

Synthesis and Study of Some Newer Polyamides for Semipermeable Membrane

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SYNOPSIS

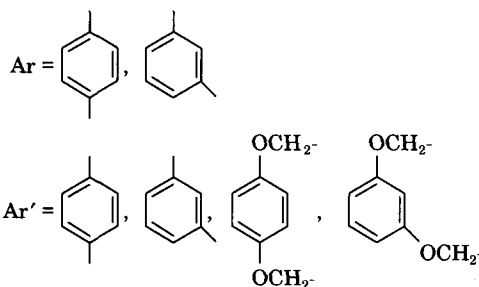
A series of novel polyamides was prepared by low temperature solution polycondensation of *N*-(*p*/*m*-aminobenzoyl aminoacetyl)-*N'*-(4/3-aminobenzoyl)hydrazine with different diacid chlorides in dry *N,N*-Dimethylacetamide (DMAC). The properties of the polyamides for membrane processing were studied with the help of infrared spectra, inherent viscosity, differential thermal, and thermogravimetric analysis. The inherent viscosities were measured in concentrated sulfuric acid at $25 \pm 5^\circ\text{C}$ and were in the range of 0.35–0.89 dL/g. The thermogravimetric data in air indicate that the initial decomposition temperature was in the range of 175–200°C. The polymer melt temperature (T_m) and glass transition temperature (T_g) were in the range of 230–450°C and 153.3–300°C, respectively.

INTRODUCTION

The significance of polyamides for semipermeable membrane processing for reverse osmosis has been well established.^{1–3} A large number of synthetic, semipermeable membranes have been developed for use in desalination as well as for use in water waste treatment. Recently, Ramchandran and Misra⁴ have initiated studies on the application of charged membranes useful in the electrodialysis process. These authors have also reported some studies on the radiation stability of cellulosic and noncellulosic, neutral, polymeric membranes, useful in reverse osmosis.⁵

We have reported earlier the synthesis of some polyamides⁶ with excellent physical properties, such as thermoxidative stability, inherent viscosity, solubility, etc. The object of the present investigation is to prepare some newer polyamides suitable for semipermeable membrane, useful for desalination by reverse osmosis.

The repeating unit of the polyamides can be represented by the following structure:



Dvornic⁷ and Preston et al.^{8,9} have reported that the polymers containing the above types of linkages exhibit interesting and potentially useful properties usually required for high performance materials. Among those worth mentioning are: high thermal and thermoxidative stability, high mechanical strength and moduli, and remarkable solute rejection capabilities of the asymmetric reverse osmosis membranes.

For these reasons the present study was undertaken and was directed towards the synthesis and study of a series of polyamides.

Table I(a) Characteristics of Monomeric Diamines

Diamines	Calculated (%)			Found (%)			Infrared Bands cm^{-1}		
	C	H	N	C	H	N	C=O (St.)	—NH (St.)	—NH (Ben.)
i. N-(<i>p</i> -aminobenzoyl aminoacetyl)-N'-(4-aminobenzoyl) hydrazine	58.7	5.1	21.4	58.2	4.8	22.2	1680	3300	1540
ii. N-(<i>m</i> -aminobenzoyl aminoacetyl)-N'-(4-aminobenzoyl)hydrazine	58.7	5.1	21.4	58.0	5.0	20.8	1660	3240	1520
iii. N-(<i>p</i> -aminobenzoyl aminoacetyl)-N'-(3-aminobenzoyl)hydrazine	58.7	5.1	21.4	57.8	5.0	21.0	1680	3210	1520

St. = Stretching vibrations; Ben. = Bending vibrations.

EXPERIMENTAL

Synthesis of Diacid Chlorides

Commercially available terephthaloyl chloride and isophthaloyl chloride were purchased from Fluka and were used as such. The 1,4/1,3 phenylene dioxy diacetyl chlorides were prepared by the method reported earlier.¹⁰

Synthesis of Diamines

Preparation of N-(*p*-Nitrobenzoyl Aminoacetyl)-N'-(4-nitrobenzoyl)Hydrazine

N-(*p*-nitrobenzoyl) aminoacetic acid hydrazide (2 mol) was dissolved in N,N-Dimethylacetamide in a three-necked flask, equipped with a condenser, mechanical stirrer, and a thermometer. *p*-Nitrobenzoyl chloride (2 mol) was added in small portions with

constant stirring for two hours. Excess solvent was distilled off under reduced pressure and concentrated solution was poured into ice-cold water. Solid product was separated. It was purified with ethanol; m.p.: 225–230°C; yield: 65%.

Preparation of N-(*p*-Aminobenzoyl Aminoacetyl)-N'-(4-Aminobenzoyl)Hydrazine

N-(*p*-nitrobenzoyl aminoacetyl)-N'-(4-nitrobenzoyl) hydrazine (1 mol) was dissolved in N,N-Dimethylacetamide. The solution was stirred with a pinch of Raney Nickel, with warming. Thereafter hydrazine hydrate (2 mol) was added dropwise with stirring. The reaction mixture was filtered and concentrated. Concentrated solution was poured into ice-cold water. Solid mass, thus obtained, was purified with ethanol; m.p.: 242–245°C; yield: 60%.

N-(*m*-aminobenzoyl aminoacetyl)-N'-(3-aminobenzoyl) hydrazine and N-(*p*-aminobenzoyl ami-

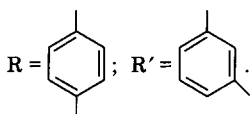
Table I(b)  **¹H NMR Spectra of Monomeric Diamines**

Diamines ^a	R ₁	R ₂	δ
i.	4-NH ₂	4-NH ₂	8.1–8.4 (m, 8H, ArH), 3.4 (bs, 4H, 2 × ArNH ₂) 4.2 (d, 2H, —CH ₂), 5.5 (bs, 1H, —CONH) 7.0–7.5 (bs, 2H, —CONHNHCO—)
ii.	3-NH ₂	3-NH ₂	8–8.6 (m, 8H, ArH), 3.8 (bs, 4H, 2 × ArNH ₂) 4.2 (d, 2H, —CH ₂), 6.0 (s, 1H, —CONH) 7.2–6.8 (bs, 2H, —CONHNHCO—)
iii.	4-NH ₂	3-NH ₂	8–8.2 (m, 8H, ArH), 3.8 (bs, 4H, 2 × ArNH ₂) 4.6 (d, 2H, —CH ₂), 5.8 (s, 1H, —CONH) 7.2–7.6 (bs, 2H, —CONHNHCO—)

^a The nomenclature of diamines i, ii, and iii is given in Table I(a).
Abbreviations: s = singlet; d = doublet; bs = broad singlet.

Table II Structure of Repeating Unit and Inherent Viscosity of Polyamides

Polymer Code	Repeating Unit	Yield (%)	Inherent Viscosity at 25 ± 5°C (dL/g)
I	+HN—R—CONHCH ₂ CONHNHCO—R—NHCO—R—CO+ _n	95	0.89
II	+HN—R—CONHCH ₂ CONHNHCO—R—NHCO—R'—CO+ _n	92	0.82
III	+HN—R—CONHCH ₂ CONHNHCO—R—NHCOCH ₂ —O—R—OCH ₂ CO+ _n	87	0.75
IV	+HN—R—CONHCH ₂ CONHNHCO—R—NHCOCH ₂ —O—R'—OCH ₂ CO+ _n	86	0.81
V	+HN—R'—CONHCH ₂ CONHNHCO—R'—NHCO—R—CO+ _n	88	0.82
VI	+HN—R'—CONHCH ₂ CONHNHCO—R'—NHCO—R'—CO+ _n	68	0.78
VII	+HN—R'—CONHCH ₂ CONHNHCO—R'—NHCOCH ₂ O—R—OCH ₂ CO+ _n	72	0.64
VIII	+HN—R'—CONHCH ₂ CONHNHCO—R'—NHCOCH ₂ O—R'—OCH ₂ CO+ _n	62	0.60
IX	+HN—R—CONHCH ₂ CONHNHCO—R'—NHCO—R—CO+ _n	65	0.47
X	+HN—R—CONHCH ₂ CONHNHCO—R'—NHCO—R'—CO+ _n	64	0.42
XI	+HN—R—CONHCH ₂ CONHNHCO—R'—NHCOCH ₂ O—R—OCH ₂ CO+ _n	65	0.38
XII	+HN—R—CONHCH ₂ CONHNHCO—R'—NHCOCH ₂ O—R'—OCH ₂ CO+ _n	61	0.35



noacetyl)-N'-(3-aminobenzoyl) hydrazine were prepared by the same method as above.

The monomers were characterized by I.R., NMR spectroscopy, and elemental analysis, (Tables Ia and Ib).

Low Temperature Solution Polycondensation

Diamine 10 g (0.03 mol) and 100 mL dry N,N-DMAC were placed in a three-necked polymerization tube, equipped with a stirring unit, a dropping funnel, and a thermometer. The reaction mixture was cooled to -20°C, and a solution of diacid chloride (0.06 mol) in dry N,N-DMAC was added dropwise with stirring. After the addition of diacid chloride, the reaction mixture was stirred well for 6 h, after which the temperature was allowed to rise to room temperature. The mixture was then neutralized by the addition of lithium hydroxide, which was needed to neutralize the HCl formed during the reaction. The viscous solution was further stirred for 8 h and then was poured into 10% aqueous methanol. Solid mass, thus obtained, was filtered and dried below 50°C.

Thermal Analysis

Thermogravimetric and differential thermal analysis were carried out in static air. The sample size was

3 to 8 mg. The heating rate and chart speed was 5°C/min. and 20 cm/h respectively.

Infrared Absorption Spectroscopy

Infrared spectra were obtained by the KBr disk method on a Jasco Model A-1 IR spectrophotometer.

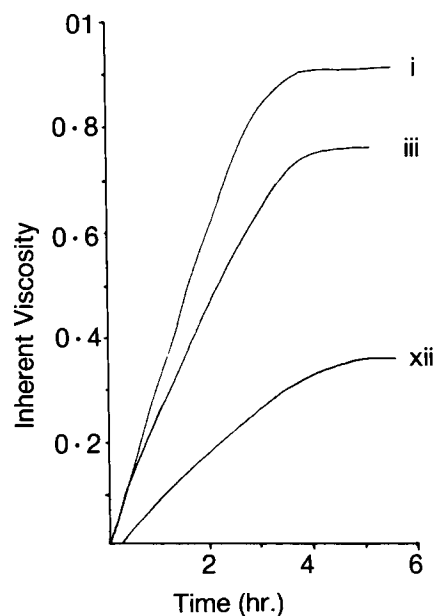


Figure 1

Table III Infrared Absorption Bands of Polyamides

Polymer Code	C=O (St.) cm ⁻¹	—NH (St.) cm ⁻¹	—NH (Ben.) cm ⁻¹	—CH (Ben.) cm ⁻¹	C—O (St.) cm ⁻¹
I	1690(S)	3240(b)	1560(m)	1420(w)	1300(m)
II	1680(m)	3200(b)	1550(w)	—	1250(m)
VI	1650(S)	3260(m)	1550(w)	1440(w)	1280(w)
IX	1680(S)	3210(b)	1530(w)	1410(w)	1260(m)

S = sharp; m = medium; b = broad; w = weak; St. = Stretching vibrations, Ben. = Bending vibrations.

RESULTS AND DISCUSSION

Inherent Viscosity

The inherent viscosities (Table II) of the polyamides were measured by observing the flow time of the polymer solution in sulfuric acid through an Ostwald-type viscometer. The concentration of the polymer solution was 0.5 g/100 mL. It was observed that the inherent viscosities vary within the range of 0.35–0.89 dL/g. Table II shows that the polyamides obtained by the condensation of diamines with terephthaloyl/isophthaloyl chlorides have higher inherent viscosities than those formed with 1,4/1,3 phenylene dioxy diacetyl chlorides. It was expected that the lower inherent viscosities of the latter type of polyamides were due to the presence of —O—R—O—linkage in the diacid chloride molecules.

The rate of polymerization (Fig. 1) of the polyamides was observed by studying the variation of inherent viscosity with time. The polymerization completion time was observed to be in the range of 3–4 h for *para* substituted polymers and 4–5 h for *meta* substituted polymers.

Infrared Spectra

The structure of the repeating unit of the polyamides reveals that the polyamides are able to exhibit a large number of free hydrogen bonding sites, which is an essential requirement for altering the structure of permeating water in reverse osmosis. The IR spectra confirmed these expectations as it was found that absorption due to N–H and C=O groups has been shifted to lower wave numbers (Table III). If these hydrogen bonding sites are free to interact with water and to modify its structure, then the polyamides would be expected to have more “bound water.” The presence of intermolecular hydrogen bonding contributes significantly to the mechanical rigidity and wet strength of membranes.

Moisture Uptake

The polymers containing a judicious combination of hydrophobic and hydrophilic characters were noted for requisite water permeation as well as for solute rejection.¹¹ The polyamides exhibited both the hydrophobic and hydrophilic groups, so good moisture uptake was expected.

Table IV Solubility of Polyamides at 25 ± 5°C

Polymer Code Solvents	Solubility											
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
H ₂ SO ₄ (conc.)	S	S	S	S	S	S	S	S	S	S	S	S
N,N-DMF	PS	S	S	SH	PS	S	S	S	SH	S	S	S
N,N-DMAC	S	S	S	S	S	S	S	S	S	S	S	S
DMSO	SH	SH	SH	S	PS	PS	S	S	S	PS	S	S
Dioxane	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins
Benzene	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins	Ins

S = Soluble at room temperature; SH = Soluble on heating; PS = Partially soluble; Ins = Insoluble.

Solubility

The solubilities of the polyamides are summarized in Table IV. Solution casting techniques primarily depend upon the solubility of the polymer candidate in a volatile, water miscible solvent. All the polyamides were soluble in sulfuric acid. The polyamides were readily soluble in polar organic solvents like DMAC, DMSO, and DMF. On the basis of these observations, it can be concluded that the polyamides exhibit a high degree of polarity due to presence of $-NH$ and $C=O$ groups.

Thermal Properties

The data obtained from thermogravimetric and differential thermal analysis are recorded in Table V. Chain stiffness and the resistance to creep deformation are the additional mechanical requirements on the barrier material, since barrier materials are exposed to high hydrostatic pressures that prevail in reverse osmosis. Figure 2 shows the change in weight of the polymer sample with change in temperature. The initial decomposition temperature of the polyamides was in the range of 175–200°C in air. The weight loss below this temperature was due to loss of moisture and solvent. The region of the steep weight loss was observed from 225°C to 350°C. It was found that the polyamides obtained from diamines and terephthaloyl/isophthaloyl chlorides have higher thermal stability than those obtained from diamines and 1,4/1,3 phenylene dioxy diacetyl chlorides. The *para* substituted polyamide (I) started to decompose at 200°C and 96% weight loss was observed at 600°C. The *meta* substituted polyamide, however, started to decompose at 185°C and it was 100% decomposed at 600°C.

Table V TGA and DTA Analysis of Polyamides

Polymer Code	IDT ^a (°C)	SWLR ^b (°C)	MWL ^c at 600°C (%)	T_m^d (°C)	T_g^e (°C)
I	200	250–350	96	450	300
II	190	225–300	98	390	260
IV	180	200–300	90	310	206.6
VI	185	230–280	100	230	153.3

^a Initial decomposition temperature.

^b Steep weight loss region.

^c Maximum weight loss at 600°C.

^d Polymer melt temperature.

^e Calculated glass transition temperature.

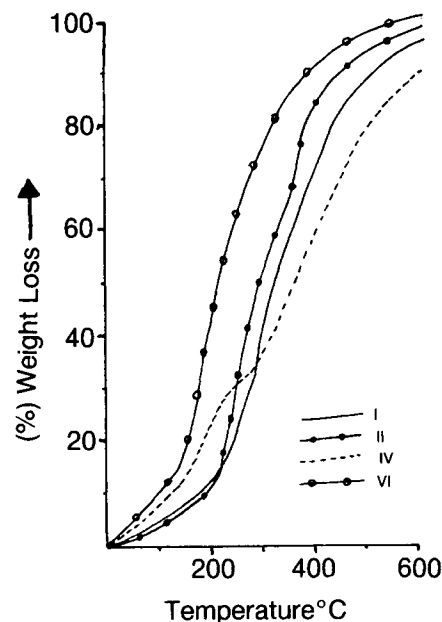


Figure 2

Polymer melt temperature (T_m) was evaluated with the help of differential thermal analysis by observing the temperature at which endothermic peaks were observed. Glass transition temperature (T_g) was calculated by using the empirical relationship:

$$T_g = \frac{2}{3} T_m$$

The empirical glass transition temperature of the polyamides was in the range of 153.3–300°C. The higher T_g values for the polyamides were due to an energy barrier of aromatic system for free rotation around bond axis. Such polyamides, having glassy rigid structures, are more suited as barrier materials for higher pressure applications and they are expected to give stable performance at elevated hydrostatic pressure.

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