

# Porous Cellulose Acetate Membrane Prepared by Thermally Induced Phase Separation

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Received 29 May 2002; accepted 12 December 2002

**ABSTRACT:** Microporous cellulose acetate membranes were prepared by a thermally induced phase separation (TIPS) process. Two kinds of cellulose acetate with acetyl content of 51 and 55 mol % and two kinds of diluents, such as 2-methyl-2,4-pentanediol and 2-ethyl-1,3-hexanediol, were used. In all polymer-diluent systems, cloud points were observed, which indicated that liquid-liquid phase separation occurred during the TIPS process. The growth of droplets formed after the phase separation was followed using three cooling conditions. The obtained pore structure was

isotropic, that is, the pore size did not vary across the membrane. In addition, no macrovoids were formed. These pore structures were in contrast with those usually obtained by the immersion precipitation method. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3951–3955, 2003

**Key words:** cellulose acetate; thermally induced phase separation; membranes; isotropic structure; effect of acetyl content

## INTRODUCTION

Cellulose acetate is one of the most useful membrane materials. Commercial reverse osmosis (RO), ultrafiltration (UF), and microfiltration (MF) membranes have been widely produced from this material. Because cellulose acetate is hydrophilic, the membrane has an advantage that the flux is unlikely to decline during operation because of solute adsorption and pore blocking,<sup>1–3</sup> compared with the hydrophobic membranes prepared from polysulfone, polyethylene, polypropylene, and so forth.

Cellulose acetate membranes have been mainly prepared by the immersion precipitation method.<sup>4</sup> The cellulose acetate solution is cast onto a support or extruded from a nozzle and immersed in a water (nonsolvent) bath. Phase separation occurs as a result of the exchange of solvent and nonsolvent. The immersion precipitation method usually gives an asymmetric membrane structure with the skin layer near the surface contacted with the nonsolvent. Moreover, macrovoids (large cavities of a conical shape) have mainly been detected in membranes prepared by this method.<sup>3</sup> The presence of macrovoids is often undesirable because the membrane tends to be fragile.

The thermally induced phase separation (TIPS) process is another way of making microporous mem-

branes.<sup>5–15</sup> In the TIPS process, a polymer is dissolved in a diluent at high temperature and then cooling the solution induces phase separation. Many microporous membranes have been prepared by the TIPS process from hydrophobic polymers such as polyethylene, polypropylene, polystyrene, and poly(vinylidene fluoride). As far as we know, however, the preparation of a hydrophilic cellulose acetate membrane by the TIPS process has not yet been reported. In this work, the TIPS process was used for the purpose of making a cellulose acetate membrane with symmetric pore structure and no macrovoids.

## EXPERIMENTAL

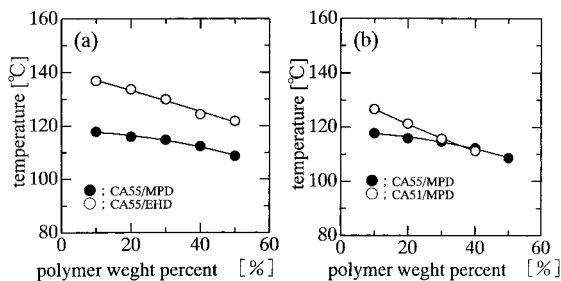
### Materials

Two kinds of cellulose acetates, with acetyl content of 55% ( $M_w = 110,000$ ,  $M_n = 33,000$ ,  $M_w/M_n = 3.3$ ) and 51% ( $M_w = 150,000$ ,  $M_n = 59,000$ ,  $M_w/M_n = 2.5$ ), were used. The former and the latter are abbreviated as CA55 and CA51, respectively. These were kindly supplied from Daicel Chemical Industries, Ltd. (Japan). Diluents were 2-methyl-2,4-pentanediol (MPD; Wako Pure Chemical Industries, Osaka, Japan) and 2-ethyl-1,3-hexanediol (EHD; Aldrich Chemical Co., Milwaukee, WI).

### Phase diagram

The cellulose acetate was mixed with diluent in a test tube. The test tube was purged with nitrogen and

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**Figure 1** Cloud point curves: (a) effect of diluent; (b) effect of kind of cellulose acetate.

sealed to prevent diluent evaporation and oxidation during melt blending. The test tube was heated in an oven at 175°C for 24 h and then quenched in ice-water to solidify the sample. The sample was sliced in desired pieces and placed between a pair of microscope coverslips. A Teflon film of 100  $\mu\text{m}$  thickness with a square opening was inserted between the coverslips. The sample with the coverslips was heated on a hot stage (Linkam, LK-600PH) at 170°C and cooled to 25°C at a controlled rate of 1°C/min. Cloud points were determined visually by noting the appearance of turbidity under an optical microscope (BX 50; Olympus, Tokyo, Japan).

A Perkin–Elmer DSC-7 apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT) was used to measure the dynamic crystallization rate and the melting temperature. The solid sample was sealed in an aluminum DSC pan, kept at 200°C for 3 min, and then cooled at 10°C/min to 25°C. After the sample was left at room temperature for 2 days, it was heated at 10°C/min to 200°C to measure the melting temperature.

### Droplet growth kinetic studies

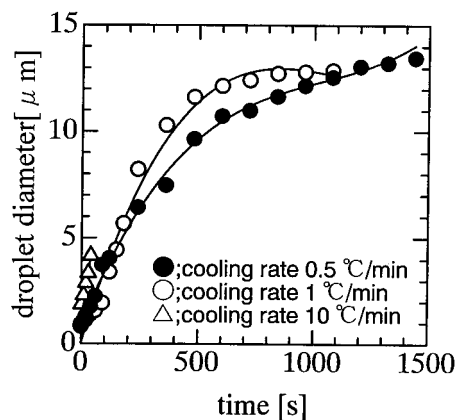
The hot stage was placed on the platform of the optical microscope. The samples with two coverslips were heated on the hot stage at 170°C and cooled to 25°C at three controlled rates of 0.5, 1, and 10°C/min. The image from the microscope was converted to a video signal. To measure the droplet size of the polymer-lean phase, which was formed after phase separation, an image analysis was used. The analysis software package was Win ROOF (Mitani Co., Fukui, Japan).

**TABLE I**  
Solubility Parameters

Substance	Solubility parameter [(MPa) <sup>1/2</sup> ]
CA55	27.83 <sup>a</sup>
MPD	19.8 <sup>b</sup>
EHD	19.2 <sup>b</sup>

<sup>a</sup> Ref. 16. Value of cellulose acetate with acetyl content of 56%.

<sup>b</sup> Ref. 16.



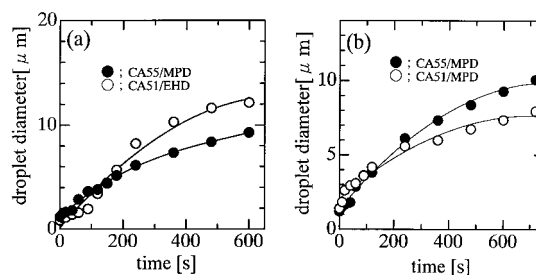
**Figure 2** Time courses of average droplet diameters in the CA55/EHD system. Polymer concentration: 20 wt %.

### Scanning electron micrographs

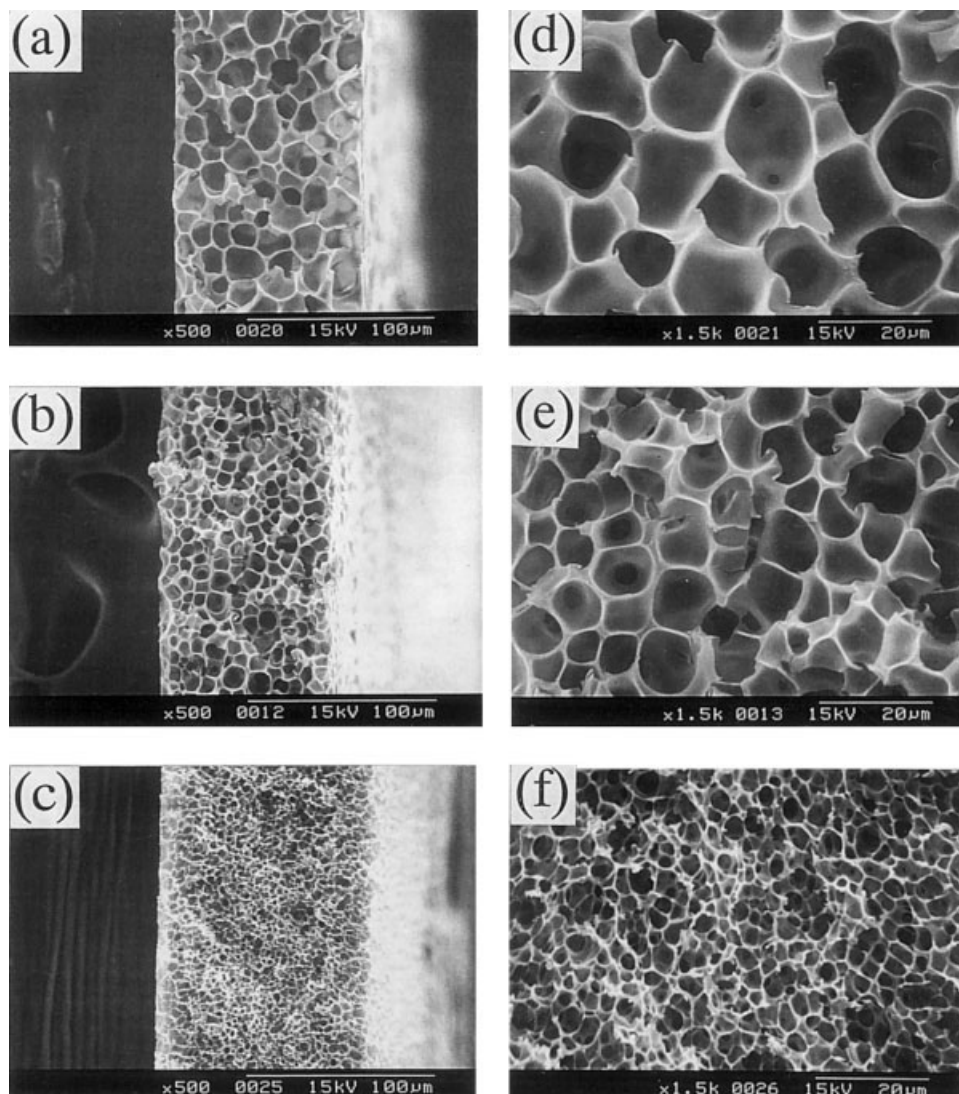
A sample similar to those used for the droplet growth kinetic studies was removed from the hot stage. The diluent was extracted with methanol and the resulting microporous membrane was dried at room temperature. The membrane was fractured in liquid nitrogen and mounted vertically on a sample holder. The sample was coated with Pt/Pd. A SEM (S-2300; Hitachi Co., Tokyo, Japan) with an accelerating voltage set to 15 kV was used to examine the membrane cross sections.

## RESULTS AND DISCUSSION

Figure 1(a) shows cloud point curves when two kinds of diluents, such as MPD and EHD, were used. The existence of cloud points shows the occurrence of liquid–liquid phase separation during cooling. The CA55/MPD system showed lower cloud points than those of the CA55/EHD system. The solubility parameters of CA55, MPD, and EHD are summarized in Table I. The parameter of MPD is a little closer to that of CA55 than to that of EHD. This means better compatibility between CA55 and the diluent, which leads to the lower cloud point curve. As shown in Figure 1(b), CA51 showed a little higher cloud point curve



**Figure 3** Time courses of average droplet diameters at a cooling condition of 1°C/min: (a) effect of diluent; (b) effect of kind of cellulose acetate. Polymer concentration: 20 wt %.



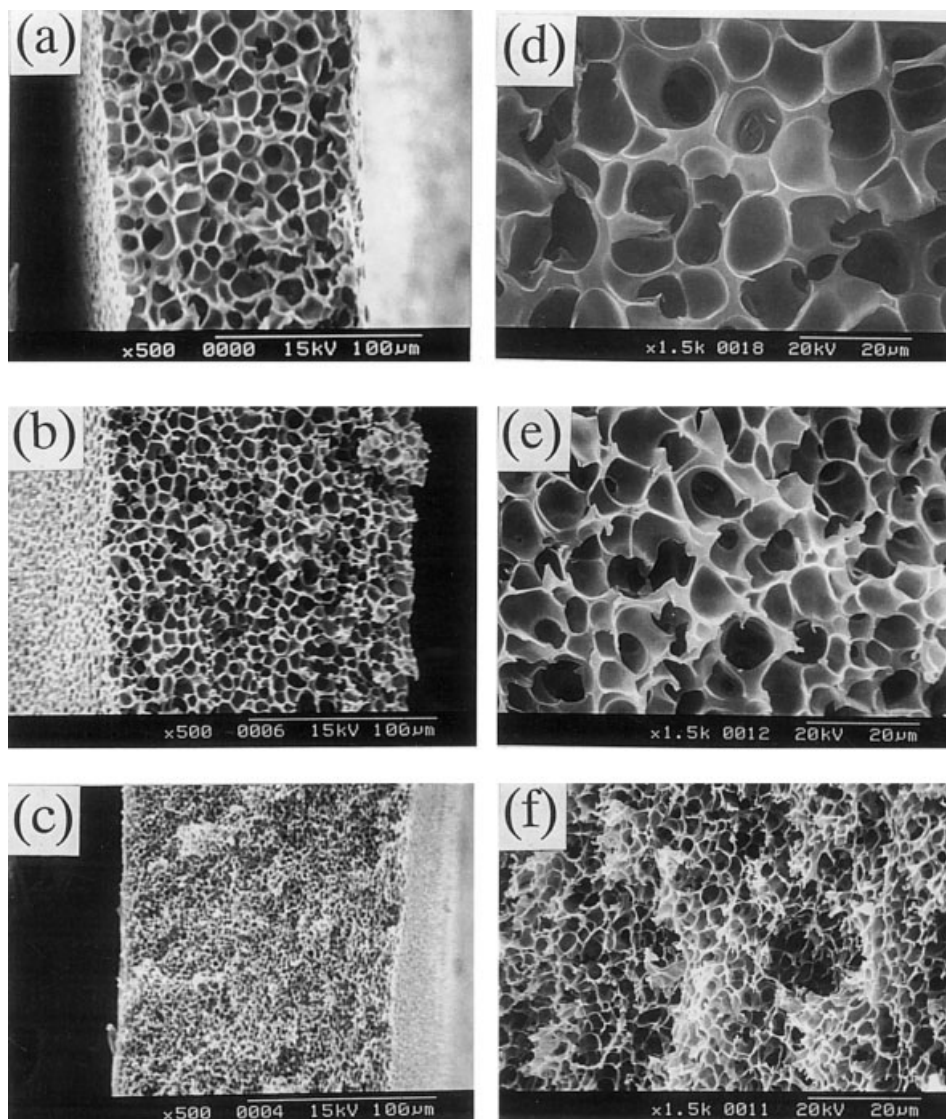
**Figure 4** Cross sections of membranes prepared at three different cooling rates in the CA55/MPD system. Polymer concentration: 20 wt %. (a), (d): cooling rate = 0.5°C/min; (b), (e): cooling rate = 1°C/min; (c), (f): cooling rate = 10°C/min.

than that of CA55 when MPD was used as diluent. The solubility parameters of the cellulose acetates with acetyl content of 48 and 56% were reported as 27.19 and 27.83 (MPa)<sup>1/2</sup>, respectively.<sup>16</sup> Thus, the parameter of CA51 can be deduced to be lower than that of CA55, although the exact value is not known. Therefore, the compatibility is expected to be better in the case of CA51 from the viewpoint of the solubility parameter difference. This predicts a tendency opposite to the experimental result shown in Figure 1(b). It is known that the polymer with the higher molecular weight shows higher cloud point arising from the entropy effect.<sup>17,18</sup> The higher molecular weight of CA51 may be the reason for the higher cloud point curve shown in Figure 1(b).

No exothermic peaks were observed in the DSC experiments for CA55/MPD samples with polymer concentrations of 10, 20, 30, and 40 wt % during cool-

ing at the rate of 10°C/min. However, all samples left at room temperature for 2 days showed endothermic peaks during heating at the rate of 10°C/min. The endothermic peak is attributable to the melting of crystallites.<sup>19</sup> These experimental results indicate that, in this system, the crystallization rate is too slow to be detected in the normal DSC process, but crystallization occurs after prolonged standing.

Figure 2 shows time courses of average droplet diameters at three different cooling rates. When the cooling rate was 10°C/min, the polymer solution became white soon after the occurrence of phase separation so that the exact measurement of the droplet diameter soon became impossible. In the initial stage, after the occurrence of phase separation, the droplet growth rate increased with the increase of cooling rate. The interfacial tension between the polymer-lean phase and the polymer-rich phase, the volume frac-



**Figure 5** Cross sections of membranes prepared at three different cooling rates in the CA51/MPD system. Polymer concentration: 20 wt %. (a), (d): cooling rate = 0.5°C/min; (b), (e): cooling rate = 1°C/min; (c), (f): cooling rate = 10°C/min.

tion of the droplet phase (polymer-lean phase), and the viscosity of the polymer-rich phase all influence the droplet growth rate.<sup>20</sup> The higher interfacial tension, the higher volume fraction of the droplet phase, and the lower viscosity of the polymer-rich phase bring about a higher droplet growth rate. At the same time, after the occurrence of phase separation, the temperature decreases in the case of the higher cooling rate condition. The interfacial tension and the volume fraction of the droplet phase increase with the decrease of temperature.<sup>21</sup> This is the reason that higher droplet growth rate was obtained in the higher cooling condition. When the droplet growth behaviors are compared in two cooling conditions of 0.5 and 1°C/min, the initial growth rate was faster in the case of 1°C/min; however, the droplet diameter became constant sooner because of the high viscosity of the polymer solution in the low-temperature region. Thus, the

final droplet diameter was larger in the case of 0.5°C/min.

Effects of kinds of diluents and polymers are shown in Figure 3(a) and (b), respectively. The CA55/EHD system showed larger droplet diameter than that of the CA55/MPD system. As shown in Figure 1(a), the former system had the higher cloud point curve. Therefore, the lower viscosity of the polymer-rich phase, brought about by the higher temperature, probably leads to the faster droplet growth. A larger droplet was obtained for CA55 than for CA51, as shown in Figure 3(b). This is also because of the lower viscosity brought about by the lower molecular weight of CA55.

Figure 4 shows the cross sections of membranes prepared at three different cooling rates for the CA55/MPD system. Whole cross sections and detailed pore structures are shown for each membrane. The obtained pore structures were isotropic, that is, pore

sizes did not vary across the membranes. In addition, no macrovoids were formed. By the immersion precipitation method, the asymmetric structure with the skin layer is usually obtained and sometimes macrovoids are formed inside the membrane. The membrane structures obtained by this TIPS process were in contrast with those by the immersion precipitation method. The pore size decreased with the increase of the cooling rate. This is the general tendency in the TIPS process.<sup>15</sup>

The membrane structures in the CA51/MPD system are shown in Figure 5. The isotropic pore structures similar to those shown in Figure 4 were also obtained. At the same cooling condition, the pore size in the CA51/MPD system was smaller than that in the CA55/MPD system. This tendency is in agreement with that shown in Figure 3(b) and is attributable to the higher molecular weight of CA51.

### CONCLUSIONS

Microporous cellulose acetate membranes were prepared by the liquid-liquid phase separation of the TIPS process. The CA55/MPD system showed a lower cloud point curve than that of the CA55/EHD system. This was explained by the better compatibility between CA55 and MPD. In the same diluent, a lower cloud point curve was obtained for CA55 than for CA51 because of the lower molecular weight.

The droplet growth process was followed using three cooling conditions. The initial droplet growth rate increased with the increase of the cooling rate. However, the final droplet size was largest in the case of the slowest cooling rate.

The obtained pore structure was isotropic and no macrovoids were formed. The CA51 showed the smaller pore size under the same experimental conditions as those of CA55.

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