid Crystals*; Friberg, S. E., Ed.; ACS Advances in Chemistry Series No. 152; American Chemical Society: Washington, DC, 1976; Chapter 7.
(34) Napper, D. H. In *Polymeric Stabilization of Colloidal Dispersions*; Ottewill, R. H., Rowell, R. L., Eds.; Academic: New York, 1983.
(35) Fahey, P. F.; Webb, W. W. *Biochemistry* **1978**, *17*, 3046.
(36) Vaz, W. L. C.; Clegg, R. M.; Hallmann, D. *Biochemistry* **1985**, *24*, 781.