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Cast Multibilayer Films from Polymerizable Lipids[†]

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ABSTRACT: Polymeric cast multibilayer films were prepared from a variety of polymerizable lipids according to two different procedures. One of these procedures is to polymerize the vesicle suspension first and then cast the film. The second procedure is to cast a film from a monomeric aqueous dispersion and then polymerize the cast film after it has been dried. The structure of these films was determined by different methods. Films from dioctadecyldimethylammonium acrylate were investigated in more detail. In films prepared according to the second procedure the lipids were oriented in multibilayer structures to a much higher degree than in films prepared from polymerized vesicles as wide-angle X-ray scattering revealed. Also, films that were polymerized after casting did not swell but remained stable in electrolyte solution. These films may thus be suitable for use in reverse-osmosis membranes. Their suitability for gas separation membranes was also tested, and the gas permeation was found to be dependent only on the molecular weight of the gas.

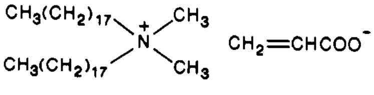
Ordered Multilayer Films

To prepare highly ordered multilayer films from amphiphiles using the Langmuir–Blodgett technique,[1,2] one usually starts from monolayers at the gas–water interface. With the help of this method highly ordered thin films can be obtained; however, the application of the Langmuir–Blodgett technique is not only limited to small film sizes. There is also a need for extremely clean water, amphiphiles, and substrate in order to get reproducible homogeneous multilayers.[3,4] Even under these perfect preconditions not all compounds can be transferred onto a substrate without a change of the ordered structure. In addition, the construction of multilayer films of larger thickness (several micrometers) is almost impossible.

To prepare ordered multilayer films a much simpler technique has recently been developed.[5,6] By this method an aqueous dispersion of amphiphiles is cast onto a substrate and the water is allowed to evaporate slowly. The resulting self-supporting films of several micrometers thickness have a multibilayer structure as was detected by DSC and X-ray scattering.[5–7]

One problem that occurs in connection with these films is that they usually dissolve again in the presence of water, just as conventional Langmuir–Blodgett multilayers do. Thus several attempts to make these films insoluble in water already have been made. These attempts include immobilization through ^{60}Co γ-irradiation[8] and immobilization as multilayered polymer films.[9] In addition, immobilization can be achieved via the salt formation of vesicles with polyelectrolytes and casting of the polyion complexes thus obtained from chloroform solution.[10] To increase the stability of the cast films poly(vinyl alcohol) often was added,[8,9] and films from polymerized aqueous lipid dispersions were also cast.[11]

In this paper cast multibilayer films from polymerizable lipids are described. The compounds investigated are summarized in Table I. Cast films from dioctadecyldimethylammonium acrylate (DODAA, 1) were investigated in more detail. In this ammonium salt the polymerizable unit is bound to the hydrophilic head group via ionic forces. Liposomes of this type of compound were reported as "liposomes in a net" or "polymer encased vesicles".[12,13] In particular, Regen and co-workers[13] investigated vesicle formation and polymerization of dioctadecyldimethylammonium methacrylate.



DODAA (1)

In most experiments cast films were prepared from monomeric aqueous dispersions and were polymerized after casting. For comparison, cast films from vesicles polymerized before casting were also investigated. To determine the structure of the films thus obtained X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and X-ray scattering were used. Attempts to determine the gas permeation properties of these cast films and their ion conductivity in electrolyte solutions were also made.

Experimental Section

Materials. Dioctadecyldimethylammonium acrylate (DODAA, 1) was prepared by ion exchange from dioctadecyldimethylammonium bromide (DODAB): 10 g (140 mmol) of acrylic acid were neutralized with 140 mL of 1 M NaOH. The resulting sodium acrylate solution was passed through a column containing 50 g of an anion-exchange resin (Amberlyst IRA 400, Cl$^-$ form) to preload the resin with the counterion acrylate. The column was washed first with water and then with methanol. DODAB (2 g, 3.2 mmol) was dissolved in 120 mL of methanol and passed through the column. Methanol was evaporated at reduced pressure, and the crude product was purified by recrystallization from 40 mL of acetone (yield: 1.6 g, 2.6 mmol, mp 55 °C). The degree of conversion to the acrylate was checked by ^{1}H NMR spectroscopy and was more than 90%.

Compound 2 was kindly provided by B. Schlarb (University of Mainz), and compound 3 was from R. Ebelhäuser (Max Planck Institut für Polymerforschung, Mainz). T. Fahmy (Max Planck Institut für Polymerforschung, Mainz) prepared compound 4, and compound 5 was prepared according to published procedures.[14]

Methods. Casting of the Multibilayer Films. Aqueous dispersions of DODAA and the other compounds were prepared by ultrasonication of 50–100 mg of lipid in 2 mL of water with a probe type sonicator (Branson B 15 sonifier, 2-min sonication time, output power 40 W). The resulting solutions, which were slightly opaque, were cast either directly on Fluoropore membranes (Sumitomo Electric Co., Japan, diameter 50 mm, pore size 0.10 μm) or were first polymerized by UV irradiation from a high-pressure mercury lamp (200 W, 4-h irradiation time under N_2 atmosphere). After casting, the water was allowed to evaporate at room temperature (2–3 days at 20–25 °C). After that, the films were dried under vacuum for 1–2 days. Part of the monomeric films were then polymerized by UV irradiation (4–6 h, depending on the thickness of the films). The degree of conversion to the polymer was confirmed by ^{1}H NMR spectroscopy: no vinyl

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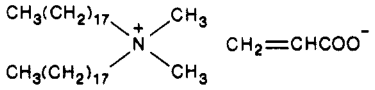
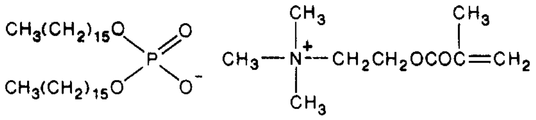
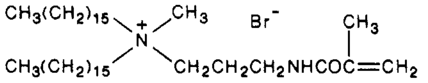
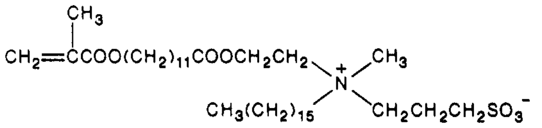
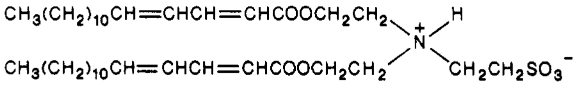
Table I
Compounds Investigated for the Formation of Cast Multibilayer Films

compd	formula	formation of cast films	ordered multibilayer structure shown by
1		yes	DSC, WAXS
2		yes	DSC
3		yes	DSC
4		no	
5		yes	DSC, WAXS

protons could be detected after the irradiation.

Characterization of the Cast Films. To characterize the cast films DSC measurements, X-ray photoelectron spectroscopy (XPS), X-ray diffraction, scanning electron microscopy, and permeability measurements were carried out.

The *phase transition* temperatures of the cast films and the aqueous dispersions were investigated by using Daini-Seikosha SSC/560 DSC equipment (heating rate 2 °C/min). To get reproducible peak shapes the aqueous dispersions were first cooled to −40 °C and were then recorded from that starting temperature. In contrast to this, the cast films could be measured starting from 0 °C.

The *surface composition* of the films was investigated by XPS. The XPS spectra were obtained on a ESCA 750 photoelectron spectrometer (Shimadzu Co., Ltd), which was operated at 8-kV acceleration voltage. The charging shift was referred to the C_{1s} line emitted from neutral hydrocarbon.

Wide-angle X-ray diffraction patterns of the cast multibilayer films were obtained by using Rigaku X-ray generator RU-200 and a toroidal focusing camera. The X-ray beams were generated with Cu Kα radiation and then filtered by nickel foil. The X-ray diffraction photographs were taken from films of about 100-μm thickness with the X-ray beam parallel to the film surface.

To study the *morphology* of the cast films, scanning electron microscopy was used. The cast films were fractured in liquid nitrogen and sputtered with gold, and the fracture surface was observed with scanning electron microscope S-430 from Hitachi Co. Ltd. (Japan).

The *stability of the cast films in aqueous environment* was checked by placing the cast films in a Teflon chamber to separate two aqueous compartments from each other and to measure the dc conductance of the film as a function of time.

The *gas permeation properties* were investigated according to the procedure of Barrer and Skirrow.[15] The films cast on Fluoropore membranes were placed in a steel cell. Oxygen, nitrogen, methane, and helium were used as permeating gases.

Results and Discussion

Films were cast from a variety of different polymerizable lipids on Fluoropore membranes. The structures of the compounds and the results of the experiments are summarized in Table I. Cast films could be obtained from the polymerizable lipids 1, 2, 3, and 5. Compound 4 could not be dispersed in water at concentrations high enough to form films.

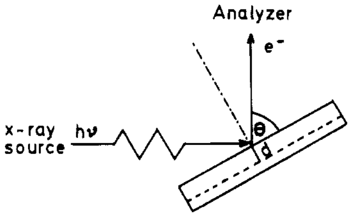


Figure 1. Schematic drawing of the relationship between the incident X-ray beam and the sampling depth, d, of the photoelectrons emitted at takeoff angle θ in the XPS measurements.

The multibilayer structure of the films from 1, 2, 3, and 5 was shown by DSC measurements. The most stable films were obtained from compound 1. Thus this lipid was chosen for a more detailed investigation.

The polymerized DODAA multibilayer films were prepared according to two different procedures. In the first procedure the aqueous dispersion was polymerized by UV irradiation and then cast on Fluoropore membranes. In the second procedure the films were cast from the monomeric aqueous dispersion of 1, and the dry films were then polymerized by UV irradiation. All cast films, the monomeric as well as the polymerized ones, were slightly turbid. However, the monomeric cast films were quite brittle, whereas the polymeric films, prepared according to both procedures, were much more stable and could be handled easily.

Structure of the Cast Films. The structure of the air-facing surface of the cast film was analyzed by X-ray photoelectron spectroscopy. To get some information about the distribution of elements from the surface into the bulk, the takeoff angle between the sample and the spectrometer was varied.[16] Figure 1 shows the relationship between the incident X-ray beam and the photoelectrons emitted. θ is the takeoff angle of the emitted photoelectrons, and d is the sampling depth, which is given by the relation[17]

$$d = 3\lambda_e \sin\theta \qquad (1)$$

where λ_e is the mean free path of the emitted photoelec-

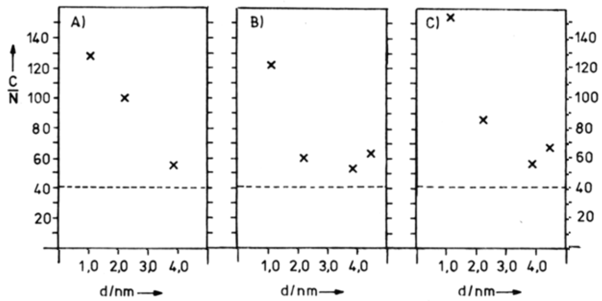


Figure 2. Results of the XPS measurements. Variation of the ratio of carbon over nitrogen (C/N) with sampling depth d on the air-facing surface of cast films from compound **1**. The dashed line indicates the ratio C/N for the lipid in the bulk phase: (A) results of measurements taken from a monomeric cast film; (B) results of a cast film polymerized after casting; (C) results of a film cast from polymerized vesicles.

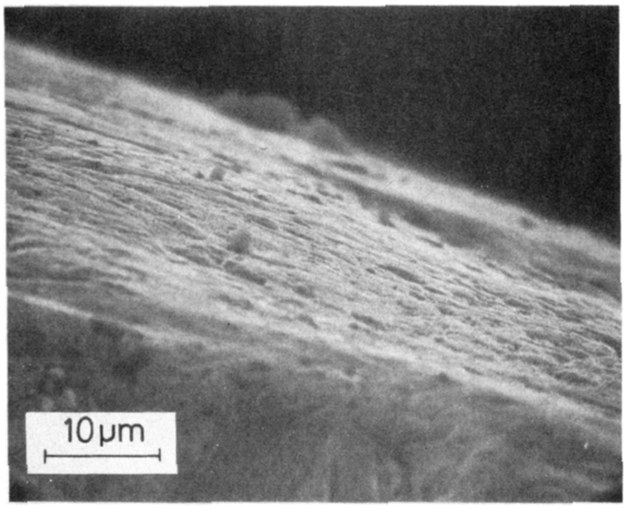


Figure 3. Scanning electron micrograph of the fractured surface of a DODAA-cast film polymerized after casting.

trons in the film (λ_e = 1.5 nm at 8-kV acceleration voltage).[18] The signal resulting from the surface increases as the takeoff angle decreases.

The ratios of the XPS signals from C_{1s} and N_{1s}, which originate from the hydrophobic hydrocarbon tail and the hydrophilic head group, were calculated from the XPS spectra taken at different takeoff angles (θ = 90°, 60°, 30°, and 15°). The sampling depths corresponding to these takeoff angles were calculated according to eq 1; the ratios C/N were plotted as a function of the sampling depth (see Figure 2). In all three plots (A, B, and C) the ratio C/N increases as the sampling depth decreases. However, as the sampling depth for at least θ = 15° (d = 1.6 nm) is less than the thickness of one monolayer, the results shown in Figure 2 give evidence that the cast films have an ordered surface with an upper monolayer which is oriented with the fatty acid chains toward the surface. This is comparable to the smectic layer found at the surface of free-standing nematic liquid crystalline films.[19]

Scanning electron microscopy provided further evidence for a multilayer structure of these films. In Figure 3 a scanning electron micrograph taken from a DODAA- (**1**-) cast film polymerized after casting is shown. It is a cross-sectional view of the edge of the cast film fractured in liquid nitrogen. The layer structure can be seen clearly. However, the layers observed in these scanning electron micrographs are much thicker than bilayers and indicative of stacked bilayers.

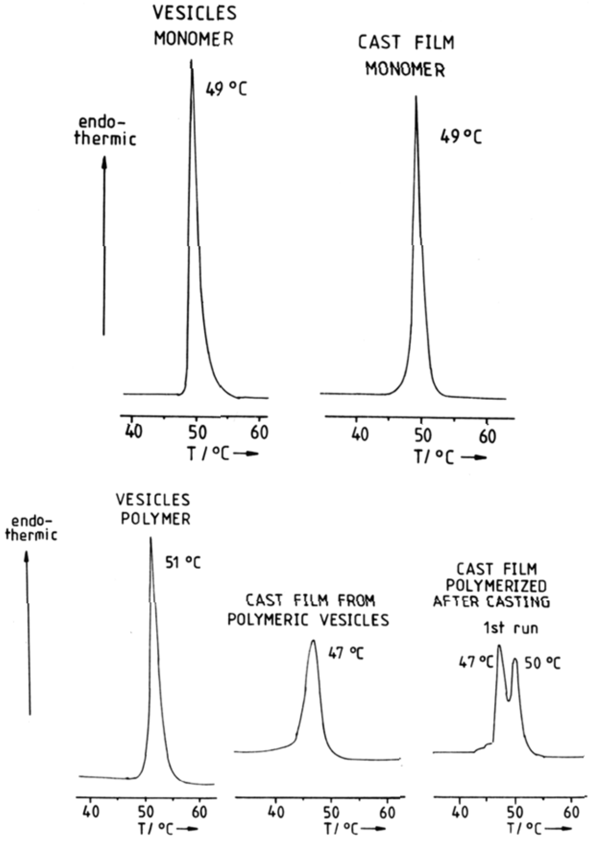


Figure 4. DSC curves of aqueous dispersions and cast films of DODAA (**1**): (top) DSC curves of monomeric vesicles and monomeric cast films are compared; (bottom) DSC curves of polymeric vesicles are compared with those from films cast from polymerized vesicles and with those from cast films polymerized after casting.

Other facts pointing to an almost undisturbed multibilayer structure of the films are detected from DSC measurements. There the phase transitions of the cast films are shifted only slightly when the aqueous dispersions are compared to the cast film. This is shown in Figure 4. The phase transition of the aqueous dispersion of monomeric DODAA as well as that of the monomeric cast film appears at 49 °C. In the polymerized aqueous dispersion the phase transition appears at 51 °C. In films cast from this polymerized aqueous dispersion the phase transition is slightly shifted toward a lower temperature (47 °C). The transition peak for the cast films is also slightly broadened. In films polymerized after casting, two transition peaks, one at 47 °C and the other at 50 °C, appear in the first heating run. After the second heating, the transition peak at 50 °C vanished. This behavior may be explained by a different order in the cast films polymerized before and after casting. In the film polymerized after casting, the order of the monomeric cast film could be retained with a 50 °C peak. This peak cannot be attributed to the residual monomer domain, since no vinyl protons are detected in a ^1H NMR spectrum. The ordering disappears after heating.

Wide-angle X-ray scattering gave final evidence for the fact that cast films exhibit a multibilayer structure. The wide-angle X-ray diffraction patterns of polymeric cast films prepared according to both procedures are shown in Figure 5. It was not possible to get any diffraction patterns from the monomeric cast films because these films were too brittle to be set on the sample stage. The X-ray beam direction was parallel to the film surface. The diffraction patterns show the orientation of the polymeric amphiphiles to be perpendicular to the film surface. On the meridian higher order reflections from the lamellar

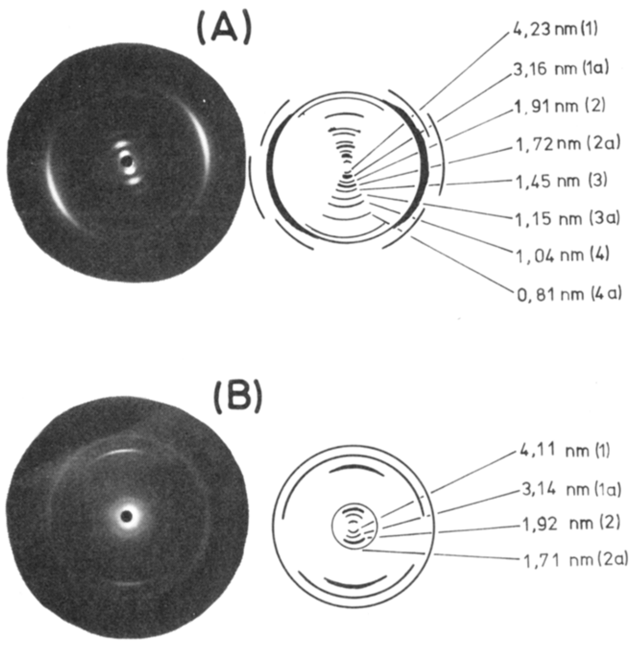
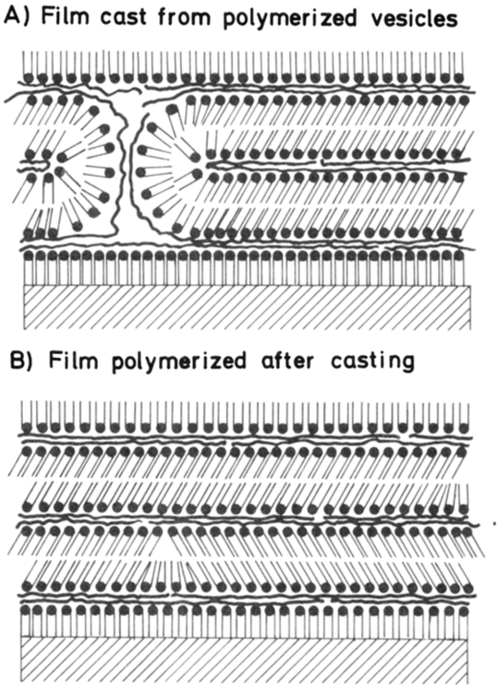
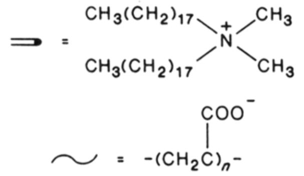


Figure 5. Wide-angle X-ray diffraction patterns of DODAA cast films: (A) diffraction pattern of a film polymerized after casting; (B) diffraction pattern of a film cast from polymerized vesicles.


A) Film cast from polymerized vesicles

B) Film polymerized after casting

Figure 6. Schematic representation of possible structures in films cast from polymerized vesicles (A) and films polymerized after casting (B).


$$\Rightarrow = (CH_3(CH_2)_{17})_2\overset{+}{N}(CH_3)_2 \qquad \sim = -(CH_2\overset{COO^-}{C})_n-$$

structure are observed. Reflections originating from two different lamellar structures with long periods of 4.2 and 3.1 nm have been detected in both cast films. These two different lamellar structures may be represented by lamellae with different tilt angles in the bilayer. In the film polymerized after casting, higher order reflections up to the fourth order were observed from both lamellar phases, whereas higher order reflections up to the second order only were detectable from the film cast from polymerized vesicles (see Figure 5). This observation supports the conclusion that the degree of order in films polymerized after casting is higher than that in films cast from polymerized vesicles. The wide-angle reflections on the equator may be related to intermolecular diffractions within the lamellae.

The higher degree of order in films polymerized after casting can easily be understood: polymerized vesicles are much more stable against fusion processes than are monomeric vesicles.[20,21] Thus they will tend to retain their vesicle structure in a drying process much more than monomeric vesicles. In a drying process the monomeric vesicle suspensions can more easily change from a vesicular to a lamellar arrangement. As a consequence the monomeric cast films exhibit a higher degree of order which can be immobilized by polymerization. In contrast to this, polymeric vesicles will tend more to retain their original vesicular structure, and thus the resulting cast films have a lower degree of order. This is schematically shown in Figure 6.

Permeation Properties. Another fact supporting the explanation given above is provided by conductivity measurements with polymeric cast films prepared according to both methods. For these investigations the cast films (diameter: 4.5 mm) were placed in a Teflon cell to separate two aqueous compartments. The dc conductance of the films was measured for several days. The conductance of both kinds of polymeric cast films was about 1 pS/cm^2. This reveals that the cast films are almost impermeable for ions, as was expected. This low conductance remained unchanged for more than 3 days for films polymerized after casting. In contrast, the films cast from polymerized vesicles became leaky after about 12 h. An additional difference between the two types of polymeric cast films was found by inspecting them after the conductivity measurements. The films cast from polymerized vesicles had swollen in the electrolyte solution after 12 h, whereas the film polymerized after casting did not show any remarkable changes in structure even after having been exposed to electrolyte solution for 3 days.

The gas permeation characteristics of multilayer films polymerized after casting were also measured. As the films cast from 50 mM aqueous dispersions of DODAA were not stable in the gas permeation measurements, films of greater thickness were prepared by casting them from 100 mM aqueous dispersions. These films (thickness: 180 μm) were placed in the permeation cell, and the gas permeation was measured at 30 °C for different gases. Figure 7 summarizes the permeability coefficients for oxygen, nitrogen, methane, and helium.

As shown in Figure 7, the permeability increases linearly with the inverse square root of the molecular weight of the gas. This indicates that the flux of gases through the membrane is due to diffusion through small pores. Thus the permeability coefficient for gases is dependent only on the molecular weight of the gas and not on its chemical nature. However, when the permeability of a gas is measured after several compression/decompression cycles, the gas flux has slightly increased. This points to the fact that these membranes are still not yet extremely stable.

Conclusion

In this paper the properties of cast multibilayer films that can be immobilized by polymerization of the counterion of the lipid (dioctadecyldimethylammonium acrylate, DODAA) are described. Cast films were prepared from monomeric as well as from polymerized aqueous

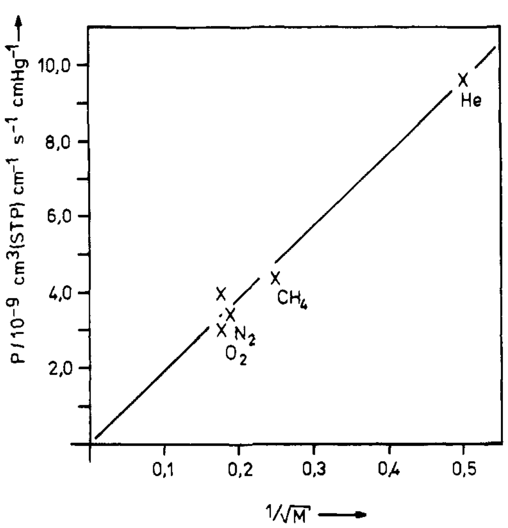


Figure 7. Permeability coefficients, P, of different gases through a polymeric cast film (compound 1, thickness 180 μm) as a function of the molecular weight, M, of the gases.

dispersions. Monomeric membranes were also polymerized by UV irradiation after having been dried. The cast films have an ordered multibilayer structure, as was demonstrated by wide-angle X-ray scattering. When cast films are prepared from polymerized vesicles, the degree of order is lower than it is in films polymerized after casting. The DODAA films cast from polymerized vesicles swell in electrolyte solution, whereas the films polymerized after casting remain stable in this environment. Thus these films may, for example, be suitable for application in reverse-osmosis membranes. With the help of gas permeation measurements it was demonstrated that the permeability depends only on the molecular weight of the gas and not on its chemical nature.

Acknowledgment. We are grateful to Tokuyama Soda Co. for their financial support for the stay of W.P. at Kyushu University.

Registry No. 1, 105336-86-5; O_2, 7782-44-7; N_2, 7727-37-9; CH_4, 74-82-8; He, 7440-59-7.

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Solid Cholesteric Films Cast from Aqueous (Hydroxypropyl)cellulose

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ABSTRACT: (Hydroxypropyl)cellulose films cast from water solutions assume a planar cholesteric arrangement, with pitches in the range 100–200 nm, depending on the casting conditions. The reflection wavelength moves into the visible range upon heating between 130 and 175 °C, the thermotropic order being characterized by a positive temperature dependence of the cholesteric pitch. This process is irreversible; the pitch values decrease only slightly on cooling. The cholesteric properties of (hydroxypropyl)cellulose films are therefore metastable and are induced either by shearing the polymer melt or by casting from the liquid crystalline solutions. The persistence of cholesteric order in the cast films at room temperature and the behavior of the optical properties on heating are consistent with dynamic mechanical measurements, which reveal an increase in the molecular mobility above 120 °C.

Introduction

In the past decade, numerous reports, reviewed in ref 1–3, have shown that most cellulose derivatives form cholesteric liquid crystalline phases in solution or in the bulk. (Hydroxypropyl)cellulose (HPC) has been widely studied because mesophases can be prepared in both water and common organic solvents. Optical anisotropy of HPC solutions has been shown to arise from a right-handed helicoidal arrangement of the polymer molecules in concentrated solution.[4,5] Strong indications have also been given that cholesteric order could be promoted on cooling HPC from the melt.[6,7]

Considerable effort has been devoted to the preparation of free-standing films exhibiting cholesteric order in view of their potential usefulness as chiroptical filters. Different routes have been studied, including (i) synthesis of thermotropic polymer liquid crystals with cross-linkable side chains,[8] (ii) incorporation of cholesteryl derivatives as side