

Interfacial Polyfunctional Condensation: Effect of the Reaction Conditions

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SYNOPSIS

1,2,4,5-Benzenetetra acyl chloride (BTAC) was prepared from pyromellitic anhydride and phosphoric chloride. The behavior in interfacial polycondensation of 4,4'-methylene dianiline (MDA) or ethylene diamine (EDA) in water with BTAC in dichloromethane with tetrabutyl ammonium chloride (TBAC) as the catalyst was examined with Fourier transform infrared spectroscopy (FTIR), fast atom bombardment mass spectroscopy (FABMS), and scanning electron microscope (SEM). A heat-resistant film can be obtained by successive heating of the resulting thin films.

Because BTAC is a tetrafunctional compound with high reactivity, the interfacial reaction is a competitive reaction of hydrolysis and amidation among the reacting groups. The optical density of FTIR spectra was employed for calculating the percentage of hydrolysis. The hydrolysis is suppressed when (1) the temperature is decreased, (2) sodium carbonate is added, (3) the proportion on the concentration of diamine is increased relative to the concentration of BTAC, (4) the diamine solution is agitated, and (5) TBAC is added to the diamine (aq).

The percentage of hydrolysis can be controlled at will, e.g., 50%. A high-resistant polyimide can be prepared through thermal treatment in a nitrogen atmosphere. By increasing the concentration of the reactants or using a good solvent, the film obtained is thicker, but in our system, the maximum thickness of the film seldom exceeded 20 μm .

INTRODUCTION

Under high temperatures, polyimide maintains excellent mechanical properties and chemical stability, so it is widely applicable to the aviation and electronics industries. However, at present, the separation industry also requires films that can sustain higher temperatures and organic solvents. Ordinary organic materials cannot meet these requirements. These are reports about using polyimide as a separation membrane. This research covers purification and concentration of organic solvents,¹ hydrogen recovery,² separation of helium and nitrogen,³ and high selectivity in the separation of carbon dioxide and methane.⁴⁻¹¹

DuPont first filed for a patent¹² on the synthesis of aromatic polyimide in 1955. Quite a lot of

research¹³⁻¹⁵ has been done concerning modification of the heat resistance and the processing properties of polyimide. Yet, so far, no one has used interfacial polymerization to synthesize polyimide. Also, the method of interface polymerization can be applied to preparing composition membranes,¹⁶⁻¹⁸ which provides higher selectivity without severely reducing membrane flux. This method is attempted for preparing polyimide membranes in this study.

Interfacial polycondensation has been reported in the literature. Most of these studies¹⁹⁻²¹ characterize the interfacial reaction of difunctional reagents and do not report on the reaction of polyfunctional reagents. In this research, the interfacial polycondensation of BTAC dissolved in dichloromethane with the diamine in water was studied. By altering various factors, such as adding a phase transfer agent, changing the temperature, adjusting PH value, applying agitation, and changing the composition, the chemical structure of the films is controlled. Heat-resistant polyimide films were prepared therefrom.

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EXPERIMENTAL

Reagents and Solvents

Methylene dianiline (MDA) was recrystallized from isopropyl alcohol. Pyromellitic dianhydride (PMDA) was purified by recrystallization with dry acetic anhydride. Ethylene diamine (EDA) was distilled at normal pressure before use. Acetic anhydride was dried by refluxing and fractional distillation over sodium acetate. Dichloromethane was dried with 4 Å molecular sieves and was stored over molecular sieves until use. Methanol was dried with 3 Å molecular sieves and was also stored over molecular sieves until use. All the solvents used were purified in the usual manner. All other reagents were of analytical grade.

Characterization

A Perkin-Elmer 1760-X FTIR spectrophotometer was used to record the spectra of KBr pellets. In a typical experiment, 20 scans per sample were averaged. For each KBr pellet, the assigned concentration of sample proportioned to KBr was 1.8:100.

A JEOL JMS-D300 mass spectrometer was used for the mass distribution studies. FABMS spectra were obtained by using a JEOL JMS-HX 110 mass spectrometer.

^{13}C -nuclear magnetic resonance spectra were recorded on a Bruker AM-300WB Fourier transform nuclear magnetic resonance (FT-NMR) spectrometer using tetramethyl silane (TMS) as the internal standard and dimethyl sulfoxide- d_6 (DMSO- d_6) as the solvent.

A Perkin-Elmer 240C elemental analyzer was used for elemental analysis. Melting points were determined by an electrothermal Buchi 510 melting point apparatus. The thickness of the film was measured with a PHILIPS 515 scanning electron microscope.

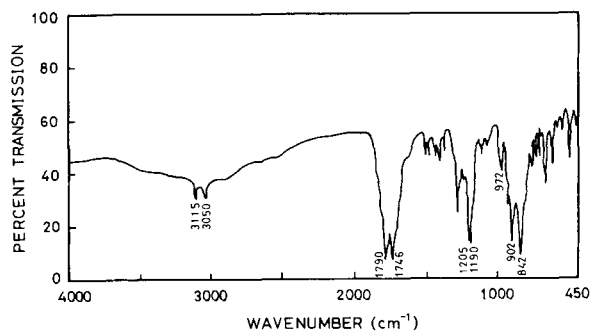


Figure 1 FTIR spectrum of BTAC.

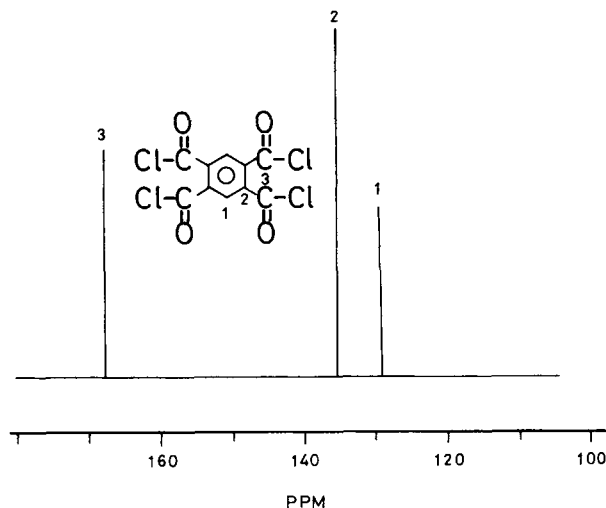


Figure 2 ^{13}C -NMR spectrum of BTAC.

Solvent Extraction

The extent of curing was tested by extraction with *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAC), and *N*-methylpyrrolidone (NMP), respectively, at room temperature^{22,23} or at high temperatures.

Preparation of 1,2,4,5-Benzenetetracarboxylic Acid Chloride (BTAC)

A mixture of 22 g of pyromellitic anhydride and 46 g of phosphoric chloride was placed in a 150 mL round-bottomed flask. The flask was equipped with a reflux condenser, the upper end of which was provided with a calcium chloride tube, and the side arm of the flask was closed with a cork. The reagents were mixed by shaking the flask and then slowly heating it. After heating in an oil bath of 160°C for 10 h, the air condenser and stopper in the end of the side arm were removed and a condenser was connected to the flask. The temperature was then raised gradually to 250°C; in the meantime, most of the phosphorous oxychloride was distilled into a receptacle. The liquid residue was distilled under reduced pressure. A little quantity of phosphorous oxychloride was distilled at the beginning, then the BTAC was distilled at the temperature of the oil bath at 220°C. The yield of colorless BTAC was 29 g (88% of the theoretical amount): mp 69–70°C; IR (KBr) cm^{-1} (Fig. 1): 3050–3115 (aromatic C–H), 1790 (C=O of the acylchloride), 1746 (C=O), 1510 (aromatic C=C), 972 (acid chloride), 1190, 902, 846 (aromatic substitute); ^{13}C -NMR (DMSO- d_6) ppm (Fig. 2): 167.6 (C=O), 135.5 (Ar), 129

Table I Condition of Interfacial Polymerization

Notation	Water Phase		
	TBAC (g/10 cc)	Na ₂ CO ₃ (g/10 cc)	Rate of Stirring (rpm)
UCUB	0	0	0
2 CLUB	0.02	0	0
1 CLUB	0.01	0	0
4 CLUB	0.04	0	0
UCB	0	0.265	0
UCUB(US)	0	0	200
2 CLUB(US)	0.02	0	200

(Ar, CH); mass: 291 (as it is subject to breaking, there is no molecular ion peak absorption, but it is cut one chromium atom); elemental analysis: C: 36.7%, H: 0.5%, Cl: 62.8%.

Preparation of Polyamic Acid

A mixture of 0.05 mol of pyromellitic anhydride dissolved in 30 mL of methanol and 0.05 mol of MDA in 30 mL methanol was placed in a 100 cc round-bottomed flask. The solution reacted in a nitrogen atmosphere at room temperature with stirring for 12 h. The solution was filtered and methanol used to rinse the filter cake. After vacuum drying, a yellowish powder was obtained. KBr pellet for IR analysis was obtained therefrom.

Aliphatic polyamic acid: The process is the same as that mentioned above, except that ethylene diamine is used instead of MDA. A whitish powder was obtained. KBr pellet for IR analysis was obtained therefrom.

Interfacial Polycondensation

We dissolved BTAC of the required concentration in dichloromethane and dissolved diamine (MDA or EDA) in water, then used a 10 mL pipet to take 10 mL of the BTAC solution and insert it into a 50 mL beaker. Next, we used a 10 mL syringe to take 10 mL of the diamine solution and inject it onto the surface of the BTAC solution along the lining walls of the beaker. Then we proceeded with interfacial polycondensation under the required conditions. The film acquired by interfacial polycondensation was rinsed with 0.001N of NaOH (aq), 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 obtained here was heated at 240°C in a nitrogen atmosphere to acquire the polyimide.

The solvents used for altering the organic phase included dichloromethane, chloroform, cyclohexane, and *n*-hexane. The various reacting conditions in the water phase is shown in Table I.

Since the solubility of the MDA in water is poor, the MDA was dissolved in 20 v/v % of the tetrahydrofuran (THF) (aq). The solution of 20 v/v % of the THF (aq) and the dichloromethane will not mix with each other; it was used as the solvent for the water phase, and a well-defined two-phase system resulted.

RESULTS AND DISCUSSION

Chemical Structure Analysis by FTIR and Solvent Extraction

As referred to in Figure 3(A), FTIR spectra of these films confirmed the presence of amic acid structure by characteristic absorptions²⁴⁻²⁶ at 3000–3500 (OH), 3280 (NH), 1720 (acid, C=O), 1655 (amide, C=O), and 1540 cm⁻¹ (NH).

The dry films are insoluble in solvents of NMP, DMAC, and DMF at room temperature and soluble

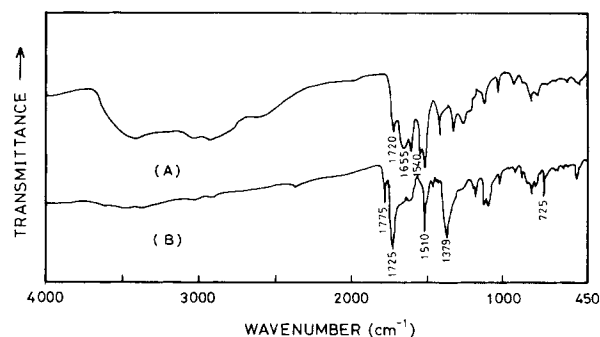


Figure 3 FTIR spectra of poly(BTAC-MDA) films on thermal treatment. (A) Before thermal treatment; (B) 6 h at 180°C and 10 h at 240°C.

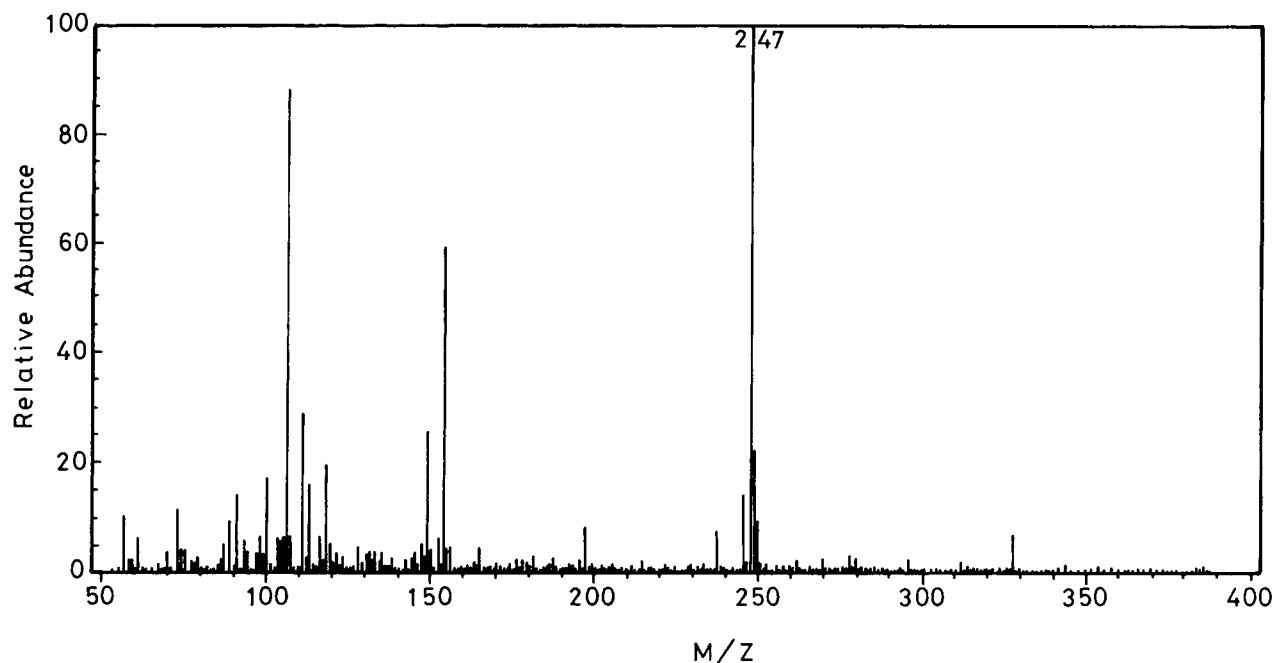


Figure 4 FABMS (Pos.) spectrum of poly(BTAC-MDA) film dissolved in NMP at 160–170°C.

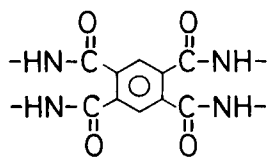
in NMP at temperatures of 160–170°C. Through FABMS analysis (Fig. 4), the maximum molecular weight when the film pyrolyzed was about 300. The molecular ion peak showed up at 246. From the FABMS and the FTIR spectrum [Fig. 3(a)], it was determined that the film had pyrolyzed into Structure I. The cross linking structure of the film was partially made with this unit.

Summarizing the analytic results of FTIR and solvent extraction, the possible reaction as shown by Scheme I may be arrived at.

Percentage of Hydrolysis Determined with Optical Density from FTIR

Beer's law is expressed as

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

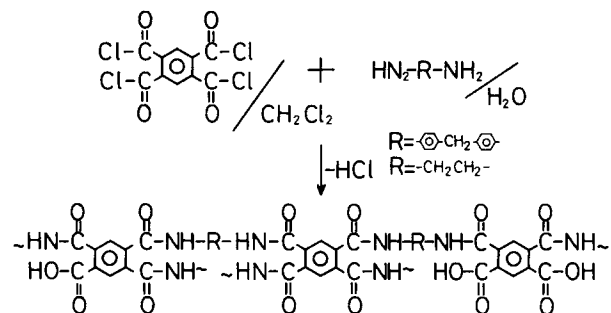


Structure I

where A is the optical density of the characteristic absorption of the sample, ϵ 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

$$\frac{A_{1720}/A_{1510}}{A'_{1720}/A'_{1510}} = \frac{\frac{\epsilon_{1720}dc_{1720}}{\epsilon_{1510}dc_{1510}}}{\frac{\epsilon_{1720}d'c'_{1720}}{\epsilon_{1510}d'c'_{1510}}} = \frac{c_{1720}/c_{1510}}{c'_{1720}/c'_{1510}} \quad (2)$$



Scheme I

Table II Percentage of Hydrolysis for Poly(BTAC-EDA)^a System

Sample	$\frac{A_{1720 \text{ cm}^{-1}}}{A_{1510 \text{ cm}^{-1}}}$	$\frac{A_{1540 \text{ cm}^{-1}}}{A_{1510 \text{ cm}^{-1}}}$	$100 \times Hy$
Polyamic acid	1.30	1.60	50.0
UCUB	1.23	1.94	43.8
UCUB(US)	0.76	1.82	34.0
2 CLUB	0.80	1.98	33.2
2 CLUB(US)	0.77	2.08	31.4
UCB	trace	2.50	trace

^a Polymerization condition: 20°C, [BTAC] = [EDA] = 0.101 M.

Table III Percentage Hydrolysis for Poly(BTAC-MDA)^a System

Sample	$\frac{A_{1720 \text{ cm}^{-1}}}{A_{1510 \text{ cm}^{-1}}}$	$\frac{A_{1540 \text{ cm}^{-1}}}{A_{1510 \text{ cm}^{-1}}}$	$100 \times Hy$
Polyamic acid	0.463	0.764	50.0
UCUB	0.384	0.830	43.3
UCUB(US)	0.362	0.804	42.6
2 CLUB(US)	0.131	0.980	18.1
1 CLUB	0.316	0.810	39.2
2 CLUB	0.273	0.795	36.2
4 CLUB	0.259	0.753	36.2

^a Polymerization condition: 20°C, [BTAC] = [MDA] = 0.061 M.

where A_{1720} is the optical density of the interfacial polymerization film at 1720 cm^{-1} (acid, C=O), A'_{1720} is the optical density of the polyamic acid at 1720 cm^{-1} (acid, C=O), A_{1510} is the optical density

of the interfacial polymerization film at 1510 cm^{-1} (Ar), and A'_{1510} is the optical density of the polyamic acid at 1510 cm^{-1} (Ar). Therefore, the mean hydrolysis percentage Hy is shown by eq. (3):

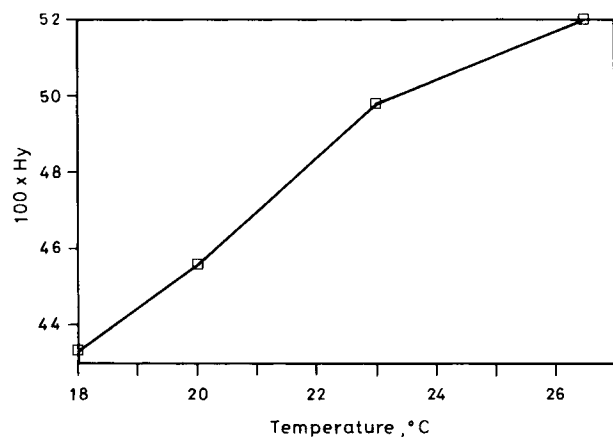


Figure 5 Percentage of hydrolysis vs. temperature for interfacial condensation of BTAC-MDA system (reaction condition: [BTAC] = [MDA] = 0.061 M).

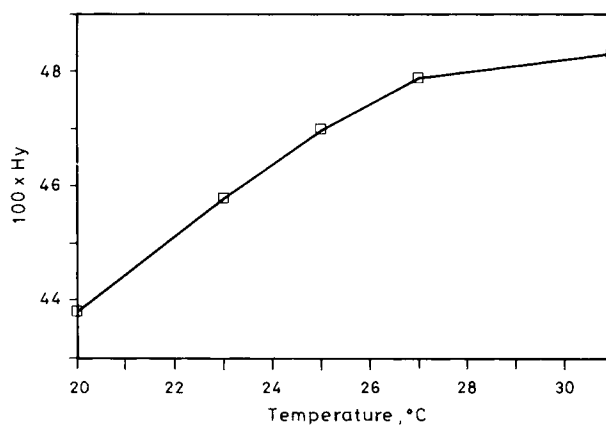


Figure 6 Percentage of hydrolysis vs. temperature for interfacial condensation of BTAC-EDA system (reaction condition: [BTAC] = [EDA] = 0.101 M).

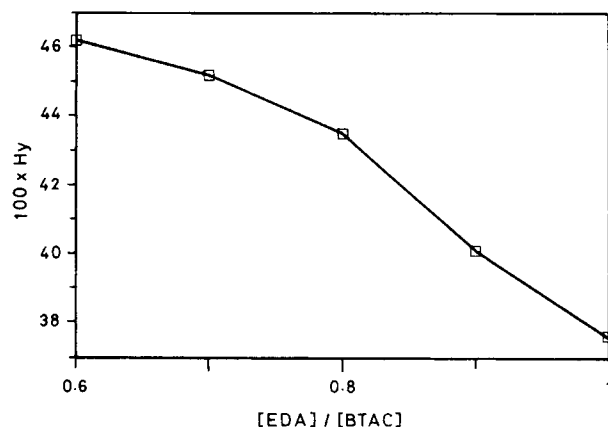


Figure 7 Percentage of hydrolysis vs. concentration for interfacial condensation of BTAC-EDA system (reaction condition: $T = 25^{\circ}\text{C}$, $[\text{BTAC}] = 0.101\text{M}$).

$$Hy = \frac{\frac{A_{1720}/A_{1510}}{A'_{1720}/A'_{1510}}}{\frac{A_{1720}/A_{1510}}{A'_{1720}/A'_{1510}} + \frac{A_{1540}/A_{1510}}{A'_{1540}/A'_{1510}}} \times 100\% \quad (3)$$

$$= \frac{\frac{c_{1720}/c_{1510}}{c'_{1720}/c'_{1510}}}{\frac{c_{1720}/c_{1510}}{c'_{1720}/c'_{1510}} + \frac{c_{1540}/c_{1510}}{c'_{1540}/c'_{1510}}} \times 100\%$$

where A_{1540} is the optical density of the interfacial polymerization film at 1540 cm^{-1} (amide, NH), A'_{1540} is the optical density of the polyamic acid at 1540 cm^{-1} (amide, NH), and Hy is the percentage of hydrolysis.

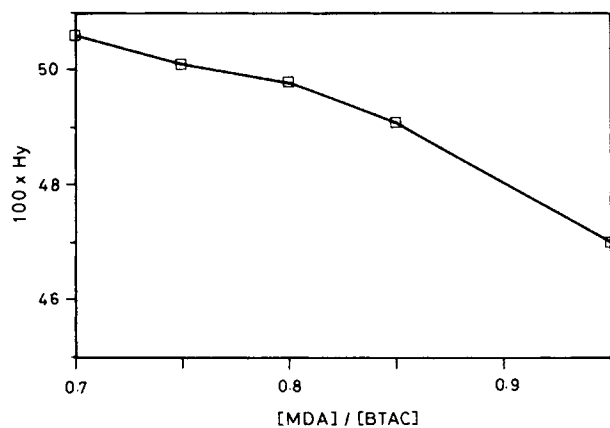


Figure 8 Percentage of hydrolysis vs. concentration for interfacial condensation of BTAC-MDA system (reaction condition: $T = 20^{\circ}\text{C}$, $[\text{BTAC}] = 0.061\text{M}$).

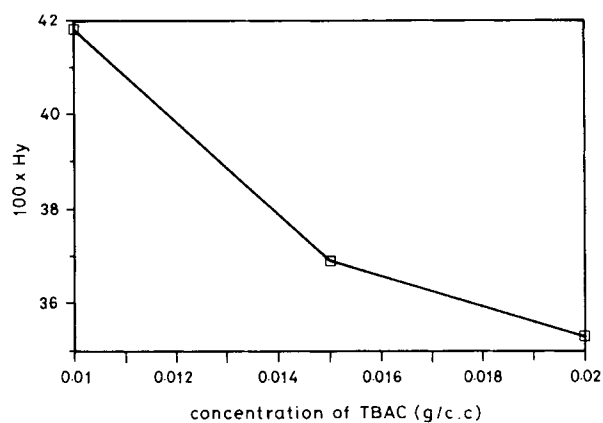


Figure 9 Percentage of hydrolysis vs. concentration of catalyst for interfacial condensation of BTAC-EDA system (reaction condition: $T = 31^{\circ}\text{C}$, $[\text{BTAC}] = [\text{EDA}] = 0.101\text{M}$).

Since diamine and water molecules are both in the aqueous solution, they may react concurrently with the BTAC. The hydrolysis percentage through eq. (3) (shown in Table II and III and Figs. 5-10) under various reaction conditions was calculated.

Effects of the Reaction Condition

As referred to in Figures 5 and 6, it is observed that hydrolysis increases along with the rise in temperature. The rate of reaction between BTAC and diamine is faster than that between BTAC and water. This indicates that the activation energy required by hydrolysis is higher than that required by amidation and that reactions with high activation energies are very temperature-sensitive. Therefore, an

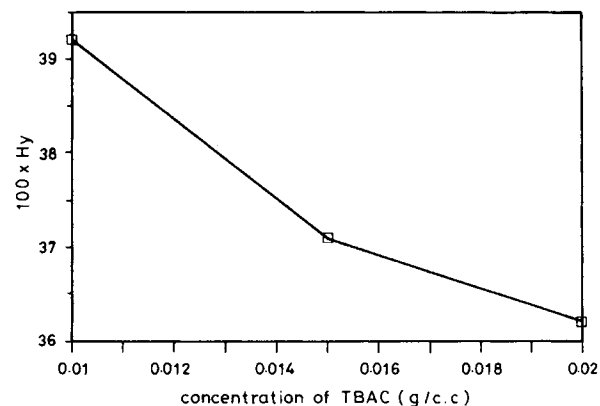


Figure 10 Percentage of hydrolysis vs. concentration of catalyst for interfacial condensation of BTAC-MDA system (reaction condition: $T = 18^{\circ}\text{C}$, $[\text{BTAC}] = [\text{MDA}] = 0.061\text{M}$).

Table IV Thermogravimetric Analysis of Poly(BTAC-MDA) and Poly(BTAC-EDA) Films in Nitrogen Atmosphere

Sample ^a	Temperature of Weight Loss (°C)	
	2%	5%
BTAC-EDA	390	430
BTAC-MDA	420	500

^a Thermal treatment: 6 h at 180°C and then 10 h at 240°C.

increase in the reaction temperature affects the rate of hydrolysis more than that of amidation. Therefore, a rise in temperature causes a concurrent increase in the hydrolysis percentage.

Referring to Table II, we see that adding sodium carbonate to the diamine aqueous solution caused a decrease in hydrolysis. The hydrochloride produced by the interfacial reaction catalyzed the hydrolysis reaction. But the presence of sodium carbonate neutralized the hydrochloride, and the reaction of hydrolysis was suppressed.

As referred to in Figures 7 and 8, when the proportion of the concentration of diamine was increased relative to that of BTAC, the hydrolysis percentage dropped. This indicates that more amidation takes place when more diamine molecules are present as expected from the law of mass action.

Referring to Tables II and III and Figures 9 and 10, we can see that when the diamine aqueous solution was agitated, or TBAC was added, the hydrolysis percentage dropped. Since the above two procedures boost diamine transfer to the interface region, the quantity of amidation increased. Therefore, it is suggested that the interfacial reaction is a diffusion-controlled reaction.

Controlling of 50% Hydrolysis

From Figures 5 and 8, it is observed that controlling 50% hydrolysis is possible in the BTAC-MDA sys-

tem. Fifty percent hydrolysis can also be obtained by interfacial reaction by adding 0.4 mL of 0.1N HCl to the EDA solution at 31°C when the concentration of the BTAC and that of the EDA are 0.061M each. However, when the obtained films had been submitted to a solvent extraction, there was still some insoluble part remaining. This indicated that some cross-linking took place. Therefore, the hydrolysis percentage indicates only a mean value.

When the film obtained went through two stages of thermal treatment: first at 180°C in a nitrogen atmosphere for 6 h, then a 240°C in nitrogen atmosphere for 10 h, it was found that the films formed the imide group [Fig. 3(B), IR (KBr) cm^{-1} : 1775, 1379, 725) and maintained good thermal stability (Table IV). We have studied the scheme of imidization, and it will be reported later.

The Effect of Solvents

The effect of solvents was examined by weighing the films obtained by a series of interfacial polycondensations while changing the solvents employed. The result is shown in Table V. Good solvents like dichloromethane, chloroform, and toluene bear swelling better, letting the diamine transfer continuously from the water phase to the organic phase to react with the BTAC. Therefore, the time needed to reach the end of the reaction with a good solvent system was longer than that for poor solvents (such as *n*-hexane and cyclohexane). Thus, the films produced were heavier in weight when a good solvent was used. The use of good solvents produced thicker films than those using poor solvents. The thickness of the films can be increased from less than 1 μm up to 20 μm by increasing concentration, but the thickness seldom exceeded 20 μm . Morgan²⁷ reported that the local concentration effect is the most important factor informing high molecular weight polymers. By similar reasoning, this system itself forms a cross-linking structure that hinders the diamine from continuously transferring and reacting with the

Table V Yield of Interfacial Polymer Films in Various Organic Solvents

Sample ^a	Yield				
	CH_2Cl_2	CHCl_3	Toluene	<i>n</i> -Hexane	Cyclohexane
Poly(BTAC-EDA) ^b	0.0172	0.0178	0.0185		
Poly(BTAC-MDA) ^c	0.0062	0.0064	0.0068	0.0016	0.0020

^a $T = 20^\circ\text{C}$, Reaction vessel: 50 mL beaker with 4.1 cm inside diameter.

^b [BTAC] = [EDA] = 0.061M.

^c [BTAC] = [MDA] = 0.00504M.

BTAC, the reaction terminates, and even thicker films cannot be made.

CONCLUSION

1,2,4,5-Benzenetetra acyl chloride is a stable product obtained from the reaction of pyromellitic anhydride and phosphoric chloride. When processing interfacial polymerization through the organic solution of the BTAC and the diamine (aq), the reaction is a competitive reaction between hydrolysis and amidation. It is possible to control the film at a mean 50% hydrolysis. Heat-resistant films with good thermal stability were formed by thermal treatment.

The hydrolysis is suppressed when (1) the temperature is decreased, (2) sodium carbonate is added, (3) the proportion of concentration of diamine is increased relative to that of BTAC, (4) the diamine solution is agitated, and (5) TBAC is added to the diamine solution. It is suggested that the reaction is a diffusion-controlled reaction.

With good solvents, the thickness of the film increases with increases in concentration of the reactants. However, the maximum thickness of the film seldom exceeds 20 μm .

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