

# Behavior of Interfacial Polycondensation on Synthesizing of Poly(amic ester)s

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## SYNOPSIS

The behavior in interfacial polycondensation of 4,4'-methylenedianiline or 4,4'-oxydianiline (ODA) in water with dimethoxycarbonyl terephthaloyl chloride (DCMTC) in dichloromethane with benzyltriethylammonium chloride (BTEAC) as a catalyst was examined with a Fourier transform infrared spectrophotometer, attenuated total reflectance, an ultraviolet spectrophotometer, and a scanning electron microscope. When the ratio of the DCMTC concentration to the ODA concentration was about 2 : 1, the interfacial polymer obtained had relatively high inherent viscosity. With the addition of a suitable amount of sodium carbonate and BTEAC, the interfacial polymer obtained had relatively high inherent viscosity. The polymer film grew toward the organic phase from the interface region until the reaction was over. The surfaces of the films adjacent to the water phase were composed of the polymer having a higher molecular weight and were denser in morphology than those of the films adjacent to the organic phase. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Early in 1944, Farbenindustrie reported the synthesis of polyurethane by interfacial polycondensation. But in 1958–1959, polyamides were successfully synthesized using a liquid–liquid interfacial polycondensation, which generated great interest. The advantage of an interfacial polycondensation is that it provides a simple and quickly synthesized polymer. Its disadvantage is that it must use highly corrosive, unstable acid chloride as a monomer. But because its reaction energy is low, polymerization can generally be conducted at a low temperature. Only a short polymerization time is needed to synthesize polymers that are thermally unstable, insoluble, volatile or contain unstable intermediate products.<sup>1</sup> This is why many polymers are successfully synthesized using this method.<sup>2–4</sup> Also, many researchers use changes in the reaction conditions (such as mixing speed, adding phase transfer catalysts, bases, etc.) to investigate the effects on inter-

facial polycondensation.<sup>5,6</sup> There have been many successful cases, especially by adding a phase transfer catalyst to speed up the reaction and increase the molecular weight of polymers. There is little information in the literature<sup>7–10</sup> on the kinetics of an interfacial process for membrane formation.

Generally, when a membrane is used for separation, it is desirable to have both high permeation and permselectivity. To achieve high permselectivity the effective thickness must be greater, but this reduces the permeation. So researchers hoped to build a composite membrane with a superthin (less than 1  $\mu\text{m}$ ), dense film to obtain high permselectivity, on porous support materials to obtain high permeation.<sup>11</sup> Successful cases were conducted through the use of interfacial polycondensation on porous support materials to create a layer of thin interfacial film.<sup>12–16</sup> The porous base material provides good permeation and mechanical properties, while the interfacial film provides good permselectivity and resistance to organic solvents. Polymers or ceramics can be used as support materials.

Aromatic polyimides contain stiff main chains. Stiffer polymers generally have a higher mobility-selectivity because they behave more like “molecular

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sieves."<sup>17</sup> Also, polyimides with high glass transition temperatures can bear a high pressure to prevent plastic deformation. They are considered important in the separation industry, therefore many researchers use a polyimide as a separation membrane.

We are interested in preparing composite membranes with a polyimide on top of a porous ceramic by interfacial polycondensation, but there has been little research on this. In previous studies, we discussed interfacial polycondensation on 1,2,4,5-benzenetetracyl chloride (BTAC) and diamines.<sup>18-21</sup> However, the BTAC contained tetra functional groups of acyl chloride which would result in a crosslinking structure of polymer. It was more difficult to analyze the thermosetting polymers. So in this research we investigated interfacial polycondensation on dimethoxycarbonyl terephthaloyl chloride (DCMTC) and aromatic diamines to form thermoplastic poly(amic ester)s. To prepare a good separation membrane, we must have sufficient understanding of the interfacial polycondensation phenomena of this system. Hence, we investigated the interfacial polycondensation phenomena through the addition of sodium carbonate, changing the reaction temperature, adding a phase transfer catalyst, and changing the concentration of monomers.

## EXPERIMENTAL

### Materials

4,4'-Oxydianiline (ODA) and 4,4'-methylenedianiline (MDA) were purified by vacuum sublimation. Pyromellitic dianhydride was recrystallized from acetic anhydride before being used. Dichloromethane was dried with 4-Å molecular sieves and was stored over molecular sieves until use. Thionyl chloride was distilled under normal pressure in inert gas. All the solvents used were purified in the usual manner. All other reagents were of analytical grade. DCMTC was synthesized according to our previous research.<sup>22</sup>

### Characterization

A Bio-Rad FTS-40 Fourier transform infrared spectrophotometer (FTIR) was used to record spectra of the KBr pellets. In a typical experiment, an average of 20 scans per sample was made. Inherent viscosities of all polymers were determined at 0.5 g/dL concentration in *N,N*-dimethyl acetamide (DMAc) at 30°C using an Ubbelohde viscometer. Attenuated

total reflectance (ATR) spectra were obtained on a Bomem DA 3.002 FTIR instrument at  $2\text{ cm}^{-1}$  resolution, with KRS-5 being used as an internal reflection element. Strips of supported film  $5 \times 0.5\text{ cm}^2$  were placed inside the ATR cell on each side of the crystal (KRS-5) so that the film surface was in contact with the crystal face. In a typical experiment, 100 scans per sample were averaged. Ultraviolet (UV) spectra were recorded on a Varian DMS 300 UV-visible spectrophotometer. The morphology of the film was measured with a Philips 515 scanning electron microscope (SEM).

### Interfacial Polycondensation

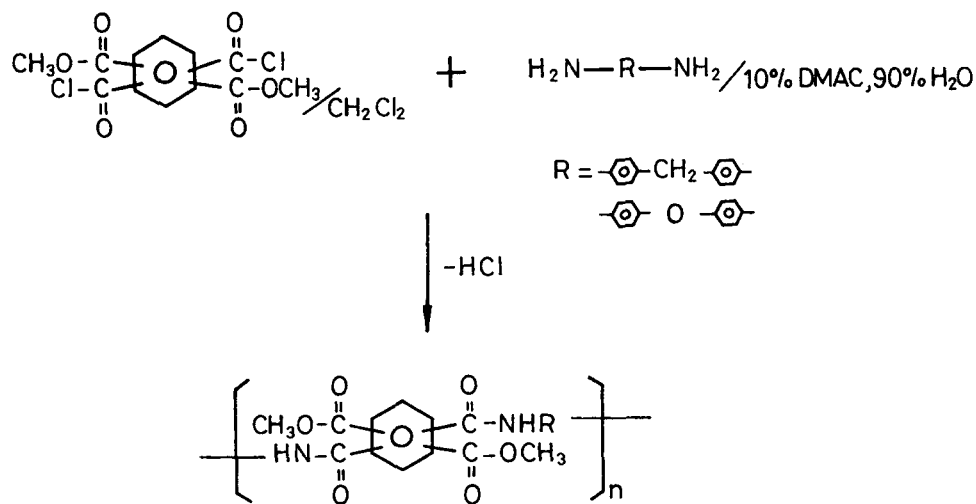
We dissolved the required amount of DCMTC in dichloromethane at 0.009*M* concentration, typically, and the diamine in 10% DMAc, 90% H<sub>2</sub>O. We used a 50-mL graduated cylinder to take 40 mL of DCMTC solution and place it into the bottom of a beaker 9 cm in diameter. Next, with a 50-mL syringe we took 40 mL of the diamine solution and injected it onto the surface of the DCMTC solution along the lining walls of the beaker. Then we proceeded with the interfacial condensation under the required conditions. The film made by interfacial polycondensation was rinsed with 0.001*N* of aqueous NaOH, then rinsed with dichloromethane until no more dissolved substances appeared. Three rinses were required for each film. Then the film was vacuum-dried, and the dry film was heated at 240°C in a nitrogen atmosphere to acquire the polyimide. The typical reaction is shown in Scheme 1.

Since the solubility of diamines in water is poor, the diamines were dissolved in 10% (v/v) of the DMAc<sub>(aq)</sub>, which would not mix with the dichloromethane. This was used as the solvent for the water phase, and a well-defined two-phase system resulted.

In the diamine competitive interfacial copolycondensation, the concentration of the ODA solution was equal to the concentration of the MDA solution, i.e., 0.0045*M*. Other procedures were the same as those described above.

### Interfacial Films Extracted by 66% DMAc<sub>(aq)</sub>

The film acquired by interfacial polycondensation was soaked with 66% DMAc in H<sub>2</sub>O for 1 h at ambient temperature. During this time, we observed that the interfacial film had contracted partially. The film was removed, and then rinsed 10 times with distilled water. The interfacial film was placed on Teflon film. Next, a current of natural air was



Scheme 1

blown onto the film overnight in order to dry it. After that, the film was vacuum-dried.

#### Soluble-diffusive Experiment of Monomer

We prepared 0.009M of the diamine in 10% DMAC, 90% H<sub>2</sub>O. We used a 100-mL graduated cylinder to take 90 mL of dichloromethane and place it into the bottom of a beaker 9 cm in diameter. Next, we used a 100-mL syringe to take 90 mL of the diamine solution and inject it onto the surface of the dichloromethane along the lining walls of the beaker. After the desired time, we used a 5-ml syringe to draw out 1 mL of dichloromethane solution from 1 cm below the interface. This was then diluted through UV to measure the concentration of diamine, using a 302-nm wavelength under the ODA system and 293-nm wavelength under the MDA system.

## RESULTS AND DISCUSSION

#### ATR Optical Density Determination of Chemical-Structure Difference between the Films' Two Sides

Beer's law is expressed as

$$A = \epsilon dc \quad (1)$$

where  $A$  is the optical density of the characteristic absorption of the sample,  $\epsilon$  is the absorption coefficient of the sample,  $d$  is the thickness of the sample, and  $c$  is the concentration of the sample.

Taking the ratio of specified optical densities, we obtain

$$\left[ \frac{A_{1662}}{A_{1728}} \right]_{\text{H}_2\text{O}} = \left[ \frac{\epsilon_{1662} d C_{1662}}{\epsilon_{1728} d C_{1728}} \right]_{\text{H}_2\text{O}} = \left[ \frac{\epsilon_{1662} C_{1662}}{\epsilon_{1728} C_{1728}} \right]_{\text{H}_2\text{O}} \quad (2)$$

where  $A_{1662}$  is the optical density of the interfacial film at 1662 cm<sup>-1</sup> (amide, C=O),  $A_{1728}$  is the optical density of the film at 1728 cm<sup>-1</sup> (acid or ester, C=O). The subscript "H<sub>2</sub>O" indicates the surface of the interfacial film adjacent to the water phase.

Under the same reasoning, the optical density ratio for the surface of the interfacial film adjacent to the organic phase could be expressed in eq. (3).

$$\left[ \frac{A_{1662}}{A_{1728}} \right]_{\text{CH}_2\text{Cl}_2} = \left[ \frac{\epsilon_{1662} C_{1662}}{\epsilon_{1728} C_{1728}} \right]_{\text{CH}_2\text{Cl}_2} \quad (3)$$

Dividing eq. (3) by eq. (2), we get eq. (4):

$$R = \frac{\left[ \frac{A_{1662}}{A_{1728}} \right]_{\text{H}_2\text{O}}}{\left[ \frac{A_{1662}}{A_{1728}} \right]_{\text{CH}_2\text{Cl}_2}} = \frac{\left[ \frac{\epsilon_{1662} C_{1662}}{\epsilon_{1728} C_{1728}} \right]_{\text{H}_2\text{O}}}{\left[ \frac{\epsilon_{1662} C_{1662}}{\epsilon_{1728} C_{1728}} \right]_{\text{CH}_2\text{Cl}_2}} = \frac{\left[ \frac{C_{1662}}{C_{1728}} \right]_{\text{H}_2\text{O}}}{\left[ \frac{C_{1662}}{C_{1728}} \right]_{\text{CH}_2\text{Cl}_2}} \quad (4)$$

**Table I Optical Density Ratio from ATR Spectra of Poly(DCMTC-MDA)**

Interfacial Film	$A_{1662}$	$A_{1728}$	$A_{1662}/A_{1728}$	R
The surface facing water phase	0.0389	0.0371	1.05	1.1
The surface facing organic phase	0.0621	0.0637	0.97	

Polymerization conditions: [DCMTC] = [MDA] = 0.009M, [Na<sub>2</sub>CO<sub>3</sub>] = 0.0021M, 0°C, 30 min.

Equation (4) indicates the difference in the chemical structures between the surface of the interfacial films adjacent to the organic phase and the surface of the interfacial films adjacent to the water phase. If there is no difference in the chemical structures between the two surfaces, the *R* value is 1; the greater the difference in chemical structure between the two surfaces, the farther the *R* value is from 1. The *R* through eq. (4) under various reaction conditions was calculated as shown in Tables I and II.

#### FTIR Optical Density Evaluation of Copolymer Composition Ratio

The chemical structure containing repeat units of the imidized polymer is shown in Figure 1. Assuming that the characteristic absorption of functional groups complies with Beer's law, from infrared (IR) spectra in Figure 2, through deconvolution technique, and using eq. (5), we might calculate the composition ratio of copolymer shown in Table III.

$$\frac{\left[\frac{A_{1250}}{A_{1500}}\right]_{\text{co}}}{\left[\frac{A_{1250}}{A_{1500}}\right]_{\text{homo}}} = \frac{\left[\frac{C_{1250}}{C_{1500}}\right]_{\text{co}}}{\left[\frac{C_{1250}}{C_{1500}}\right]_{\text{homo}}} = \frac{\frac{y}{3x + 3y}}{\frac{1}{3}} = \frac{y}{x + y} \quad (5)$$

where  $A_{1250}$  is the optical density of the interfacial film at 1250 cm<sup>-1</sup> (ether, C=O), and  $A_{1500}$  is the optical density of the film at 1500 cm<sup>-1</sup> (aromatic, C=C). The subscript "homo" indicates a homopolymer system, and the subscript "co" indicates a copolymer system. The *x* and *y* were shown in Figure

1. The copolymer was prepared via a competitive interfacial polycondensation under the same concentrations of ODA and MDA.

#### Effect of Reaction Conditions on Films' Inherent Viscosity

The result in Figure 3 shows that the inherent viscosity of either poly(DCMTC-ODA) or poly(DCMTC-MDA) increases as the concentrations of the monomers increase. It is attributed to the higher collision rate between acid chloride and amine, so that a higher inherent viscosity of the film was obtained. When the concentration of diamine was lower, the hydrolysis side reaction of acyl chloride (DCMTC) on the interface might be more competitive, and the inherent viscosity of the interfacial film was reduced.

The result in Figure 4 shows that under the poly(DCMTC-MDA) system when (DCMTC)/(MDA) = 1, the inherent viscosity of the interfacial polymer obtained was the highest. In the poly(DCMTC-ODA) system, when the concentration ratio between DCMTC and ODA was about 2:1, the inherent viscosity of the interfacial polymer obtained was the highest. This means that there was an optimum concentration ratio of monomer in both systems. This may be because if the concentration DCMTC is too high, the hydrolysis side reaction for the functional groups of acid chloride increases, producing even more acid-ester chain ends. Thus the molecular weight of the resulting interfacial film cannot continue to grow. When the concentration of DCMTC is too low, more diamine monomers exist on the interface, preventing further polymerization

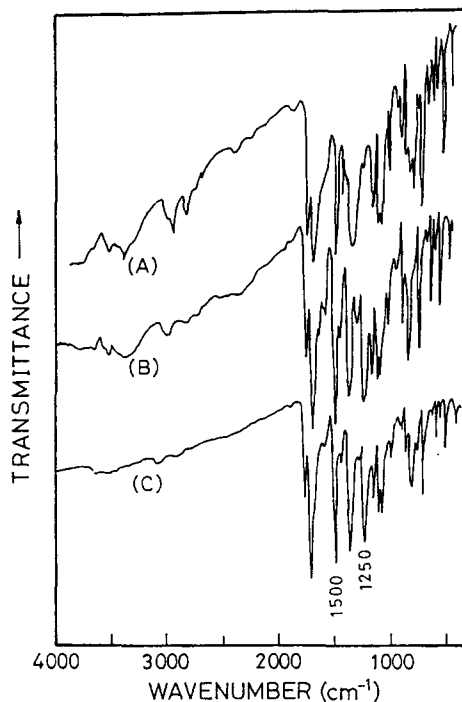
**Table II Optical Density Ratio from ATR Spectra of Poly(DCMTC-MDA) Rinsed with 66% DMAc<sub>(aq)</sub>**

Interfacial Film	$A_{1662}$	$A_{1728}$	$A_{1662}/A_{1728}$	R
The surface facing water phase	0.0402	0.0366	1.10	1.05
The surface facing organic phase	0.0465	0.0441	1.05	

Polymerization conditions: [DCMTC] = [MDA] = 0.009M, [Na<sub>2</sub>CO<sub>3</sub>] = 0.0021M, 0°C, 30 min.

of the resulting interfacial film. As to the difference between the most suitable concentration ratios of monomer between poly(DCMTC-ODA) and poly(DCMTC-MDA), the reason is shown in Tables III and IV. Referring to Table IV, we found that the rate of the ODA soluble-diffusing in dichloromethane is approximately twice as fast as that of the MDA soluble-diffusing in dichloromethane. From the composition of the copolymer in Table III, we also find that in conducting a competitive interfacial copolycondensation under the same concentrations of ODA and MDA, the quantity of chemical structures containing repeat units of poly(DCMTC-ODA) in the copolymer film formed is approximately 2.43 times that of poly(DCMTC-MDA). From these results, we can understand that the reason for the difference in the suitable concentration of monomer between the poly(DCMTC-ODA) and the poly(DCMTC-MDA) is mainly due to the difference in the soluble-diffusion rate of diamines. Therefore, different systems have different suitable concentration ratios of monomer for interfacial polycondensation.

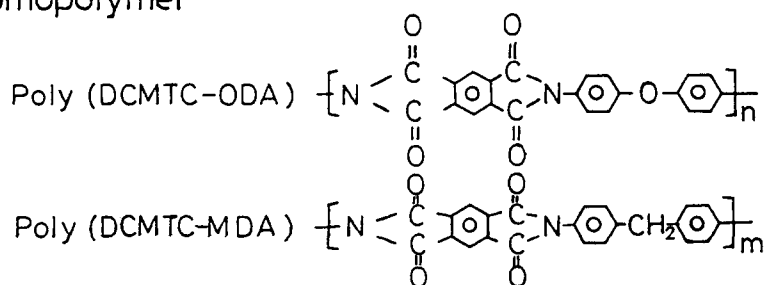
Referring to Figure 5, we found that there was a suitable concentration range for adding sodium carbonate to either poly(DCMTC-ODA) or poly(DCMTC-MDA) system. Adding an appropriate amount of sodium carbonate could neutralize the hydrogen chloride produced during interfacial polycondensation. It could therefore suppress the hydrolysis side reaction, and thus a higher molecular weight of interfacial polymer could be obtained. But



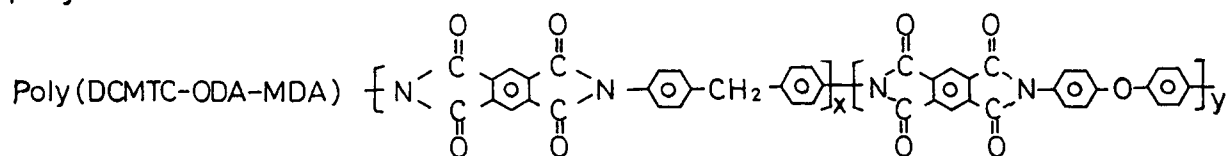
**Figure 2** FTIR spectra of polyimide film. (A) Poly(DCMTC-MDA); (B) poly(DCMTC-ODA); (C) poly(DCMTC-ODA-MDA).

when excessive sodium carbonate is added, the excess of sodium carbonate present could promote the weak nucleophilic reagent water under hydrolysis of nucleophilic substitution. That is, it accelerated hydrolysis so that the molecular weight of interfacial polymer was lower.

### Homopolymer



### Copolymer



**Figure 1** The chemical structure containing repeat units of the polymer.

**Table III Optical Density Ratio from FTIR Spectra of Copolymer and Homopolymer**

Polymer	$A_{1250}$	$A_{1500}$	$A_{1250}/A_{1500}$	$y/x^a$
Co <sup>b</sup>	0.237	0.447	0.529	2.43
Homo <sup>c</sup>	0.068	0.084	0.746	

<sup>a</sup> The ratio between the chemical-structure-containing repeat unit of poly(DCMTC-ODA) and the chemical-structure-containing repeat unit of poly(DCMTC-MDA) in the copolymer film.

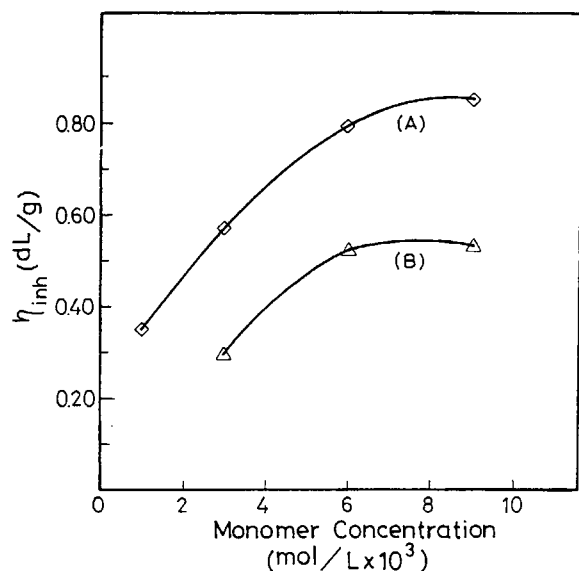
<sup>b</sup> Poly(DCMTC-ODA-MDA).

<sup>c</sup> Poly(DCMTC-ODA).

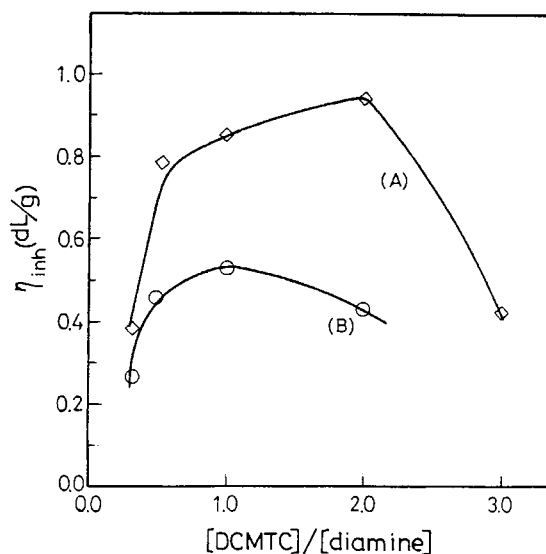
Referring to Figure 6, we find that the inherent viscosity of the interfacial polymer formed from either poly(DCMTC-ODA) or poly(DCMTC-MDA) system had a suitable concentration range for adding benzyltriethylammonium chloride (BTEAC). BTEAC assists the transfer of diamine from the water phase to the organic phase, increasing the formation rate of the interfacial film. From this we can see that the diffusion plays a very important role in interfacial polycondensation. But when excess BTEAC was added, the hydrolysis was increased by IR spectroscopic characterization of end groups. It is probably because BTEAC also promotes the diffusion of water molecules, because increasing the hydrolysis side reaction lowers the molecular weight of the interfacial film.

### Behavior of Interfacial Polycondensation

In interfacial polycondensation below 20°C, we observed that bubbles accumulated below the interfacial film and that the accumulation of bubbles increased over time. We also observed that the accumulation of bubbles increased when the thickness of the film increased. When the temperature was higher, the diffusion of monomer and the rate of reaction increased so that the interfacial film was formed faster. The hydrogen chloride produced by the reaction had to dissolve into the water phase and diffuse out. The hindrance of the film showed this procedure, creating a pileup of bubbles in the organic phase. These bubbles were produced on the surface of the film on the organic phase side, and the indicated pH was about 2-3. Therefore, the bub-



**Figure 3** Effect of monomer concentration on interfacial condensation (polymerization conditions: 0°C, 30 min). (A) Poly(DCMTC-ODA): [ODA] = [DCMTC], [Na<sub>2</sub>CO<sub>3</sub>] = 0.0021M; (B) poly(DCMTC-MDA): [MDA] = [DCMTC], [Na<sub>2</sub>CO<sub>3</sub>] = 0.0021M.



**Figure 4** Effect of monomer-concentration ratio on interfacial condensation (polymerization conditions: [Na<sub>2</sub>CO<sub>3</sub>] = 0.0021M, 30 min). (A) Poly(DCMTC-ODA): [ODA] = 0.009M, at 0°C; (B) poly(DCMTC-MDA): [MDA] = 0.009M, at 0°C.

**Table IV** Effect of Diffusion for Diamine at 0°C

Time (min)	[ODA] <sup>a</sup> × 10 <sup>5</sup> (M)	[MDA] <sup>b</sup> × 10 <sup>5</sup> (M)
2	37.8	19.6
5	78.6	34.4
10	165.4	73.2

<sup>a</sup> Sample taken: 1 cc at 1 cm below interface position.

<sup>b</sup> Initial diamine concentration in water phase: 0.009M.

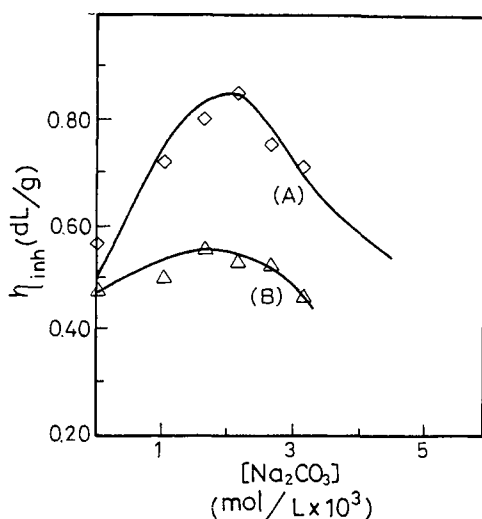
bles were possibly hydrogen chloride vapor produced by the interfacial reaction.

At low temperatures, the rate of reaction decreased so that the interfacial film was formed more slowly. Therefore, the hydrogen chloride produced by the reaction was dissolved into the water phase and diffused out, so that the accumulation of bubbles was not observed. From the above result, we understand that the bubbles were formed in the organic phase below the interfacial film. Therefore, the interfacial polycondensation of this system possibly occurred in the organic phase.

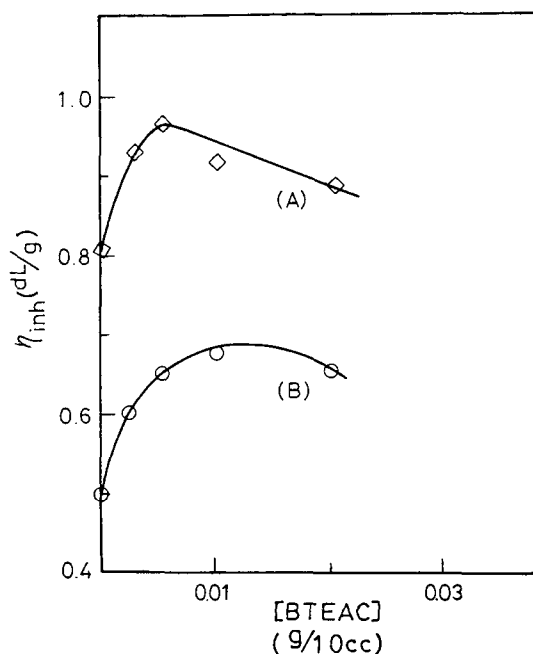
### Morphology and Chemical Structure of Interfacial Films

Figure 7 shows the ATR spectra of the interfacial film under different conditions. In this experiment, we pulled up the Teflon dish to hold the film produced by the polycondensation, thus enabling both

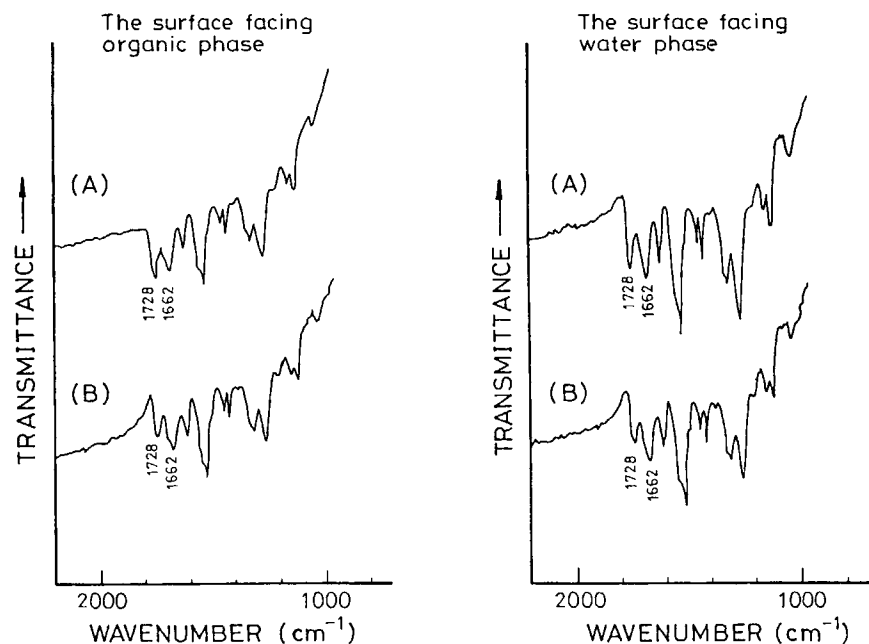
sides of the film to remain in a stable position. The detailed procedures were shown in our previous study.<sup>20</sup> We assume that the characteristic absorption of functional groups complied with Beer's law. From the results in Figure 7, and using eqs. (1) to (4), we calculated the optical density ratio of the characteristic absorption of the functional groups. The results are arranged in Tables I and II. Comparing the values of  $(A_{1662}/A_{1728})_{\text{H}_2\text{O}}$  and  $(A_{1662}/A_{1728})_{\text{CH}_2\text{Cl}_2}$  in Table I, we understand that the chemical structure of the surface of the films adjacent to the water phase showed more characteristic absorption of the amide groups. The chemical structure of the surface of the films adjacent to the organic phase showed more characteristic absorption of the



**Figure 5** Effect of sodium carbonate on interfacial condensation at 0°C for 30 min. (A) Poly(DCMTC-ODA): [ODA] = [DCMTC] = 0.009M; (B) poly(DCMTC-MDA): [MDA] = [DCMTC] = 0.009M.



**Figure 6** Effect of phase-transfer-catalyst concentration on interfacial condensation (polymerization conditions: 0°C, 3 min). (A) Poly(DCMTC-ODA): [ODA] = [DCMTC] = 0.009M; (B) poly(DCMTC-MDA): [MDA] = [DCMTC] = 0.009M.



**Figure 7** ATR spectra obtained from both sides of poly(DCMTC-MDA) films. (A) Not rinsed; (B) rinsed with 66% DMAC<sub>(aq)</sub>.

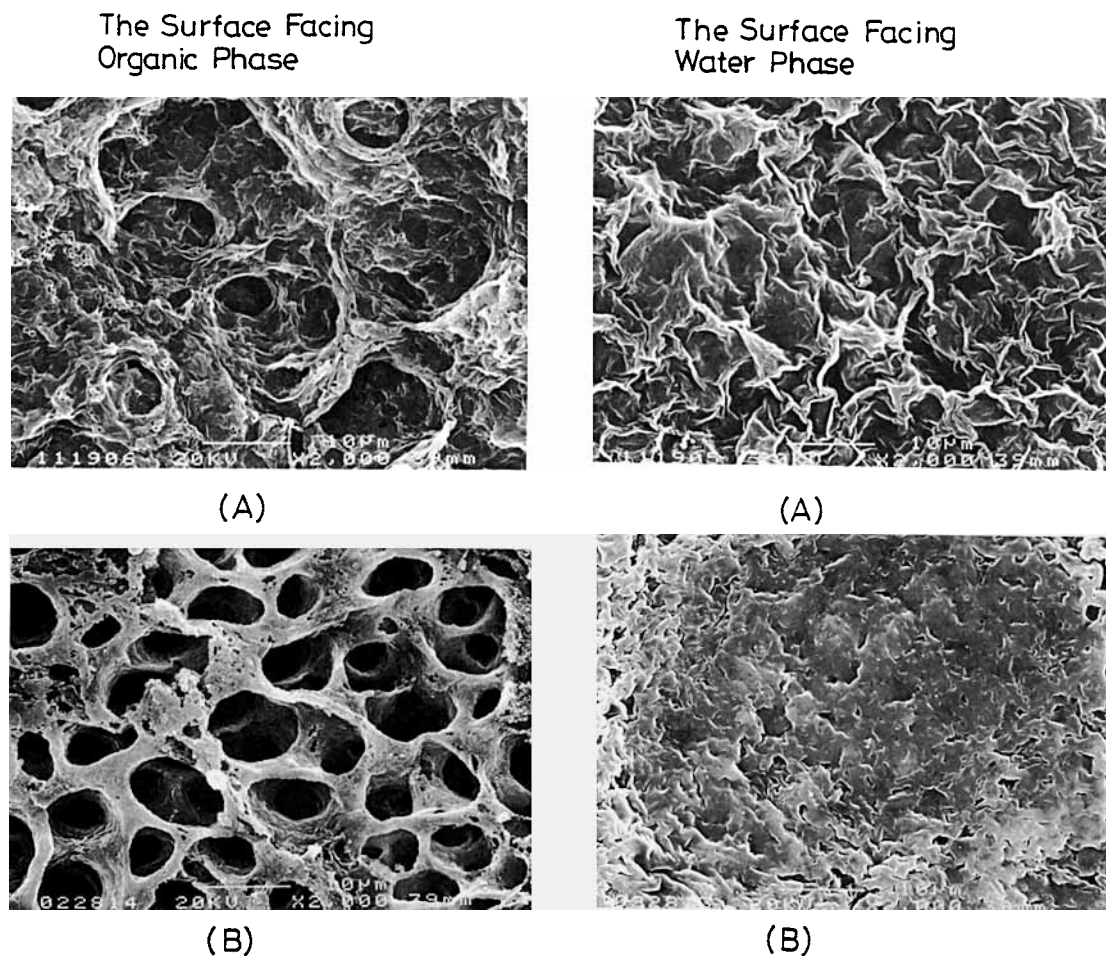
acid groups. The reasons for the different chemical structures on the two sides of the film were the characteristic features of this interfacial polycondensation: (1) the hydrogen chloride produced by the interfacial reaction was dissolved almost completely into the water phase and diffused out during the initial reaction stage; (2) the reactivity and solubility of the diamine are greater than those of water, and the amidation from DCMTC and the diamine is the primary reaction at the initial stage; (3) the concentration of diamine on the interface adjacent to the organic phase was very low during the later stages of the reaction; (4) the diamine and the hydrogen chloride diffused slowly due to the hindrance of the interfacial film at the later reaction stages; and (5) the slow diffusion in reason 4 created a pileup of hydrogen chloride in the organic phase adjacent to the film, and so hydrolysis of DCMTC was increased at the later reaction stages. This also proved that the film was growing toward the organic phase from the interface region until the reaction was over.

From the SEM photos in Figure 8, we observed that the morphology of the surface of the films adjacent to the water phase was denser. This dense morphology may be due to homogeneous reaction at the initial reaction stage, proceeding mostly from the amidation from DCMTC and the diamine. However, the morphology of the surface of the films adjacent to the organic phase was loose and porous.

This porous morphology may be due to heterogeneous reaction at the later reaction stages, proceeding from the amidation and the hydrolysis side reaction. Owing to the hindrance of the interfacial film at the later reaction stages, which created a pileup of hydrogen chloride in the organic phase adjacent to the film, the hydrolysis of DCMTC was increased. Once hydrolysis had occurred in the chain end of polymers, the hydrolysis chain end of the polymers was inactive in polycondensation. Therefore the molecular weight of polymer could not grow, which resulted in more pores in the film. A typical reaction is shown in Scheme 2.

The interfacial films extracted by 66% DMAc in H<sub>2</sub>O solution, and the results, are arranged in Table V. We observed that, in both poly(DCMTC-ODA) and poly(DCMTC-MDA) systems, the inherent viscosity of the interfacial polymer increased after extraction. Comparing the *R* values of the polymers in Tables I and II, we find that the difference in chemical structure of the two sides of the films extracted with 66% DMAc<sub>(aq)</sub> is smaller than that of the films extracted without 66% DMAc<sub>(aq)</sub>. Due to increased inherent viscosity of the polymer extracted with 66% DMAc<sub>(aq)</sub> (shown in Table V), we understand that the polymer of smaller molecular weight was removed from the interfacial film in this procedure. The reason for the change in the different chemical structures of the two sides of the film was





**Figure 8** SEM photomicrographs from both sides of poly(DCMTC-ODA) films. (A) Not rinsed; (B) rinsed with 66% DMAC<sub>(aq)</sub>.

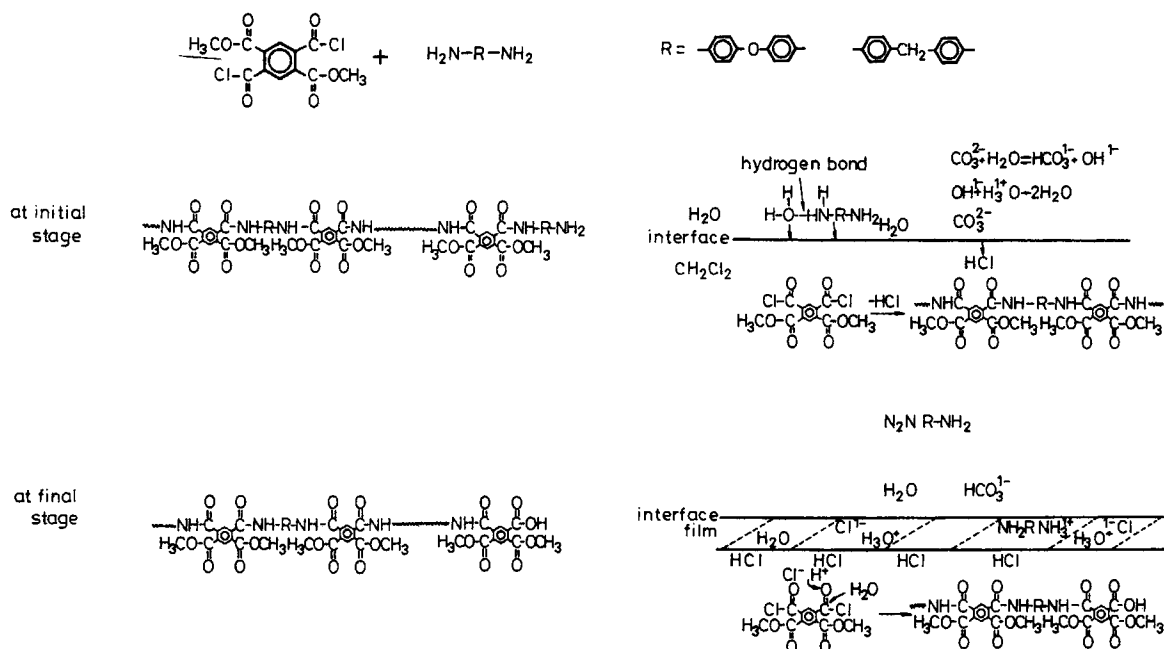
the extraction of the polymer of smaller molecular weight. The surface of the films adjacent to the organic phase contained a high quantity of the polymer with small molecular weight, formed via hydrolysis, than the surface of the films adjacent to the water phase. Because the polymer of small molecular weight was removed, the chemical structures of the two sides of the film became similar. The SEM photo in Figure 8 shows that after extraction, the pores on the surface of the film adjacent to the organic phase became larger in morphology. This clearly shows that more polymers were being removed from the surface of the film adjacent to the organic phase.

Summing up the above results, we understand that the film formation started from the interface and grew toward the organic phase. The surfaces of the films adjacent to the water phase were denser and composed of higher average molecular weight polymer than the surfaces of the films adjacent to

the organic phase. In other words, the surfaces of the films adjacent to the organic phase were composed of lower average molecular weight polymer with high porosity. The molecular weight at the organic side could be lower due to depletion of the diamine. Thus, the hydrolysis side reaction became a stronger factor. Therefore, the low molecular weight at the organic side might be due to the hydrolysis side reaction.

## CONCLUSIONS

In the poly(DCMTC-ODA) system, the concentration ratio between DCMTC and ODA was about 2 : 1, and the interfacial film obtained had the highest inherent viscosity. When the concentration of DCMTC was equal to the concentration of MDA, the interfacial film obtained had the highest inherent



Scheme 2

viscosity. The difference between the two was mainly due to the difference in the soluble-diffusive rate of the diamines. The addition of sodium carbonate could suppress the hydrolysis but an excess of sodium carbonate promoted the hydrolysis of acyl chloride (DCMTC). The addition of BTEAC promoted the diffusion of the diamine and water, and therefore an excess of BTEAC would accelerate the hydrolysis of acyl chloride (DCMTC).

The film grew toward the organic phase from the interface region until the reaction was over. The surface of the films adjacent to the water phase was composed of higher average molecular weight polymer and was denser in morphology. However, the surface of the films adjacent to the organic phase

was composed of lower average molecular weight polymer with high porosity. This might be attributed to the hydrolysis side reaction.

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**Table V** The Viscosity of Interfacial Films Rinsed with 66% DMAc<sub>(aq)</sub>

MDA <sup>a</sup> (M)	ODA <sup>b</sup> (M)	Rinsed with 66% DMAc <sub>(aq)</sub>	$\eta_{inh}$ (dL/g) <sup>c</sup>
0.009	—	No	0.53
0.009	—	Yes	0.58
—	0.009	No	0.85
—	0.009	Yes	0.90

Interfacial conditions: 0°C, 30 min, [Na<sub>2</sub>CO<sub>3</sub>] = 0.0021M.

<sup>a</sup> [MDA] = [DCMTC] = 0.009M.

<sup>b</sup> [ODA] = [DCMTC] = 0.009M.

<sup>c</sup> Measured at 30°C at a concentration of 0.5 g/dL in DMAc.

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