

Interfacial Polyfunctional Condensation: Curing Reaction

YAW-TERNG CHERN and LEO-WANG CHEN*

Institute of Materials Engineering, National Taiwan University, Taipei, Taiwan 10764, Republic of China

SYNOPSIS

Heat treatment of films obtained by interfacial condensation of 4,4'-methylene dianiline (MDA) or ethylene diamine (EDA) in water and 1,2,4,5-benzenetetra acyl chloride (BTAC) in dichloromethane were studied by Fourier transform infrared spectroscopy (FTIR), ¹H- and ¹³C-nuclear magnetic resonance (NMR), fast atom bombardment mass spectrometry (FABMS), an elemental analyzer, and differential scanning calorimetry (DSC). The reaction scheme for forming the polyimide is presented. Films were synthesized from the aromatic diamine and from the aliphatic diamine system. Both must go through two-stage thermal treatment to form the structure of the imide. The first stage of this reaction is the imidization of the polyamic acid, and the second is the reaction to imidization of the functional amide group linked to the neighboring carbon on the benzene ring. After thermal treatment, the films will maintain good heat resistance. The difference between the mentioned interfacial synthetic polyimide and the conventional synthetic polyimide is that no isoimide and anhydride groups are found in the former. But the thickness of the film is limited by the nature of interfacial polymerization. In our reaction system, the maximum thickness of the film did not exceed 20 μm.

INTRODUCTION

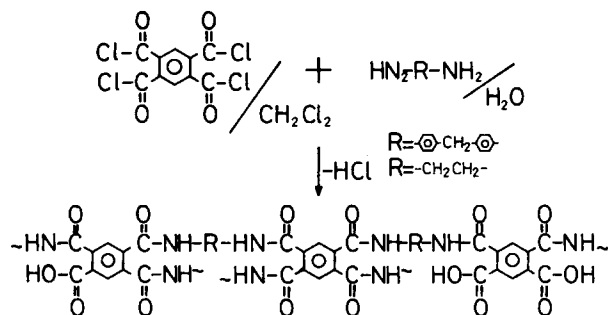
Polyimide maintains excellent mechanical properties and chemical stability under high temperatures and is widely used in the aviation and electronics industries. However, at the present time, the separation industry also requires films that can be used at higher temperatures and in organic solvents. Ordinary organic materials cannot meet these requirements. There are some reports of research using polyimide as the separation membrane. Interfacial polymerization may be applied to the preparation of composite membranes.^{1,2} The membrane provides high selectivity but is not subject to severe drops in flux as is the separating film.

Early in 1955, DuPont filed the first patent³ for synthesizing aromatic polyimides. Much research⁴⁻⁶ has been done on modifying the heat resistance and processing properties of polyimides.

In our previous study, we discussed the interfacial polycondensation reaction in which BTAC was dissolved in dichloromethane, and EDA or MDA, dissolved in water. The typical reaction scheme is shown in Scheme I.⁷ It is similar to the synthesis of polyimide: First, an intermediate product like polyamic acid is formed; then further heating is needed to produce the polyimide. The reaction mechanism directly affects the chemical structure⁸⁻¹¹ of the film. Anhydride and isoimide groups are typical byproducts of synthetic polyimide production, which can affect heat resistivity, chemical stability, and separation of gases in the polyimide. Therefore, it is important to understand the reaction mechanism of our reaction system. There have been many studies¹²⁻¹⁴ done on the imidization of polyamic acid. However, no reports related to our reaction system have been written.

In our research, we set the different reaction conditions and employed DSC and FTIR for analyzing the reaction scheme. Thermogravimetric analysis (TGA) was employed for analyzing the heat resistance of the film, and scanning electron microscope (SEM), for analyzing the morphology of the film.

* To whom correspondence should be addressed.



Scheme 1

EXPERIMENTAL

Reagents and Solvent

4,4-Methylene dianiline (MDA) was recrystallized from isopropyl alcohol. Ethylene diamine (EDA) was distilled at normal pressure before use. Dichloromethane was dried with 4 Å molecular sieves and stored over molecular sieves until use. Methanol was dried with 3 Å molecular sieves and was stored over molecular sieves until use. The BTAC was synthesized in a way similar to that described in a previous paper.⁷ All 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 spectra of the KBr pellets. In a typical experiment, an average of 20 scans per sample were made. FABMS spectra were obtained by using a JEOL JMS-HX 110 mass spectrometer. ¹H- and ¹³C-NMR 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 D₂O as the solvent. A Perkin-Elmer 240C elemental analyzer was used for elemental analysis.

Melting points were determined in an electrothermal Buchi 510 melting-point apparatus. DSC and TGA were performed on a DuPont 990 thermal analyzer system. A sample of about 5 mg was heated in nitrogen at 10°C/min. The electron micrograph was taken with a PHILIPS 515 scanning electron microscope. The polymer film was coated with gold by sputter deposition prior to the measurement to improve the resolution of the micrograph.

Interfacial Synthesis

We dissolved the required amount of BTAC in dichloromethane and the diamine in water, then used a syringe to take 10 mL of the diamine solution and inject it onto the solution of BTAC along the lining walls for interfacial polycondensation. After that, the obtained film was first rinsed with water or 0.001 N of NaOH (aq) and further rinsed with dichloromethane until there was no more dissolved matter, and then it was vacuum dried. The film was analyzed with DSC for its heating reaction, and its morphology was observed with SEM.

As for its heat treatment, first the film was heated under 180°C in nitrogen for 6 h and then heated under 240°C in nitrogen atmosphere for 10 h. The films after heat treatment were rinsed with dichloromethane and water to eliminate the byproduct. Then, the films were vacuum-dried. Finally, we used TGA to analyze the thermal stability, and FTIR, to observe the change in chemical structure.

RESULTS AND DISCUSSION

Poly(BTAC-MDA) Film Rinsed with Water and Dichloromethane

As referred to in Figure 1, it was found that there are two endothermic peaks: the first peak in the range of 100–200°C and the second peak in the range of 220–300°C. In Figure 2, the FTIR spectra of the

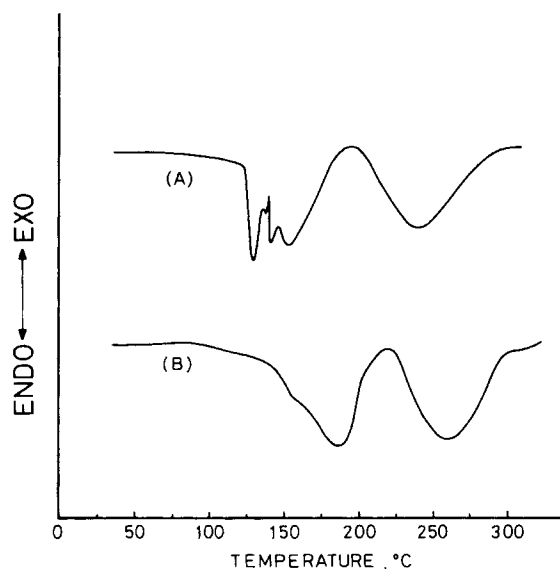


Figure 1 DSC thermograms of poly(BTAC-MDA) films in nitrogen atmosphere (heating rate: 10°C/min). (A) Rinsed with water and dichloromethane; (B) rinsed with 0.001 N of NaOH (aq) and dichloromethane.

non-heat-treated sample and the sample treated at 180°C in a nitrogen atmosphere for 6 h are compared. The spectra of the latter show the decreasing of the characteristic absorption¹⁵⁻¹⁷ of the amic acid, i.e., [cm^{-1} (KBr): 3300 (NH, OH), 1655 (C=O), 1540 (NH)]. However, the characteristic absorption of the imide group, i.e., the 1775, 1379, and 725 cm^{-1} , is observed. From the results mentioned above, it is suggested that the first heat-absorption peak is caused by imidization of the polyamic acid. Its heat-absorbing position is similar to what another study¹⁸ had reported. The film was further heated under 240°C in nitrogen atmosphere for 10 h. Colorless crystals were produced on the surface of the film. These were purified by recrystallization with distilled water. After analysis, it was ascertained to be MDA hydrochloride salt. Its properties are as follows: mp: 265–266°C; IR (KBr) cm^{-1} : 3430, 3550 (NH), 1910 (primary amine salt), 1610 (NH), 1500 (Ar, C=C); ¹H-NMR(D₂O): 7.15–7.27 (8H, Ar), 4.63 (6H, NH₃⁺), 3.94 (2H, CH₂); ¹³C-NMR (D₂O) ppm: 144.62 (Ar), 132.10 (Ar, CH), 130.45 (Ar), 125.62 (Ar, CH), 42.42 (CH₂); elemental analysis: C: 57.23%, H: 5.78%, N: 10.00%, Cl: 26.99%, FABMS (*m/e*) 198. (As it is subject to breaking, the MDA fragment is recognizable by a molecular ion peak.)

The fact that the interfacial polycondensation reaction may yield hydrochloride suggests that it exists in the film in the form of a salt of amine hydrochloride. Since the film was rinsed with water only, complete elimination of the hydrochloride is not possible. It is reasonable to assume it to be MDA hydrochloride salt.

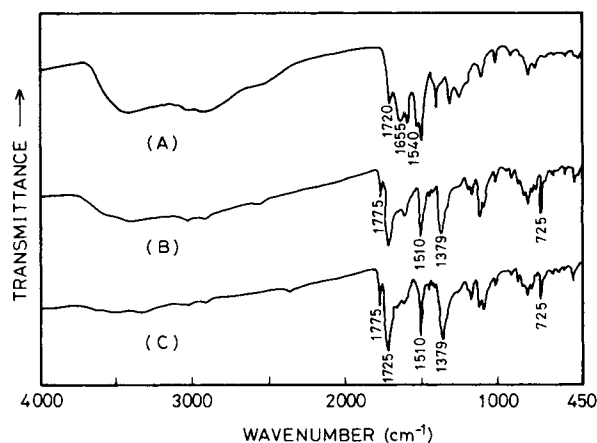


Figure 2 FTIR spectra for poly(BTAC-MDA) films on different thermal treatment. (A) Before thermal treatment; (B) 6 h at 180°C; (C) 6 h at 180°C and 10 h at 240°C.

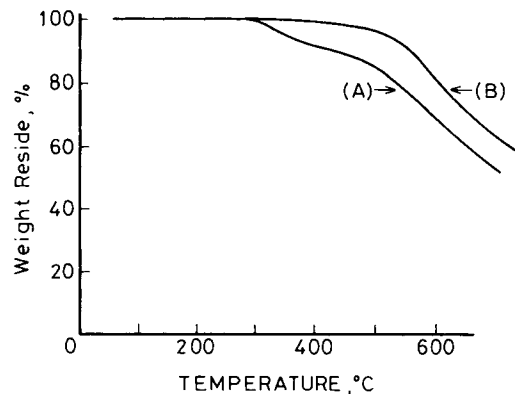


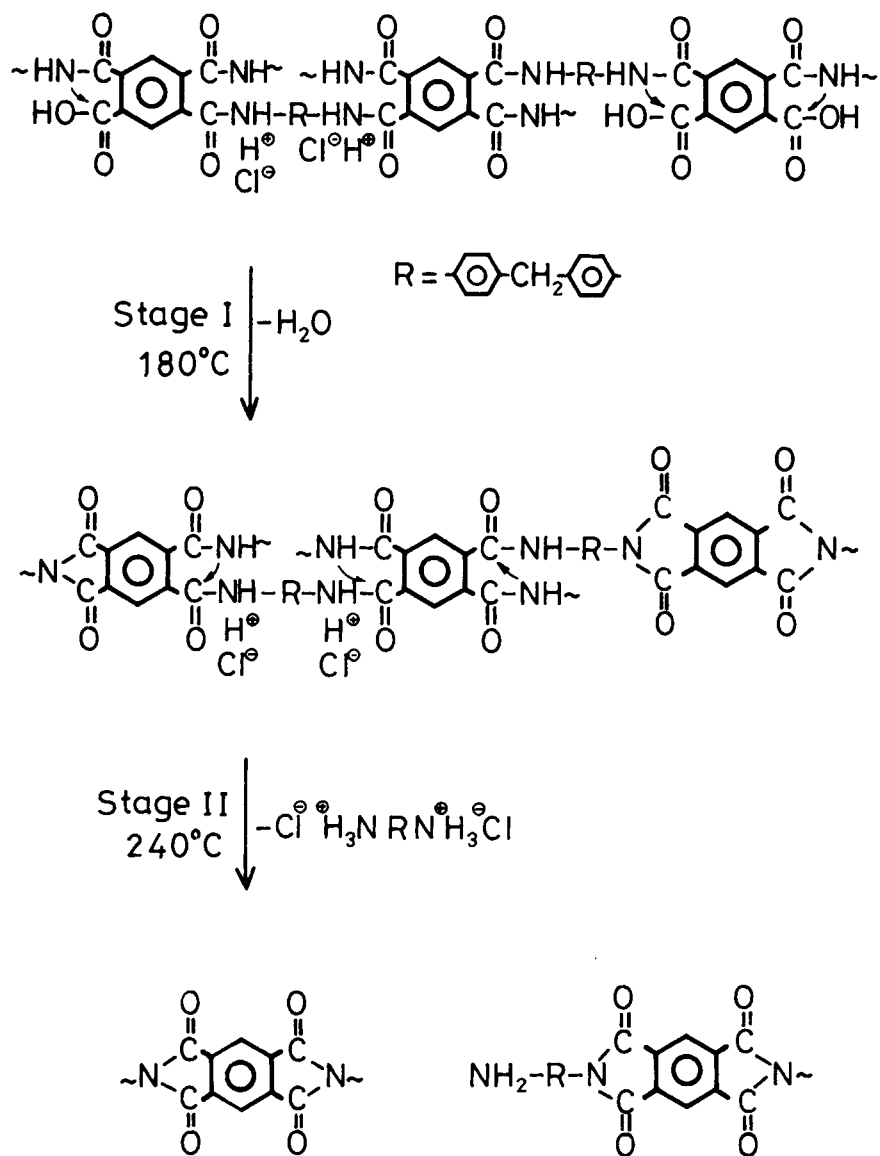
Figure 3 TGA thermograms of poly(BTAC-MDA) film in nitrogen atmosphere on different thermal treatment. (A) 6 h at 180°C; (B) 6 h at 180°C and 10 h at 240°C.

Figure 2 shows the comparison of FTIR spectra of the first thermally treated film and the second thermally treated film. It was found that the latter characteristic absorption of the amide group [cm^{-1} (KBr): 3350 (NH), 1540 (NH)] became less intensive and that of the imide group [cm^{-1} (KBr): 1775, 1379, 725] became more intensive. The isoimide group [cm^{-1} (KBr): 1820–1950, 921–934] and anhydride group [cm^{-1} (KBr): 1850] are byproducts in the ordinary manufacture of the polyimide. But in our experiment, we did not find the IR characteristic absorption in the isoimide and anhydride groups of film.

Referring to Figure 3, we found that the heat resistance of the film that had been through the first thermal treatment stage, as well as the thermal cracking temperature of the film, is lower than 350°C. The thermal cracking temperature is taken by measuring the temperature at 5% weight loss. Because the film contains amide groups, the heat resistance of the film is poor. When the film has been through the secondary stage of thermal treatment, its thermal cracking temperature is nearly 500°C. This is similar to what other studies^{19,20} have reported. Summarizing the above results, the heat absorption of the band at 220–300°C is the imidization of the adjacent carbon on the benzene ring linked with functional groups of amide. The typical reaction is shown in Scheme II.

Poly(BTAC-MDA) Film Rinsed with NaOH (aq) and Dichloromethane

As referred to in Figure 1, we also observed two heat-absorbing bands. However, the temperature of the second heat-absorbing band of the film that had been



Scheme II

rinsed with the NaOH (aq) is about 20°C higher than that of the film that had been rinsed with H₂O. This is because the film that had been rinsed with water retained some hydrochloride that had been produced by the interfacial reaction. Also, the hydrochloride provides hydrogen ions, which attach

themselves to carbonyl oxygen and thus render the molecule vulnerable to attack by the weakly nucleophilic reagent, the secondary amide group; that is, the hydrogen ions may catalyze the reaction of cyclization, so the imidization proceeds more easily. When using FTIR to analyze the chemical structure

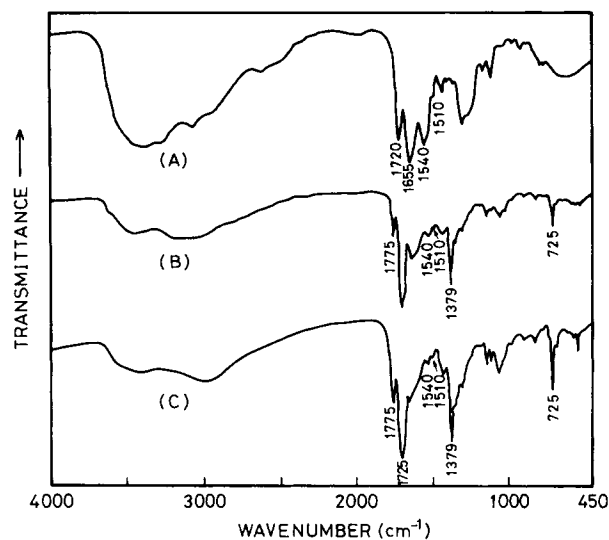


Figure 4 FTIR spectra for poly(BTAC-EDA) films on different thermal treatment. (A) Before thermal treatment; (B) 6 h at 180°C; (C) 6 h at 180°C and then 10 h at 240°C.

of the film and TGA to analyze the heat resistance of the film, the results are similar to those stated previously. Therefore, there is no reference chart

Table I Optical Density Ratio of Poly(BTAC-EDA) Films

Sample ^a	Optical Density Ratio	
	$\frac{D_{1540 \text{ cm}^{-1}}}{D_{1510 \text{ cm}^{-1}}}$ ^b	$\frac{D_{1775 \text{ cm}^{-1}}}{D_{1510 \text{ cm}^{-1}}}$
(A)	2.13	0
(B)	1.24	1.30
(C)	1.16	2.46

^a Thermal treatment: (A) before thermal treatment; (B) 6 h at 180°C; (C) 6 h at 180°C and then 10 h at 240°C.

^b D is the optical density of the characteristic absorption of the sample.

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

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

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

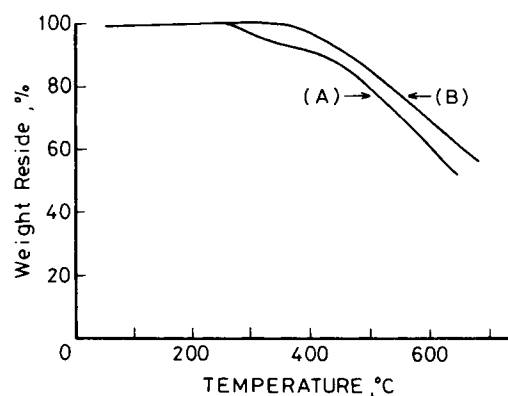


Figure 5 TGA thermograms of poly(BTAC-EDA) films in nitrogen atmosphere on different thermal treatment. (A) 6 h at 180°C; (B) 6 h at 180°C and then 10 h at 240°C.

given. So, from the above results, we may understand that even without the hydrogen ions, the film may form polyimides by thermal treatment.

Poly(BTAC-EDA) Film System Rinsed with NaOH (aq) and Dichloromethane

Referring to Figure 4 and Table I, we found from the FTIR analysis that the film that had been through two stages of heat treatment and the film that had been through only the first stage of heat treatment are different in their chemical structure. The former shows lower characteristic absorption of the amide group and higher absorption of the imide group.

Referring to Figure 5, we found from the diagram of TGA that the thermal stability drops markedly when the polyimide contains amide groups. We also

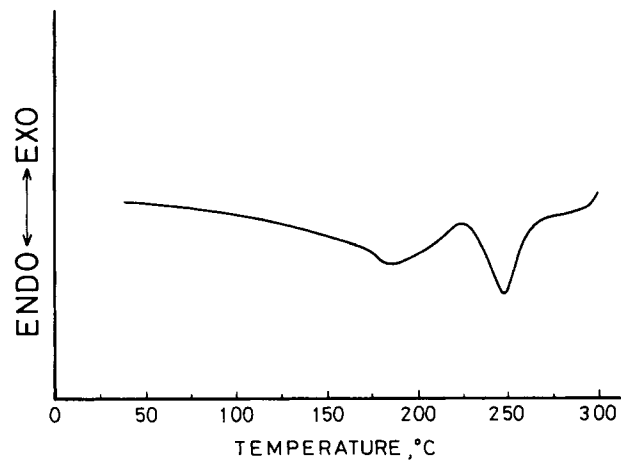
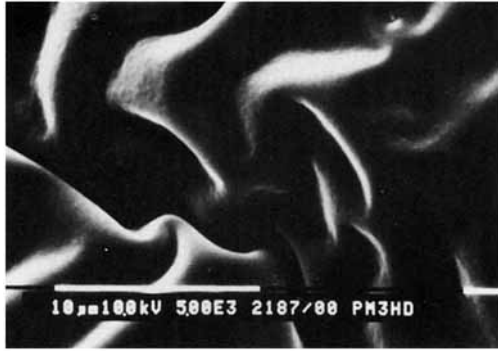
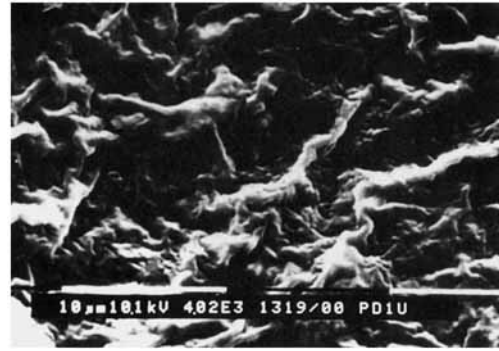


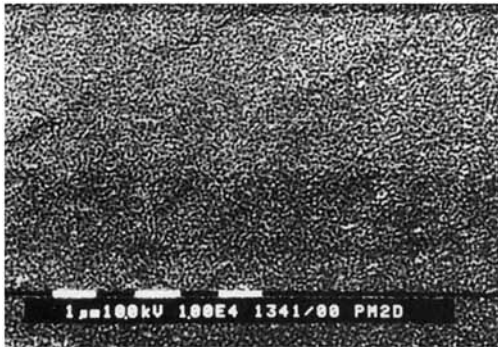
Figure 6 DSC thermograms of poly(BTAC-EDA) film in nitrogen atmosphere (heating rate: 10°C/min).



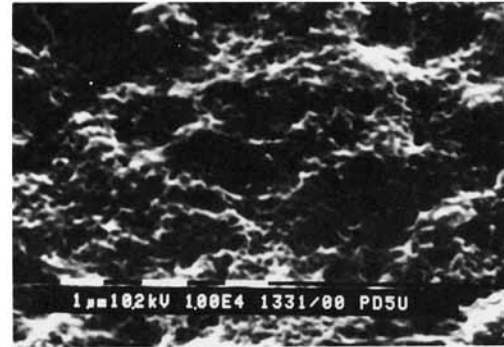
(A)



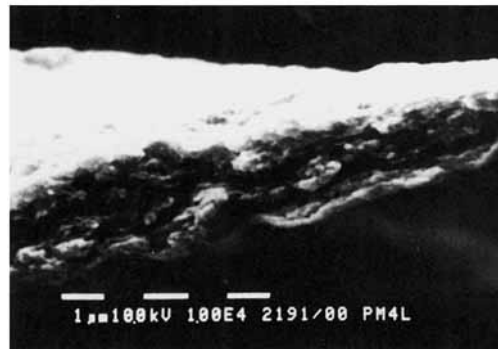
(C)



(B)



(D)



(E)

Figure 7 SEM of interfacial polycondensation films. (A) Poly(BTAC-MDA) film, obtained at 5°C, organic face side, 5000X; (B) poly(BTAC-MDA) film, obtained at 31°C, organic face side, 10,000X; (C) poly(BTAC-EDA) film, obtained at 5°C, water-phase side, 4000X; (D) poly(BTAC-EDA) film, obtained at 31°C, water-phase side, 10,000X; (E) cross section of poly(BTAC-MDA) film obtained at 5°C, 10,000X.

found that the higher the extent of imidization, the better the heat resistance of the film. Referring to Figure 6 and summarizing the above results, it is suggested that the first heat-absorbing band is caused by imidization of polyamic acid and the second heat-absorbing band by cyclization of the neighboring carbon on the benzene ring linking with the amide groups with the formation of a five-member imide ring. Table II shows that the heat resistance of the imide on the aromatic diamine system is better than that of the imide on the aliphatic diamine system.

Morphology

Referring to Figure 7(A) and (C), we found that the photos of the films show no holes under 10,000 \times magnification and that the surface is corrugated and wavy. This was probably caused by nonhomogeneous shrinkage during the drying stage. Referring to Figure 7(B) and (D), we found that the surface of the films are microporous when processing of the interfacial polycondensation reaction at 30 $^{\circ}$ C. This was probably caused by dichloromethane vaporizing.

Referring to Figure 7(E), we found that the thickness of poly(BTAC-MDA) film is about 2.2 μ m. The thickness of poly(BTAC-EDA) film is about 10 μ m. When the film obtained is not over 20 μ m in thickness, since interfacial polycondensation reaction results in a film of high molecular weight forming at once and hindering the transfer of reagents, the reaction cannot proceed. Therefore, the thickness of the film is limited.

CONCLUSION

In the BTAC-MDA and BTAC-EDA systems, the film is formed by an interfacial polycondensation reaction and the polyimide can be formed through two-stage thermal treatment. The temperature of the first stage is about 180 $^{\circ}$ C, and the imidization of the polyamic acid occurs at this temperature. The temperature of the second stage is about 240 $^{\circ}$ C, and the imidization of the neighboring carbon on the benzene ring linking with the amide groups occurs at this temperature.

The polyimide contains no byproducts of the isoimide and anhydride groups; thus, it maintains good heat resistance. The thermal cracking temperature for BTAC-MDA film is 500 $^{\circ}$ C. As for the BTAC-EDA film, the thermal cracking temperature is 430 $^{\circ}$ C. The thickness of the film in the BTAC-MDA system is about 2.2 μ m and about 10 μ m in

the BTAC-EDA system. However, the increasing concentration of reactants increases the thickness of the film. But, by virtue of the nature of interfacial polycondensation, the maximum thickness of the film obtained from our system is less than 20 μ m.

We would like to express thanks to Mr. J. C. Ding, Department of Chemical Engineering, Ming-Chi Institute of Technology, for his TGA experiments during this study. The authors wish to acknowledge the financial support of the National Science Council, R.O.C.

REFERENCES

1. F. F. Stengnard, *J. Membrane Sci.*, **36**, 257 (1988).
2. H. K. Lonsdale, *J. Membrane Sci.*, **33**, 121 (1987).
3. P. M. Heigenisher and N. J. Johnston, ACS Symp. Ser. 132, American Chemical Society, Washington, DC, 1980, p. 3.
4. F. W. Harris, A. Pamidimukkala, R. Gupta, S. Das, T. Wu, and G. Mock, *J. Macromol. Sci. Chem.*, **A21**(8,9), 1117 (1984).
5. R. W. Lauver, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 2529 (1979).
6. P. M. Hergenrother, N. T. Wakelyn, and S. J. Havens, *J. Polym. Sci. Polym. Chem.*, **25**, 1093 (1987).
7. Y. T. Chern and L. W. Chen, to appear.
8. D. Garoia, *J. Polym. Sci. Polym. Phys.*, **25**, 2275 (1987).
9. J. C. Johnston, M. A. B. Meador, and W. B. Alston, *J. Polym. Sci. Polym. Chem.*, **25**, 2175 (1987).
10. C. A. Pryde, *J. Polym. Sci. Polym. Chem.*, **27**, 711 (1989).
11. A. P. Mellissaris and J. A. MiKroyannidis, *J. Polym. Sci. Polym. Chem.*, **27**, 245 (1989).
12. M. J. Brekner and C. Feger, *J. Polym. Sci. Polym. Chem.*, **25**, 2479 (1987).
13. H. G. Linde and R. T. Gleason, *J. Polym. Sci. Polym. Phys.*, **26**, 1485 (1989).
14. B. D. Silverman, J. W. Bartha, J. G. Clabes, and P. S. Ho, *J. Polym. Sci. Polym. Chem.*, **24**, 3325 (1986).
15. E. Pyun, R. J. Mathisen, and C. S. P. Sung, *Macromolecules*, **22**, 1174 (1989).
16. H. Ishida, S. T. Wellinghoff, E. Baer, and J. L. Koenig, *Macromolecules*, **13**, 826 (1980).
17. H. Imajo, K. Kurita, and Y. Iwakura, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 2189 (1980).
18. S. E. Delos, R. K. Schellenberg, J. E. Smedley, and D. E. Kranbuel, *J. Appl. Polym. Sci.*, **27**, 4295 (1982).
19. N. D. Ghatge, B. M. Schinde, and U. P. Mulik, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3359 (1984).
20. G. D. Khune, *J. Macromol. Sci. Chem.*, **A14**(5), 687 (1980).

Received August 21, 1990

Accepted August 31, 1990