Polymer Bulletin 36, 609–616 (1996)

Polymer Bulletin

The behavior of interfacial polycondensation on synthesizing of poly(amic-ester)s: homogeneity of the interfacial films

Yaw-Terng Chern*, Bae-Shyang Wu, Chin-Min Huang

Department of Chemical Engineering, National Taiwan Institute of Technology,
Taipei, Taiwan 106, Republic of China

Received: 18 December 1995/Revised version: 22 January 1996/Accepted: 30 January 1996

Summary

The behavior in interfacial polycondensation of 4,4´-methylenedianiline (MDA) or 4,4 -oxydianiline (ODA) in water with dimethoxycarbonylterephthaloyl chloride (DCMTC) in dichloromethane with benzyltriethylammonium chloride (BTEAC) as the catalyst was examined with a Raman imaging microscope, and scanning electron microscope.

The surfaces of the polymers adjacent to the water phase had higher average molecular weight than the surfaces of the polymers adjacent to the organic phase. Moreover, the morphology of the films also changed from dense to porous along the thickness direction of the films. To obtain an interfacial film more homogeneous in morphology and molecular weight, the reaction time of interfacial condensation should not exceed 5 minutes in this system. The interfacial films were anisotropic. The chain axis of the poly(amic-ester)s mainly oriented perpendicularly to the interface in the direction of membrane growth.

Introduction

In principle, composite membranes allow the properties of the dense, separating layer and the porous support layer to be optimized individually to a greater extent.[1] A number of patents have described an asymmetric coating layer, which is a simple dense top layer, applied to an already formed asymmetric support layer.[2-4] The method of interfacial polycondensation can be applied to composite membrane being prepared. This provides higher selectivity without severely reducing membrane flux. Rozelle et al. and Cadotte developed interfacial polycondensation for manufacturing composite reverse-osmosis membranes.[5,6] Rapid advances in this technology in the 1970s led to the commercialization of the highly successful FT-30 composite membrane.[7,8] Thus, much research on interfacial polycondensation has been reported in the literature.[9-14] Interfacial polycondensation has become one of the most successful methods for manufacturing composite membranes.[15]

There have been several studies that have focused on improving membrane performance by using composite membranes.[16-19] However, there have been relatively few studies of interfacial polycondensation layers. Enkelmann and Wegner established the time-conversion curves, and derived an equation by measuring the increase in membrane thickness with reaction time.[20] They also found that the polymer chains mainly oriented perpendicularly to the interface in the direction of membrane growth. Mikos and Kiparissides presented a mathematical model to describe these phenomena, and predict the

---

* Corresponding author

structural characteristics of the produced polymer by polymerization of methyl methacrylate with water.[21] Chai and Krantz found that real-time data on the effects of trimesoyl chloride and m-phenylenediamine concentration, as well as reaction time on the interfacial polycondensation membrane-formation process, were obtained using light reflection and pendant-drop tensiometry.[6] In previous studies, we found that the interfacial reaction of this system takes place in the organic phase.[22] We also found that the films formation started from the interface and grew toward the organic phase.[22] To prepare a good separation membrane, we must have sufficient understanding of the interfacial polycondensation phenomena of this system. Thus, the objectives of this study were to investigate the effect of reaction time on the homogeneity of the interfacial film and to determine the reaction conditions necessary to obtain a film more homogeneous in morphology. While at the same time, we analyze the anisotropy of the interfacial films.

Experimental

Materials

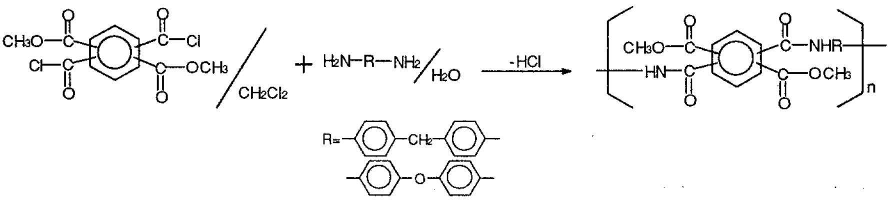
Dimethoxycarbonylterephthaloyl chloride (DCMTC) was synthesized in a previous study.[23] 4,4´-Oxydianiline (ODA) and 4,4´-methylenedianiline (MDA) were purified by vacuum sublimation. Dichloromethane was dried with 4Å molecular sieves and was stored over molecular sieves until use. All the solvents used were purified in the usual manner. All other reagents were of analytical grade.

Characterization

Inherent viscosities of all polymers were determined at 0.5 g/dL concentration in N,N-dimethylacetamide (DMAc) at 30°C by using an Ubbelohde viscometer. The morphology of the film was measured with a Philips 515 scanning electron microscope (SEM). Raman measurements were carried out on a Renishaw 2000 Raman imaging microscope equipped with a Polaroid sheet. The Raman spectra were recorded at 1 cm^{-1} resolution.

Interfacial polycondensation

We prepared 0.009 M of DCMTC in dichloromethane and an aqueous solution of 0.009 M of the diamines. The latter contained 0.0021 M of aqueous Na_2CO_3 and 10 vol.% of DMAc in distilled water. We used a 50 ml graduated cylinder to take 40 ml of DCMTC solution and place it at the bottom of a beaker 9 cm in diameter. Next, we used a 50 ml syringe to take 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 interfacial polycondensation under the required conditions. The film acquired by interfacial polycondensation was rinsed with 0.001 N of aqueous NaOH, then rinsed with dichloromethane until no more dissolved substance appeared. Then the film was vacuum-dried. The typical reaction was shown in Scheme I.



Scheme I

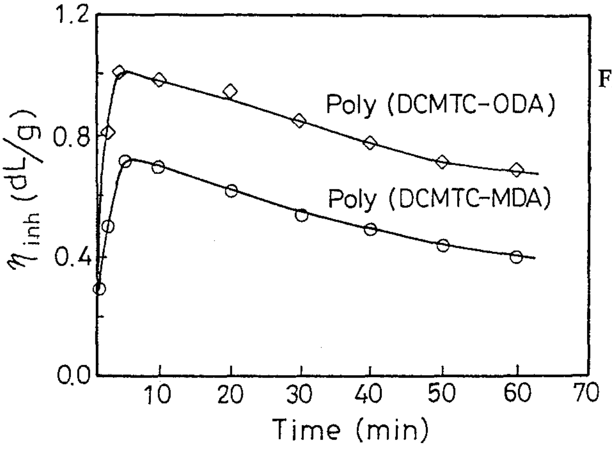


Figure 1. Effect of reaction time for interfacial polycondensation. Polymerization conditions:0 °C, [Na_2CO_3]=0.0021M; for Poly(DCMTC-ODA): [DCMTC]=[ODA]=0.009M ; for Poly(DCMTC-MDA):[DCMTC]=[MDA]= 0.009M.

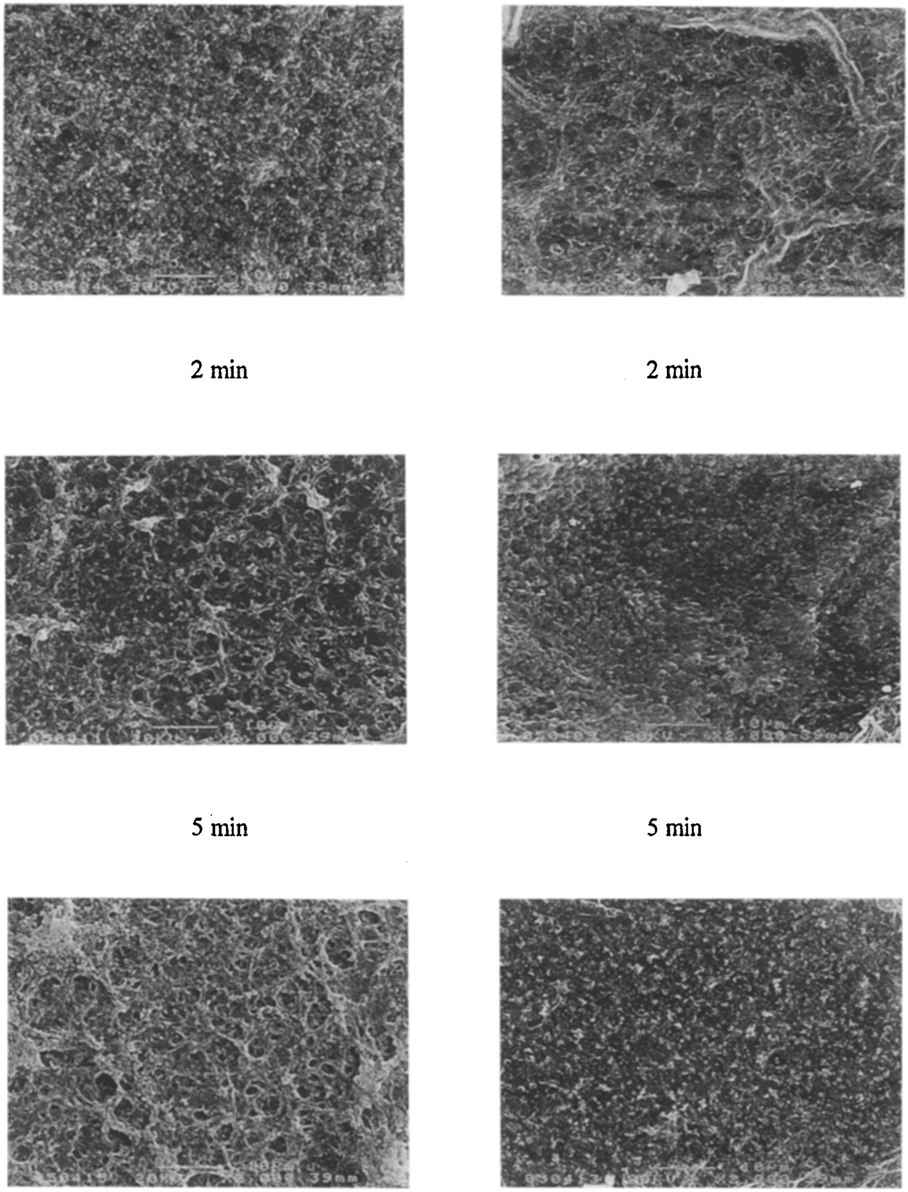
Since the solubility of the diamines in water is poor, the diamines were dissolved in 10 (v/v)% of the aqueous DMAc. The solution of 10 (v/v)% of the aqueous DMAc and the dichloromethane will not mix with each other. It was used as the solvent for the water phase, and a well-defined two-phase system resulted.

Results and Discussion

Effect of Reaction Time

Referring to Figure 1, at first the inherent viscosity of the polymers increased as the reaction time increased. At about 5 minutes, the inherent viscosity of the polymers was at maximum. When the reaction time exceeded 5 minutes, the inherent viscosity of the polymers declined as the reaction time increased. The reasons for the inherent viscosity of the polymers decreased during the reaction might be due to the following factor: (i) the hydrochloride produced by the interfacial reaction; (ii) the diamine and the hydrochloride diffused slowly due to the hindrance of the interfacial film at the later reaction stages; (iii) the concentration of diamine on the interface adjacent to the organic phase was low during the later stages of the reaction; (iv) the slow diffusion in (ii) created a pile-up of hydrochloride which could be observed in the organic phase adjacent to the film, and so hydrolysis of DCMTC was increased at the later reaction stages; (v) once hydrolysis had occurred in the chain end of polymers, the hydrolysis chain end of the polymers was inactive in polycondensation. In previous studies, we found that the film formation started from the interface and grew toward the organic phase.[22] Thus, we can infer that the surfaces of the polymers adjacent to the water phase had higher average molecular weight than the surfaces of the polymers adjacent to the organic phase.

From the photos of SEM in Figure 2, we can see that there were small pores in the two sides of the interfacial film after a reaction time of 2 minutes. At this period, the growth of the interfacial film was not yet complete. The photo of SEM at 5 minutes shows that almost the complete surface of the films adjacent to the water phase was dense in morphology. When the reaction time exceeded 5 minutes, the surfaces of the films adjacent to the water phase did not change much in morphology as the reaction time increased. It still retained its dense morphology, but the surfaces of the films adjacent to the organic phase became porous in morphology at 5 minutes. When the reaction time exceeded 5



The Surface Facing Organic Phase

The Surface Facing Water Phase

2 min

2 min

5 min

5 min

20 min

20 min

Figure 2. SEM photomicrographs 2000X of Poly(DCMTC-ODA) films with various reaction time.

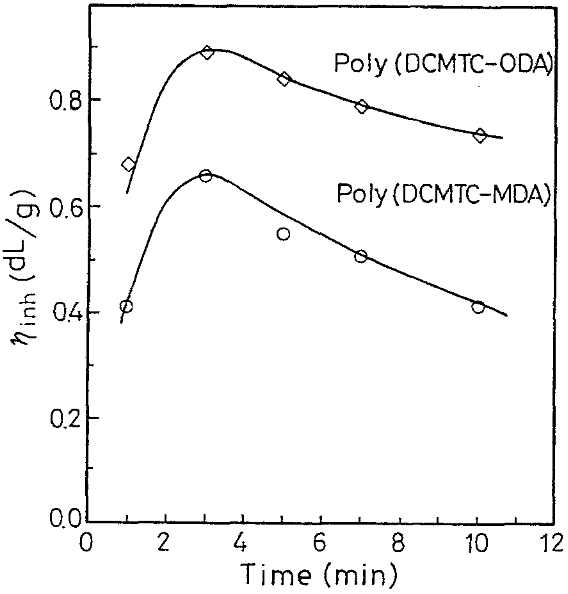


Figure 3. Effect of reaction time for interfacial polycondensation with 0.02 g/10cc of aqueous BTEAC. Polymerization conditions: 0°C; for Poly(DCMTC-ODA): [DCMTC]=[ODA]= 0.009M; for Poly(DCMTC-MDA): [DCMTC]=[MDA]= 0.009M.

minutes, the surfaces of the films adjacent to the organic phase were still porous in morphology. The porous structure formed on the surface of the films adjacent to the organic phase might be due to the hydrolysis side-reaction that terminated the growth of the polymer chain. From the results discussed above, we can infer that the reaction time of interfacial polycondensation should not exceed 5 minutes in order to obtain more dense interfacial film.

Summing up the above results, we understand that the molecular weight of the polymer as it relates to thickness was not homogeneous. The surfaces of the polymers adjacent to the

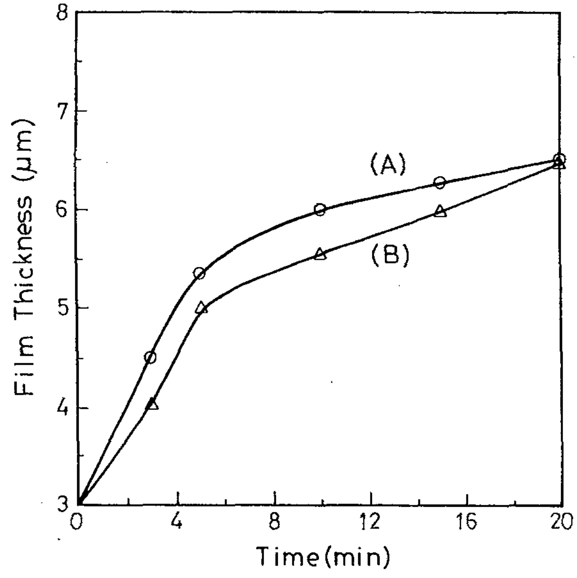


Figure 4. Effect of catalyst on the film thickness of Poly(DCMTC-MDA) (polymerization condition: 0°C, [DCMTC]=[MDA]= 0.009 M): (A) with 0.02 g/10 cc of aqueous BTEAC; (B) without adding BTEAC.

water phase had higher average molecular weight than the surfaces of the polymers adjacent to the organic phase. Moreover, the morphology of the films also changed from dense to porous along the thickness direction of the films. Therefore, the morphology and molecular weight were not homogeneous in the thickness direction of the films. To obtain an interfacial film more homogeneous in morphology and molecular weight, the reaction time of interfacial condensation should not exceed 5 minutes in this system.

Referring to Figure 3, with adding BTEAC, at first the inherent viscosity of the polymers increased as the reaction time increased. At about 3 minutes of reaction time, the inherent viscosity of the polymer was at maximum in both Poly(DCMTC-ODA) and Poly(DCMTC-MDA) systems. When the reaction time exceeded 3 minutes, the inherent viscosity of the polymer declined as the reaction time increased. Comparing the results of Figures 1 and 3, when BTEAC was added to this system the maximum inherent viscosity of polymer was achieved at 3 minutes of reaction time instead of 5 minutes. This was probably because BTEAC promoted the diffusion of diamines.Referring to Figure 4, at first the film growth rate (namely film thickness) with adding BTEAC was faster than that without adding BTEAC. The results also explain BTEAC promoted the diffusion of diamines.

Anisotropy of Interfacial Films

The effect of anisotropy on a selected absorption band of the Raman spectra of the interfacial film was characterized by the polarization ratio R, defined as $R=A_{//}/A_{\perp}$, $A_{//}$ and $A_{\perp}$ being the absorbances measured with radiation polarized parallel and perpendicular to the film surface, respectively.

A representative Raman spectra of the interfacial film is shown in Figure 5. The stretching vibrations of C=O and N-H groups in polyamides involve changes in dipole moment that are almost exactly perpendicular to the chain axis.[24] Thus, two absorption bands, at 1328 cm^{-1} and 1656 cm^{-1} were characteristic of the overall chain orientation. The 1328 cm^{-1} band was assigned to the N-H band and the C-N stretch of the amide group. The 1656

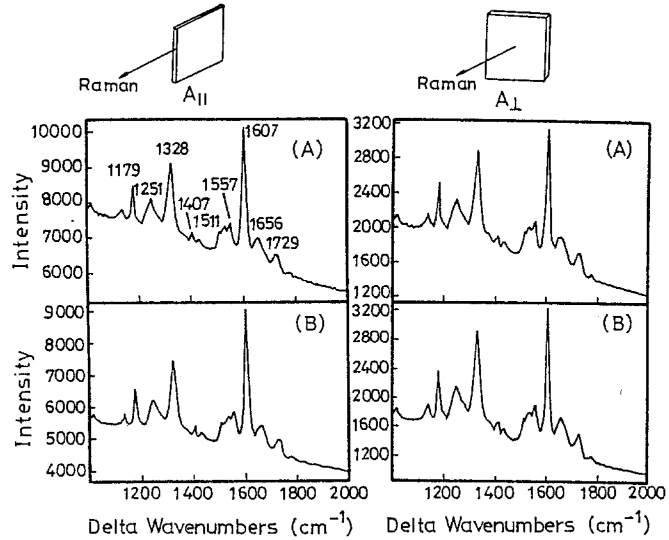


Figure 5. Raman spectra of Poly(DCMTC-ODA) films prepared at 10 minutes of reaction time: (A) The surface facing water phase; (B) The surface facing organic phase.

Table 1. The Effect of Anisotropy on a Sectected Absorption Bands of the Raman Spectra for Poly(DCMTC-ODA) Films[a].

Reaction Time(min)	Surface[b]	Raman Frequencies					
		1328 cm^{-1}			1656 cm^{-1}		
		$A_{\parallel}$	$A_{\perp}$	R	$A_{\parallel}$	$A_{\perp}$	R
2	W	218	177	1.23	90	44	2.05
	O	200	166	1.20	73	38	1.92
5	W	770	340	2.26	220	105	2.10
	O	1010	472	2.14	250	138	1.81
10	W	1740	875	1.99	485	220	2.20
	O	1920	1158	1.66	510	285	1.79
30	W	1870	1050	1.78	525	244	2.15
	O	1575	1145	1.38	510	300	1.70

[a] Polymerization condition:[DCMTC]=[ODA]=0.009M, Na_2CO_3=0.002M, Reaction temperature=0°C.

[b] W:the surface of the films adjacent to the water phase; O: the surface of the films adjacent to the organic phase.

cm^{-1} band was assigned to the C=O stretch of the amide group. From the Raman spectra of interfacial film, we calculated the polarization ratio of the characteristic absorption of the functional groups. The results are arranged in Table 1. Referring to Table 1, we found that the R value is above one (1). Thus, the interfacial films were anisotropic samples. Moreover, all the surfaces of the films adjacent to the water phase were greater in the polarization ratio of the two absorption bands than the surfaces of the films adjacent to the organic phase at same reaction time. The stretching vibrations of the C=O and N-H groups in polyamides involve changes in dipole moment that are almost exactly perpendicular to the chain axis; the corresponding bands are weak for polarized radiation vibrating along the chain axis and strong for that vibrating perpendicular to the axis.[24] Thus, the chain axis of the poly(amic-ester)s mainly oriented perpendicularly to the interface in the direction of membrane growth. This was probably because the direction of polymer chains had connections with the diffusive directions of the monomers. These results are consistent with literature.[20]

Conclusions

The interfacial films obtained were not homogeneous. The surfaces of the polymers adjacent to the water phase had higher average molecular weight than the surfaces of the polymers adjacent to the organic phase. Moreover, the morphology of the films also changed from dense to porous along the thickness direction of the films.

In both Poly(DCMTC-ODA) and Poly(DCMTC-MDA) systems, the inherent viscosity of the polymers was at a maximum of about 5 minutes of reaction time. When BTEAC was added, the inherent viscosity of the polymers was at a maximum of 3 minutes. This was probably because BTEAC promoted the diffusion of the diamines.

From the results of polarization ratio, we understood the films were anisotropic samples. The polarization ratios 1328 cm^{-1} and 1650 cm^{-1} at the surfaces of the films adjacent to the water phase were greater than that at the surfaces of the films adjacent to the organic phase at the same reaction time. The chain axis of the poly(amic-ester)s mainly oriented perpendicularly to the film surface and parallel to the direction of membrane growth.

Acknowledgements

We are grateful to the National Science Council of the Republic of China for their support of this work (Grant: NSC 82-0405-E-011-049).

References

1. Koros WJ, Fleming GK (1993) J.Membrane Sci., 83: 1.
2. Makino H, Kusuki Y, Harada T, Shimazaki H, Isida T (1985) US Patent 4,528,004.
3. Makino H, Kusuki Y, Harada T, Shimazaki H, Isida T (1984) US Patent 4,440,643.
4. Bikson B, Nelson J (1989) US Patent 4,826,599.
5. Cadotte JE (1981) US Patent 4,277,344.
6. Chai GY, Krantz WB (1994) J.Membrane Sci., 93: 175.
7. Cadotte JE, Petersen RJ, Larson RE, Erickson EE (1980) Desalination, 32: 23.
8. Larson RE, Cadotte JE, Petersen RJ (1981) Desalination, 38: 473.
9. Bartels CR, Kreuz KL (1987) J.Membrane Sci., 32: 291.
10. Cadotte JE, King RS, Majerle RJ, Petersen RJ (1981) J.Macromol.Sci. Chem., A15(5): 727.
11. Ueda U, Oishi Y, Sakai N, Imai Y (1982) Macromolecules,15: 248.
12 Tagle LH, Diaz FR, Maza MPDL, Vega JC (1986) J.Polym.Sci.Polym. Chem.Ed., 24: 495.
13. Tagle LH, Diaz FR, Riveros PE (1986) Polymer J., 18: 501.
14. Morgan PW (1965) Condensation Polymers by Interfacial and Solution Methods, Interscience, New York,.
15. Cadotte JE (1985) ACS Symp.Ser,269, Chap. 12.
16. Sugawara S, Konno M, Saito S (1989) J.Membrane Sci., 44: 151.
17. Sundet SA, Arthur SD, Campos D, Eckman TJ, Brown RG (1987) Desalination, 64: 259.
18. Desai NV, Rangarajan R, Rao AV, Gary DK, Ankleshwaria BV, Mehta MH (1992) J.Membrane Sci., 71: 201.
19. Hurndall MJ, Jacobs EP, Sanderson RD (1992) Desalination, 86: 135.
20. Enkelmann V, Wegner G (1976) Makromol.Chem., 177: 3177.
21.Mikos AG, Kiparissides C (1991) J.Membrane Sci., 59: 205.
22. Chern YT, Wu BS, J .Appl. Polym. Sci., accepted.
23. Chern YT (1995) Makromol.Chem.Phys., 196: 3217.
24. Billmeyer FW, Jr. (1984) Textbook of Polymer Science,3th ed.,John Wiley and Sons,New York,NY,p.295 .