Chlorination and Oxidation of Aromatic Polyamides. I. Synthesis and Characterization of Some Aromatic Polyamides

SHAOYU WU,[1,*] GUODONG ZHENG,[1] HUIQIN LIAN,[1] JING XING,[1] and LIANFANG SHEN[2]

[1]Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022 and [2]State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan, 430071, People's Republic of China

SYNOPSIS

The synthesis is described of some aromatic polyamides based on unsubstituted, and methyl-, carboxy-, and sulfo-substituted diamines by interfacial polycondensation. Some of them are crosslinked and some of them contain heterocyclic aromatic rings. Their chemical structures are characterized by IR and ^{13}C solid-state NMR spectra and the spectra are interpreted. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyamides possess suitable high performance for reverse osmosis membranes used for seawater desalination and ultrapure water preparation.[1] Since the DuPont company determined that polyamides (PAs) were the most suitable materials for reverse osmosis membranes, many studies on them have been reported,[2] especially since Cadotte et al. of Filmtec prepared outstanding performance composite membranes by an *in situ* interfacial polymerization reaction on the surface of a porous polysulfone substrate.[3] PA thin film composite membranes, such as FT-30 from Filmtec, A-15 from Dupont, and the UTC series from Toray,[4] have achieved a major position in the market of reverse osmosis membranes. Their ultrathin active layers are all PAs made by interfacial polycondensation. In this study some aromatic PAs for composite reverse osmosis membranes were synthesized by interfacial polycondensation, some of them containing special substituents or heterocyclic aromatic rings and some of them crosslinked. Their chemical

structures were characterized by IR and ^{13}C solid-state NMR spectra.
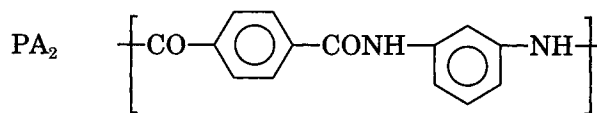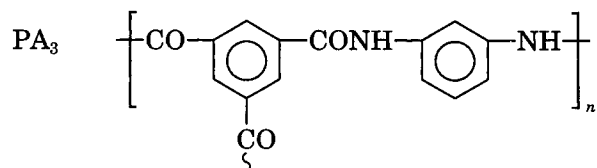
EXPERIMENTAL

Synthesis of PAs

All PAs were prepared by the interfacial polycondensation method developed by Morgan.[5] Their structures are as follows:
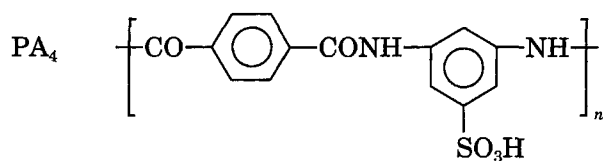

PA$_1$
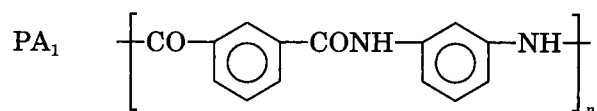
poly(-1, 3-phenylene isophthalamide)
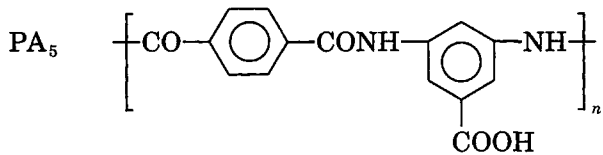
PA$_2$

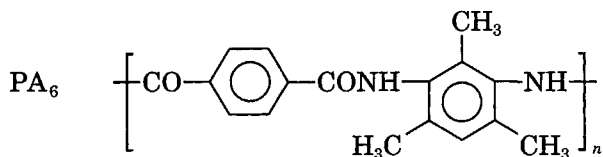poly(-1, 3-phenylene terephthalamide)

PA$_3$

poly(-1, 3-phenylene trimesoylamide)

PA$_4$ $\left[\!CO\!-\!\langle\bigcirc\rangle\!-\!CONH\!-\!\langle\bigcirc\rangle\!-\!NH\right]_n$
        SO$_3$H

poly(-sulfo-3, 5-phenylene terephthalamide)

PA$_5$ $\left[\!CO\!-\!\langle\bigcirc\rangle\!-\!CONH\!-\!\langle\bigcirc\rangle\!-\!NH\right]_n$
        COOH

poly(-carboxy-3, 5-phenylene terephthalamide)

PA$_6$ $\left[\!CO\!-\!\langle\bigcirc\rangle\!-\!CONH\!-\!\langle\bigcirc\rangle\!-\!NH\right]_n$
        CH$_3$
        H$_3$C   CH$_3$

poly(-2, 4, 6-trimethyl-1, 3-phenylene
terephthalamide)

PA$_7$ $\left[\!CO\!-\!\langle\bigcirc\rangle\!-\!CONH\!-\!\langle N \rangle\!-\!NH\right]_n$
        OH
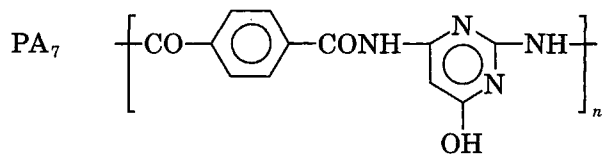
poly(-4-hydroxy-2, 4-pyrimididylidene
terephthalamide)

PA$_8$ $\left[\!CO\!-\!\langle\bigcirc\rangle\!-\!CONH\!-\!\langle N \rangle\!-\!NH\right]_n$
        NH
        S

poly(-2, 4, 6-pyrimididylidene terephthalamide)

PA$_9$ $\left[\!CO\!-\!\langle\bigcirc\rangle\!-\!CONH\!-\!\langle N \rangle\!-\!NH\right]_n$
        NH
        S
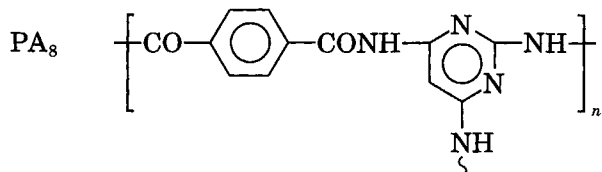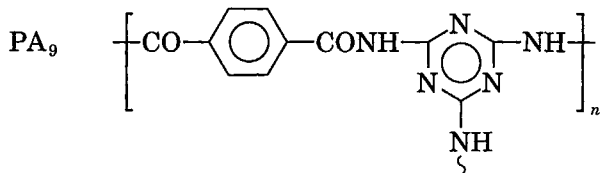
poly(-2, 4, 6-1, 3, 5-triazolylidene terephthalamide)

Table I   Conditions of Interfacial Polycondensation of Polyamides (PAs)

| PA | Phase | | T (min) | η_{inh} (dL/g) |
	Aqueous	Organic		
PA$_1$	5 mmol diamine 100 mL water 0.05 mol NaOH	5 mmol acid chloride 100 mL hexane	10	1.02
PA$_2$		Same as PA$_1$	10	1.23
PA$_3$	7 mmol diamine 100 mL water 0.05 mol NaOH	5 mmol acid chloride 100 mL hexane	10	
PA$_4$	5 mmol diamine 80 mL water 10 mL acetone 0.05 mol NaOH	5 mmol acid chloride 50 mL hexane	30	0.45
PA$_5$	5 mmol diamine 80 mL water 20 mL THF 0.05 mol NaOH	5 mmol acid chloride 50 mL hexane	30	0.51
PA$_6$		Same as PA$_4$	30	0.48
PA$_7$	5 mmol diamine 100 mL water 20 mL THF 0.05 mol NaOH	7 mmol acid chloride 50 mL hexane 10 mL THF	30	0.38
PA$_8$	5 mmol triamine	Same as PA$_6$	30	
PA$_9$	10 mmol triamine TMAHDB	10 mmol acid chloride	15	

T, reaction time; TMAHDB, trimethylamine hexadecane bromide. Reaction temperature was 20°C.

Table II   IR Spectral Data of Some Polyamides (PAs) Not Containing Substituent Groups in Diaminobenzene

Frequency (cm^{-1})			
PA$_1$	PA$_2$	PA$_3$	Assignment
3430	3421	3424	N — H stretching (free)
	3312		N — H stretching (H-bonded)
3066	3062	3070	Aromatic C — H stretching
1652	1646	1668	Amide I
1608	1607	1609	C = C ring stretching
1540	1538	1541	Amide II
1487	1486	1488	C = C ring stretching
1441		1445	C = C ring stretching
1416	1420	1419	Aromatic C — N stretching
1249	1281	1246	Interaction of N — H bending and C — N stretching (amide II)
783	782	779	Out of plane bending of C — H bonds of aromatic rings
716	720	731	Out of plane of amide I
688	683	674	Deformation of N — H
584	592	576	C = O out of plane

Table III   IR Spectral Data of Polyamides (PAs) Containing Substituent Groups

Frequency (cm^{-1})			
PA$_4$	PA$_5$	PA$_6$	Assignment
3456		3418	N — H stretching (free)
3330	3385	3324	N — H stretching (H-bonded)
3064	3063	3063	Aromatic C — H stretching
		2924	C — H stretching in CH$_3$
	1791		C = O stretching in COOH
1687	1686	1645	Amide I
1570	1609	1572	C = C stretching
1530	1554	1524	Amide II
1505		1490	C = C stretching
1423	1426	1426	Aromatic C — N stretching
1296	1287	1285	Amide II
1233			S = O stretching in SO$_3$H
1025	1017		1, 3, 5-substituted in aromatic rings
778	775	781	Out of plane bending of C — H bonds of aromatic rings
731	731	731	Out of plane of amide I
634	657	687	Deformation of N — H
582	567	564	Out of plane of C = O

Table IV   IR Spectral Data of Polyamides (PAs) Containing Heterocyclic Rings

Frequency (cm^{-1})			
PA$_7$	PA$_8$	PA$_9$	Assignment
3423		3474	N—H stretching
	3337		N—H stretching (H-bonded)
3067	3089	3009	C—H stretching in benzene
1690	1695	1685	Amide I
	1663	1645	Ring breathing of heterocyclic rings
1608	1607	1610	C=C stretching in benzene
1508	1512	1511	Amide II
1424	1458	1466	C—N stretching
1286	1294	1286	Amide II
1202	1198	1209	Ring breathing of heterocyclic rings
780	827	792	Out of plane bending C—H bonds of benzene
732	724	733	Out of plane N—H bending
699	646	640	Deformation of N—H
565	541	571	C=O out of plane

Table V   Chemical Shifts and Assignments of ^{13}C Solid-State NMR

Structure of PA	Chemical Shift and Assignment							
CO—⬡(6,2,3,7)—CONH(1,4)—⬡(5,8,9)—NH	Chemical shift	165	136	129	126	120	116	112
	Assignment	C$_1$	C$_2$	C$_{3,4,9}$	C$_7$	C$_6$	C$_8$	C$_5$
CO—⬡(2,4)—CONH(1)—⬡(3,6,5,7)—NH	Chemical shift	165	136	132	127		118	
	Assignment	C$_1$	C$_2$	C$_3$	C$_{4,7}$		C$_{5,6}$	
CO—⬡(4,2,3,CO)—CONH(1)—⬡(5,3,6,7)—NH	Chemical shift	165	136	130	123	119	116	
	Assignment	C$_1$	C$_2$	C$_4$	C$_7$	C$_3$	C$_{5,6}$	
CO—⬡(2,6)—CONH(1,3)—⬡(4,5,7,SO$_3$H)—NH	Chemical shift	165	140	136	130	123	118	
	Assignment	C$_1$	C$_4$	C$_2$	C$_{3,6}$	C$_7$	C$_5$	
CO—⬡(2,6)—CONH(1,3)—⬡(4,5,7,COOH)—NH	Chemical shift	165	138	135	130	116		
	Assignment	C$_1$	C$_{3,4}$	C$_2$	C$_{6,7}$	C$_5$		
CO—⬡(3,4)—CONH(1,2)—⬡(N,2,5,6,N,OH)—NH	Chemical shift	166	137	129	117			
	Assignment	C$_1$	C$_{2,3}$	C$_4$	C$_{5,6}$			

The conditions of polymerization are summarized in Table I.

All PAs were washed with an aqueous solution of HCl, distilled water, and acetone successively, then dried under vacuum at 60°C for 24 h. The inherent viscosity was determined on a 0.5 g/dL solution in concentrated sulfuric acid at 20°C.

IR Spectroscopy

The IR spectra were recorded on a U.S. Digilab FT 20E IR spectrometer. The samples were made by the KBr pellet technique.

^{13}C Solid-State NMR Spectroscopy

^{13}C solid-state NMR spectra were obtained using a Swiss Bruker MSL-400-PFT-NMR spectrometer.

RESULTS AND DISCUSSION

IR Spectra

A summary of appropriate frequency assignments of those PAs not containing substituents in the diaminobenzene is presented in Table II.

PA$_1$–PA$_3$ exhibit strong absorption bands between 3421 and 3430 cm^{-1} attributed to the N—H stretching vibrations. PA$_2$ exhibits an H-bonded N—H stretching vibration at 3312 cm^{-1}. The band between 3062 and 3078 cm^{-1}, which corresponds to the C—H stretching vibration, characterizes an aromatic system. Amide I from the C=O stretching vibration, which is located in the area between 1646 and 1668 cm^{-1}, is the typical absorption band of amide.[6] Amide II, from the coupling of N—H bending and C—N stretching of C—N—H groups, is located near 1540 cm^{-1}, between 1216 and 1281 cm^{-1}, and is the typical absorption band of amide too. The three strong absorptions near 1608, 1487, and 1441 cm^{-1} are assigned to C=C stretching vibration in the benzene structure. Other corresponding absorption bands are shown in Table II.

It is interesting to note that only PA2 in this group shows a strong H-bonded N—H stretching peak at 3312 cm^{-1}, which may result from its symmetrical structure from the acid chloride.

We find from Table II that the effect of structure on vibration frequencies of amide I is obvious. PA$_2$, because of its resonance effect, shows the lowest frequencies for the absorption band of all the PAs studied.

The IR spectral data of PAs that contain some special substituents are given in Table III.

Apart from the same assignments as PA$_1$–PA$_3$, PA$_4$–PA$_6$ show special absorption bands, for example, the 1233 cm^{-1} is the S=O stretching vibration frequency of SO$_3$H in PA$_4$. PA$_5$ exhibits a strong absorption band at 1791 cm^{-1}, which results from C=O stretching in COOH; and 2924 cm^{-1} is assigned to C—H stretching in —CH$_3$.[7] Another obvious difference is that PA$_4$–PA$_6$ exhibit special absorption bands owing to the effect of multisubstitution on benzene: 1025 and 1017 cm^{-1} of PA$_4$ and PA$_5$ are the typical absorption frequencies of 1,3,5-substituted benzene.[7]

The IR spectral data of PAs that contain heterocyclic aromatic rings are presented in Table IV.

Besides typical absorption bands of amide and benzene, PA$_7$–PA$_9$ exhibit some special bands that

Chemical shift (ppm)
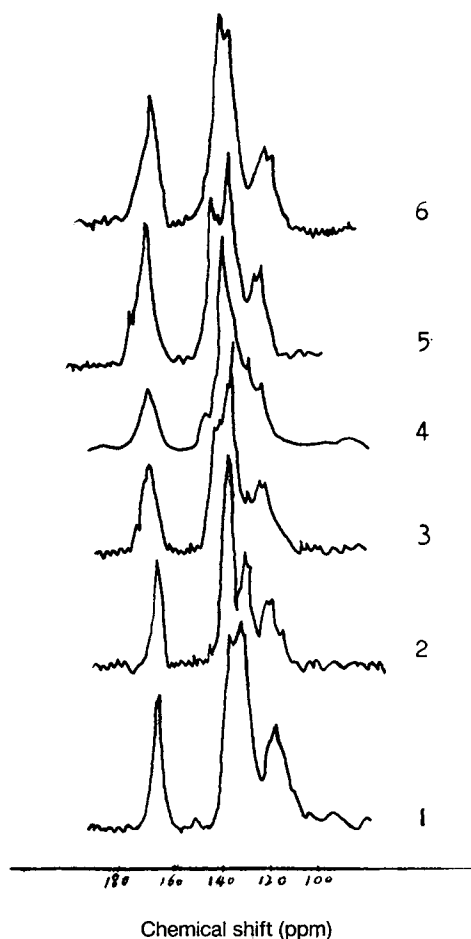
Figure 1   Spectra of ^{13}C solid-state NMR of polyamides: (1) PA$_1$, (2) PA$_2$, (3) PA$_3$, (4) PA$_4$, (5) PA$_5$, and (6) PA$_7$.

relate to heterocyclic aromatic rings, such as the heterocyclic aromatic ring breathing bands located near 1650 and 1200 cm^{-1}.[8]

^{13}C Solid-State NMR Spectra

High-resolution ^{13}C solid-state NMR was a useful tool for examination of molecular structure in the solid state for the past decade.[9] This tool was used for this study to characterize the chemical structure of PAs. Relevant data and spectra are presented in Table V and Figure 1.[10]

From Table V and Figure 1 we find that the chemical shift of the carbon of C$=$O is in the lowest field in every PA and is not affected by different structures. Some of the C bands are difficult to resolve because of their proximate chemical shifts.

REFERENCES

1. R. J. Petersen, *J. Membr. Sci.,* **83,** 81 (1993).
2. S. D. Arthur, *J. Membr. Sci.,* **46,** 243 (1989).
3. J. E. Cadotte, R. S. King, R. J. Majerle, and R. J. Petersen, *J. Macro. Sci.-Chem.,* **A15,** 727 (1981).
4. R. J. Petersen and J. E. Cadotte, in M. E. Poter, Ed., *Handbook of Industry Membrane Technology,* Noyes Publications, Park Ridge, NJ 1990 p. 307.
5. P. W. Morgan, *Condensation Polymers,* Plenum, New York, 1965.
6. Y. P. Khanna and E. M. Pearce, *J. Polym. Sci., Polym. Chem. Ed.,* **19,** 2799 (1981).
7. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules,* Chapman & Hall, London, 1978.
8. Tanner, *Spectrochim. Acta,* **8,** 9 (1956).
9. J. Schaefer and E. O. Stejeskel, *J. Am. Chem. Soc.,* **98,** 1031 (1976).
10. J. L. Nieto, J. G. de la Campa, and J. der Abajo, *Macromol Chem.,* **183,** 557 (1982).