

Synthesis of Liquid Crystalline Triheptyl Cellulose and Its Blend Thin-Film Composite Membrane for Air Separation

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SYNOPSIS

Liquid crystalline triheptyl cellulose (THC) was synthesized directly from cellulose acetate and heptyl bromide with dimethyl sulfoxide as a single-component solvent. Synthetic conditions were studied with respect to reaction temperature, time, and yield. The molecular structure and liquid crystalline character of the THC obtained as sticky, soft, and birefringent solids at room temperature were investigated by IR, NMR, elemental analysis, and a polarizing microscope. The composite membranes consisting of a THC/ethyl cellulose blend as a dense thin selective layer and polyethersulfone as a porous thick support layer were fabricated and their air-separation performances were studied by a constant pressure-variable volume method. The data show that the air-separation performances increase dramatically with operating parameters such as pressure and temperature. No apparent dependence of air-separation ability on operating time and THC/ethyl cellulose ratio was observed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The utility of polymeric membranes for air separation has advanced substantially during the past decades. Membrane-based air-separation technology is competitive with conventional separation processes for certain ranges of composition and flux of oxygen- or nitrogen-enriched air (OEA or NEA). Oxygen-containing OEA, 28–40%, has been used in both medical and industrial fields. In designing air-separation membranes, the fabrication of new composite membranes possessing both high OEA flux and high air-separation capability seems quite interesting.

In our recent study, a liquid crystalline triheptyl cellulose (THC)/ethyl cellulose (EC) blend membrane showed a better air-separation property.^{1,2} However, this THC/EC thick membrane suffers from a relatively low OEA flux. In this article, the synthesis of THC exhibiting both lyotropic and thermotropic liquid crystalline behaviors even at

room temperature is reported. The air-separation properties of the THC/EC blend thin-film composite membrane are studied in different operating conditions to enhance the OEA flux through the membranes while maintaining a higher oxygen over nitrogen separation capability.

EXPERIMENTAL

The THC was prepared directly from cellulose acetate, sodium hydroxide, and *n*-heptyl bromide with dimethyl sulfoxide as a single-component solvent according to the reported method.³ The intrinsic viscosities [η] of THC in chloroform were measured with an Ubbelohde viscometer at 25°C. IR spectra were obtained with a Pye Unicam SP2000 IR spectrometer by a deposited film technique from a THC-chloroform solution. A 200 MHz ¹H-NMR spectrum was recorded on a Bruker AC-P-200 spectrometer in CDCl₃ solvent. Elemental analysis was carried out with an MT-3-type instrument. Melting temperature and liquid crystalline were observed using a Jiang-Nan XPT-6-type polarized microscope with a hot stage.

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A selective thin film whose thickness averaged 1 μm was prepared from a casting solution of the THC/EC blend in tetrahydrofuran. A porous polyethersulfone membrane (total thickness 120 μm) with a mean pore size of 15–45 nm was selected as a thick support layer. Air-separation performances were measured using a constant pressure-variable volume method.⁴ The pressure on the permeation-gas side of the membrane was maintained at atmospheric pressure, and the pressure difference between the feed-gas and the permeation-gas sides, at 0.05–0.49 MPa. An effective membrane area is about 50 cm^2 . Once compressed, air was charged into the testing system. The performance of the composite membranes can be evaluated at various temperatures, pressure differences, and operating times. To evaluate the membrane performance for the separation of a constant air composition containing 21% oxygen, the feed flux was maintained at significantly higher levels than was the permeate flux. This was done to maintain a uniform air composition across the membrane surface.

RESULTS AND DISCUSSION

The etherification conditions, yield, $[\eta]$, and melting temperature T_m of eight heptyl celluloses are given in Table I. It can be seen that the highest etherification temperature and the longest etherification time applicable are 90°C and 12 h, respectively, to prepare highly substituted heptyl cellulose. The etherification time strongly influences the degree of substitution (DS) of resulting heptyl cellulose. As the etherification time is prolonged, the DS values increase while the T_m decreases. The preparation yield with this synthetic method can reach 50–96%. All the heptyl celluloses listed in Table I are insoluble in the reaction system and become milk white

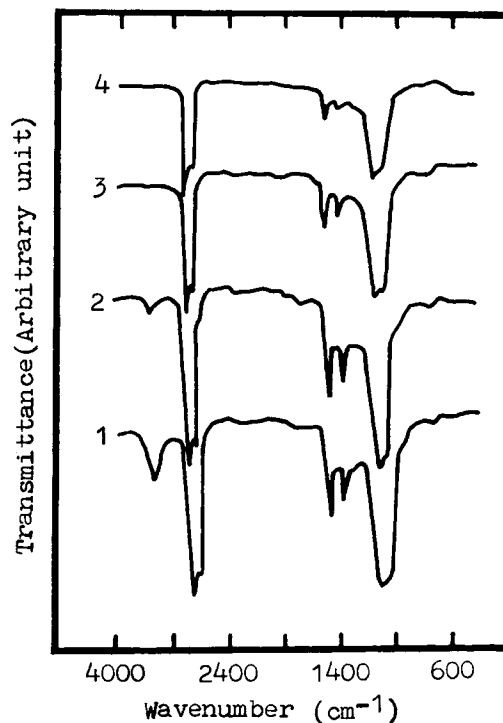


Figure 1 IR spectra of four heptyl celluloses with various degrees of substitution under different synthetic conditions. For numbers of the curves, refer to Table I.

as they are formed during etherification. Although insoluble in polar solvents, highly substituted heptyl celluloses are readily soluble in nonpolar hydrocarbon, ester, and ether. The attractive forces between a large number of nonpolar heptyl side chains on the cellulose main chains and nonpolar solvent molecules are similar to those between individual heptyl on the cellulose and the individual solvent molecule according to the familiar generation “like dissolves like.”

Figure 1 illustrates the typical IR spectra of four heptyl celluloses obtained in different synthetic

Table I Synthesis of *n*-Heptyl Celluloses

No.	Etherification			Form	$[\eta]$ (mL/g)	DS	T_m (°C)
	Temp (°C)	Time (h)	Yield (%)				
1	20–90	6	55	Faint yellow	47	2.6	125
2	17–90	8	90	Gummy, soft	55	2.8	80
3	15–90	9	50	Clear white	36	3.0	75
4	15–86	10	92	Gummy, soft	31	3.0	65
5	12–86	10	54	Gummy, soft	42	3.0	60
6	10–85	11	78	Gummy, soft	44	2.9	50
7	10–83	11	96	Gummy, soft	42	2.9	45
8	10–90	12	81	Gummy, fluid	26	2.9	20

conditions.⁵ The strong absorptions around 2970 and 2840 cm^{-1} are due to the C—H stretching vibrations of heptyl substituents and the cellulose skeleton, respectively. Both broad and strong absorptions in the range from 1050 to 1160 cm^{-1} arise from C—O stretching vibrations. The sharp absorption peaks around 1480, 1390, and 770 cm^{-1} are attributed to —CH₂— scissoring and rocking vibrations in the plane, respectively. The weak absorption around 1780 cm^{-1} is attributed to a C=O stretching vibration in the residual ester groups, whereas the weak absorption around 3520 cm^{-1} is due to O—H stretching vibration. The higher wavenumber of the O—H group is due to weaker hydrogen bonding in highly substituted heptyl celluloses. Table I also lists

the DS, which is roughly estimated by the absorption areas due to hydroxyl groups in the IR spectra of the heptyl celluloses.

To characterize the structure and property of heptyl cellulose further, we investigated the molecular structure by ¹H-NMR and elemental analysis. No resonance peak for the hydroxyl group was observed by high-resolution ¹H-NMR spectrometry for heptyl cellulose no. 4 because of its complete substitution. Elemental analysis results indicated that heptyl cellulose no. 4 has a DS value of 2.8. The differences between the DS values calculated from the above three measurements are small.

Most of the heptyl celluloses obtained under these synthetic conditions, being condensed, gummy, soft,

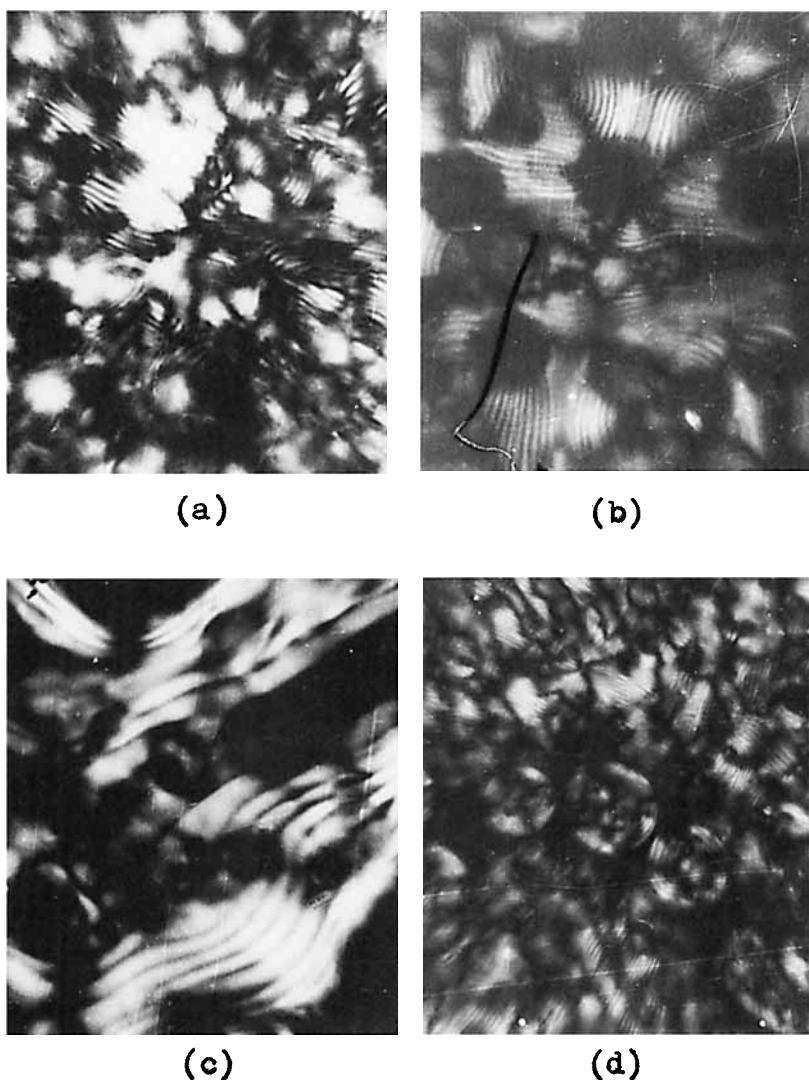


Figure 2 Photomicrographs of THC showing a “fingerprint” texture for the cholesteric liquid crystalline phase at 25°C in four solvents: (a) dichloromethane; (b) *sym*-tetrahydroethane; (c) butanone; (d) tetrahydrofuran, at 500× magnification.

and birefringent even at room temperature, exhibit typical thermotropic liquid crystalline behavior above their T_m . The lyotropic liquid crystalline character of the concentrated solutions of heptyl cellulose no. 8 could be directly confirmed by polarizing microscopic observations of the striation lines attributed to the cholesteric helical repeat, as observed in Figure 2. It can be seen that they are present as a "fingerprint" texture or a grainy appearance characteristic of a cholesteric polydomain structure. Shear-induced melt birefringence is noticeable upon pulling the coverglass, but such birefringence relaxes quickly. It has been found that heptyl cellulose no. 8 has the lowest $[\eta]$ and lowest T_m , which is suitable for the preparation of higher-performance liquid crystalline blend membrane. It is certain that the excellent liquid crystallinity of triheptyl cellulose is responsible for its usefulness as functional membranes for gas separation.

In Figure 3, the variation of the flux Q_{OEA} and oxygen concentration Y_{O_2} in the OEA through the THC/EC blend thin-film composite membranes as a function of THC content in the range 0–30 wt % is presented. As observed, Y_{O_2} increases with increasing THC content from zero to 20 wt %. The remarkable fluctuation of Q_{OEA} may be attributed to the higher sensitivity of Q_{OEA} to the slight variation of thin film thickness at higher temperature. Similar variations of Q_{OEA} and Y_{O_2} with THC content at 30°C were experimentally achieved as described in our previous article,⁶ which demonstrates the important role of the addition of a small amount of

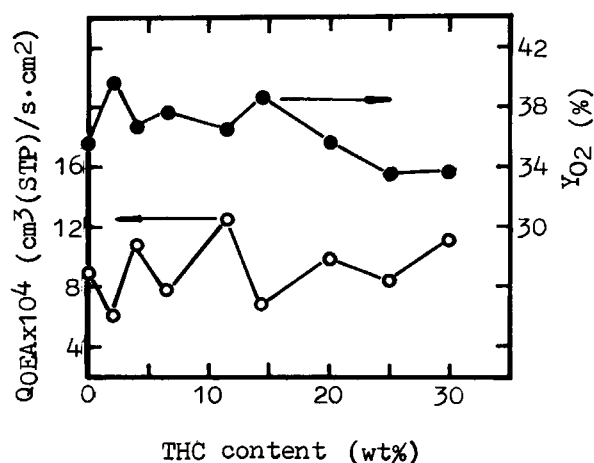


Figure 3 Effect of the THC content in THC/EC thin-film composite membranes on air-separation capabilities at 40°C and the pressure difference of 0.41 MPa after the operation of 24 h.

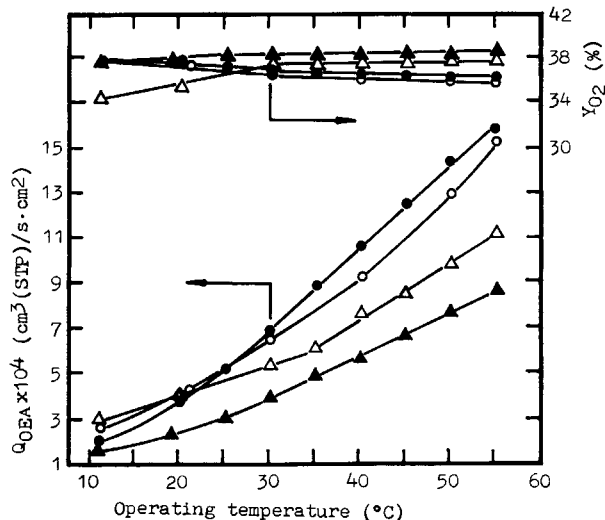


Figure 4 Effect of operating temperature on the air-separation capabilities through the THC/EC thin-film composite membranes with different THC/EC ratios: (○) 0/100; (●) 4/96; (△) 7/93; (▲) 15/85, at the pressure difference of 0.41 MPa after operation for 24 h.

THC to EC in improving the air-separation capability of the membranes.

The variation of Q_{OEA} and Y_{O_2} vs. operating temperature is presented in Figure 4 for a series of THC/EC ratios. These experiments were carried out at the transmembrane pressure difference of 0.41 MPa and after the operating time of 24 h. The Q_{OEA} for four composite membranes increases with temperature, especially at higher temperature. Of all these composite membranes, the THC/EC (4/96) thin-film composite membrane shows the highest value of Q_{OEA} at temperature higher than 25°C, which may be attributed to the thinnest thickness of the THC/EC (4/96) composite membrane.

On the contrary, Y_{O_2} decreases slightly for the THC/EC (0/100) and (4/96) thin-film composite membranes but increases slightly for THC/EC (7/93) and (15/85) thin-film composite membranes with increasing operating temperature. At a given operating temperature higher than 25°C, Y_{O_2} increases slightly with an increase in THC content from zero to 15 wt %, which is agreeable with the results observed in Figure 3. As shown in Figure 4, all the membranes in the temperature range from 11 to 55°C have a Y_{O_2} of greater than 34% and thus are essentially defect-free.

Figure 5 presents the relationship between the air-separation parameters and pressure difference for the membranes with different THC/EC ratios at various temperatures. For each set of data, Q_{OEA}

is directly proportional to the pressure difference. Thus, the air permeation behavior through the membranes may be explained by the solution-diffusion mechanism.⁷ At a fixed THC/EC ratio of 12/88, the dependence of Q_{OEA} on the pressure difference becomes stronger with increase in the temperature from 35 to 40°C. An increase in pressure difference results in a higher Y_{O_2} for the same membrane, whereas the dependence of Y_{O_2} on the pressure difference becomes weaker with an increasing pressure difference. It can be predicted from Figure 5 that Q_{OEA} might reach the higher value of about $5 \times 10^{-3} \text{ cm}^3 \text{ (STP)}/\text{s cm}^2$ under the pressure difference of 1.0 MPa across the THC/EC (12/88) thin-film composite membrane at 40°C. Summarizing, a higher operating pressure difference across the membrane will give both higher Q_{OEA} and higher Y_{O_2} for the same membrane.

In Figure 6, the variations of Q_{OEA} and Y_{O_2} as a function of operating time for the membranes with different THC contents from 12 to 20 wt % is presented. It is important to notice that Q_{OEA} declines slightly and Y_{O_2} increases slightly with increasing operating time for THC/EC (12/88) composite membrane, but that Q_{OEA} and Y_{O_2} for another two

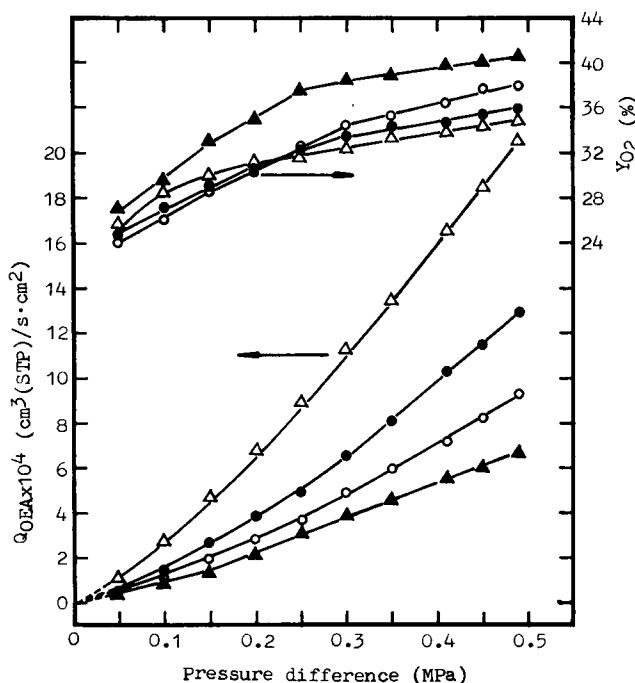


Figure 5 Effect of pressure difference on the air-separation capabilities through the membranes with different thin-film compositions of the following THC/EC ratios: (O) 0/100 at 30°C; (●) 12/88 at 35°C; (Δ) 12/88 at 40°C; (▲) 15/85 at 35°C, after operation for 24 h.

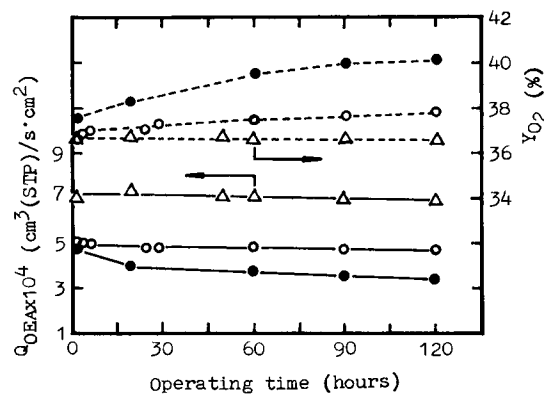


Figure 6 Effect of operating time on the air-separation abilities of the composite membranes with different thin-film compositions—THC/EC ratios: (O) 12/88; (●) 15/85; (Δ) 20/80 at 30°C, at a pressure difference of 0.41 MPa.

membranes remain almost constant, at least during the period of observation in the laboratory.

These results show no appreciable change in the membrane structure during the continued operation period, indicating a promising long-time stability that is also displayed by thick dense THC/EC blend membranes.¹ This good stability of air-separation capability during the continued operation is an important factor in the applicability of the membranes.

CONCLUSIONS

Highly substituted heptyl cellulose could be directly prepared by reacting cellulose acetate with sodium hydroxide and heptyl bromide in dimethyl sulfoxide. The degree of substitution and properties of heptyl celluloses obtained thus could be altered by the variation of etherification conditions. Triheptyl celluloses show both thermotropic and lyotropic cholesteric liquid crystalline behaviors even at room temperature and in some nonpolar solvents, respectively. The triheptyl cellulose/ethyl cellulose blend thin-film composite membranes with a porous polyethersulfone as a support layer demonstrate a case where their air-separation capabilities vary significantly with operating temperature, pressure difference, and good stability, which must be taken into account properly in designing a membrane-based air-separation system. An oxygen-enriched air flux of $6.6\text{--}20.0 \times 10^{-4} \text{ cm}^3 \text{ (STP)}/\text{s cm}^2$ and its oxygen concentration of 34–40% through the composite membranes could be obtained at 35–40°C and the operating pressure difference of 0.49 MPa.

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