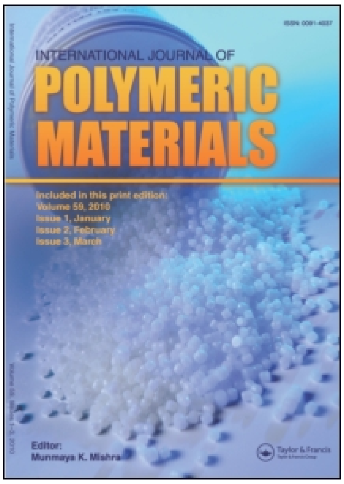

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# Synthesis and Characterisation of Aromatic Polyamide Hydrazide Polymers for Membrane Applications

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# Synthesis and Characterisation of Aromatic Polyamide Hydrazide Polymers for Membrane Applications

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The synthesis and characterisation of aromatic polyamide hydrazide polymers are reported in this paper. The polymers were synthesised from meta- and para-amino benzhydrazide and iso- and terephthaloyl chlorides by low temperature solution condensation polymerization reaction in *N*,*N*-dimethyl acetamide solvent at −10°C. Polymers having inherent viscosities in the range of 0.10 to 0.67 dl/g were obtained by varying the monomer concentration, stoichiometric ratio and also by employing multimonomer systems in suitable concentration ratios. The polymers are characterised by their inherent viscosity, moisture uptake, elemental composition, IR spectra and thermal stability.

KEYWORDS: Polyamide hydrazide, Reverse Osmosis, Membranes, Polymer synthesis, Polymer characterisation.

## 1. INTRODUCTION

The criteria for the selection of polymers suitable for making membrane for reverse osmotic separation is now clearly recognised[1–4] and it is presently possible to design polymer structure for membrane making to meet specific separation requirements.

The salient features of polymers suitable as barrier materials are the inherent chemical, mechanical and thermal properties and their processability. The appropriate chemical structure combines polar and nonpolar functional groups with a polymeric network. Polymers with adequate molecular weight are known[2] to ensure tough membranes. The chain stiffness characterised by high glass transition temperature is an additional mechanical requirement for barrier applications. Processability of the polymers in terms of solubility and tractability is also one of the major requirements for barrier applications. The rapidly expanding family of nitrogen-containing polymers has made available a special class of membranes suitable for a broad spectrum of membrane applications. This class of polymers is characterised by amide/imide linkages between various aromatic/heterocyclic structural units.

Aromatic polyamides,[5] polyamide hydrazide,[6] polybenzimidazole[7] polymers are reported to be superior to conventional cellulose acetate membranes with respect to high pressure and high temperature service conditions apart from their inherent chemical and bacterial stability. Some studies are recently reported[8–17] on the synthesis, characterisation and membrane transport properties of polyamide hydrazide polymers.

Most polymers considered for barrier applications are the products of polycondensation reactions between complimentary bifunctional compounds or self-condensation of cyclic intermediates containing both functional groups by conventional techniques of melt, solution and interfacial polycondensation.[18] It is well known that polymers of high molecular weight suitable for film formation are usually obtained if adequate attention is paid to the purity of monomers, stoichiometric equivalence of reactants, removal of nonpolymeric reaction products, temperature, time etc. However, a systematic study of the effect of these various reaction parameters on the polymer molecular weight is desirable. In this paper, the studies on the synthesis of a simple aromatic polyamide hydrazide polymer under varying reaction conditions are reported.

## 2. EXPERIMENTAL

Aromatic polyamide hydrazide polymer was synthesised by low temperature polycondensation reaction of meta- and para-amino benzhydrazide and iso- and terephthaloyl chloride in dimethyl acetamide solvent medium which also acts as an acid acceptor. P-amino benzoic acid hydrazide (PABH melting point 222°C–224°C) was obtained from Fluka A.G and was directly used after recrystallisation from demineralised water and ethyl alcohol mixture. The m-amino benzhydrazide (melting point 91–92°C) was synthesised from m-amino benzoic acid (obtained from Ferac Berlin, W.G) by converting it to methyl ester and by subsequent reaction with hydrazine and purification by recrystallisation. Isophthaloyl (IPC) and terephthaloyl chlorides (TPC melting points 44°C and 83°C respectively) were similarly obtained from Fluka A.G, and were distilled under vacuum and were recrystallised from dry hexane. Dimethyl acetamide (DMAc) was fractionally distilled under reduced pressure (boiling point 56–58°C at 11 mm Hg pressure) and stored over molecular sieve 4A. The polymerisation reaction was carried out under nitrogen atmosphere at $-10$°C using ice-salt mixture in a reaction vessel fitted with a mechanical stirrer.

The polymer samples were characterised by estimating their solution viscosity, elemental composition and moisture uptake. The solution viscosity was measured in dimethyl acetamide at $30 \pm 0.5$°C using Zeitfuch viscometer. The results are expressed as $\eta_{\text{inh}}$. The infrared spectroscopy of the polymer samples was recorded by KBr pelletisation using Perkin–Elmer Model 577 infrared spectrometer. The thermal stability of the polymers was carried out in air by recording thermogravimetric (TGA) and differential thermal analysis (DTA) spectra at a heating rate of 10°C/min using ULVAC SINKU-RIKO thermal analyser. The sample size was about 10 mg.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Synthesis of polymer

Solution polycondensations are known[19] to be affected by several reaction variables involving the characteristics inherent in the pure materials as well as the physical conditions. Purity of the reactants and solvents, equivalence of reactants, degree of mixing, time and temperature of the reaction are controlled to ensure completeness of the reaction with maximum yield.

*3.1.1. Effect of monomer concentration* The effect of monomer

TABLE I

Effect of monomer concentration

| S. no. | Concentration (M)<br>PABH | IPC | $\eta_{inh}$(dl/g) |
|---|---|---|---|
| 1 | 0.2 | 0.2 | 0.23 |
| 2 | 0.4 | 0.4 | 0.43 |
| 3 | 0.8 | 0.8 | 0.57 |
| 4 | 1.6 | 1.6 | 0.27 |

concentration on the polycondensation reaction between p-amino benzhydrazide (PABH) and isophthaloyl chloride (IPC) was studied. The $\eta_{inh}$ values obtained for the resultant polymer samples in the various cases are shown in Table I. It can be seen from this table that the inherent viscosity values decline at lower and higher monomer concentrations. The viscosity values reach a maximum at optimum intermediate concentrations. The lower viscosity observed at higher concentrations may be due to the difficulty in stirrability and temperature control. The poor viscosity values obtained at low concentrations could be due to some interfering side reactions because of traces of impurities.

*3.1.2. Effect of time and temperature* The reaction between amine and acid chloride functional groups was reported[18] to be fast with the rate constants in the order of $10^2$–$10^6$ l/mole sec, and hence is expected to be completed in a few minutes at room temperature. The $\eta_{inh}$ and % yield increase[20] sharply in a few minutes of reaction time and attain a saturation limit. In our studies, it was observed that the increase in reaction time from 30 minutes to several hours produced similar results which indicate that the reaction between p-aminobenzhydrazide and isophthaloyl chloride are fast enough with the rate constants comparable to what is reported[18] elsewhere for simple aromatic diamine and diacid chloride systems.

The reaction between amine hydrazide and diacid chloride being exothermic, high molecular weight polymers are obtained when reactions are carried out at room temperature or below. The % yield and $\eta_{inh}$ values are reported[20] to decrease with increase in reaction temperature. Although reaction rates and polymer solubility may increase with increase in temperature, the possibility of increase of rate of interfering side reactions lowers the obtainable viscosity. The polymerisation reactions in our study are invariably carried out at low temperature. However, room temperature polycondensation reaction produced the polymer in a finely powdered form with very low viscosity.

*3.1.3. Effect of stoichiometric ratio* The effect of molar ratio of the benzhydrazide and diacid chloride was studied. The molar concentration of PABH was kept at 0.42 M and diacid chloride concentration was varied from 0.35 M to 0.93 M. The results are shown in Table II. It can be seen from the results that the $\eta_{inh}$ values of the polymer is affected sharply when the molar ratios depart from unity. It is also interesting to note that the presence of excess amino hydrazide significantly decreases $\eta_{inh}$.

It is known that the presence of complementary reacting functional groups at the two ends of the growing polymer chain ensures high molecular weight. This criteria is fulfilled by taking near stoichiometric equivalence of reactants. The possibility of formation of smaller macromolecules with nonreacting similar end groups is enhanced by the presence of one of the reactants in excess. In this case, the presence of excess amino hydrazide insulates the growing polymer chains by end capping and further the amine and hydrazide end groups become inactive by salt formation with the liberated acid. This could be the reason for the extreme sensitivity of the reaction to the presence of excess amine hydrazide.

TABLE II
Effect of stoichiometric ratio

| S. no. | Stoichiometric ratio PABH/IPC | $\eta_{inh}$ (dl/g) |
|---|---|---|
| 1 | 1.2 | 0.10 |
| 2 | 0.67 | 0.19 |
| 3 | 1.0 | 0.43 |

*3.1.4 Effect of multimonomer reacting systems* The polymerisation reactions were carried out using different acid chloride and the effect of multimonomer reacting systems were studied. P-amino benzhydrazide was made to react with isophthaloyl chloride and

TABLE III

Effect of different acid chlorides

| S. no. | MABH | Conc. of monomers (M)<br>PABH | IPC | TPC | $\eta_{inh}$ (dl/g) |
|---|---|---|---|---|---|
| 1 | — | 0.2 | 0.2 | — | 0.23 |
| 2 | — | 0.2 | 0.14 | 0.06 | 0.33 |
| 3 | — | 0.2 | — | 0.2 | 0.38 |
| 4 | — | 0.8 | 0.6 | 0.2 | 0.62 |
| 5 | 0.8 | 0.2 | 0.8 | 0.2 | 0.67 |

terephthaloyl chloride and the mixtures of both. The $\eta_{inh}$ values obtained are shown in Table III. It can be seen from the results that higher viscosity values were obtained by replacement of isophthaloyl chloride with terephthaloyl chloride. Similar increase in viscosity for the polymerisation of all para substituted monomers are reported elsewhere.[10,15] Reaction between mixtures of meta and para substituted diacid chlorides also showed enhanced viscosity. It can be seen from the results that use of three monomer systems at optimum molar concentration (0.8 M) yielded a maximum $\eta_{inh}$ value of 0.62 dl/g. Four monomer reacting systems involving meta- and p-amino benzhydrazide, iso- and terephthaloyl chlorides were also studied and the resulting polymer showed $\eta_{inh}$ of 0.67 dl/g. This polymer exhibits film forming characteristics.

### 3.2. Characterisation of polymers

The characterisation data of typical polymer samples obtained from p-amino benzhydrazide and isophthaloyl chloride (Polymer I), p-amino benzhydrazide and terephthaloyl chloride (Polymer II) p-amino benzhydrazide and tere- and isophthaloyl chlorides (Polymer III), meta- and p-amino benzhydrazide and iso- and terephthaloyl chloride (Polymer IV) are shown in Table IV. The samples were characterised in terms of % moisture regain (at 65% RH and 30°C), $\eta_{inh}$ and elemental composition.

*3.2.1. Elemental composition and % moisture regain* The polymers exhibit a % moisture regain in the range of 4.87 to 4.97. This is comparable to 5% moisture regain reported[2] at 65% RH and 22°C for a simple aromatic polyamide (Nomex) polymer. It is

TABLE IV
Characterisation of Polyamide Hydrazide Polymers

| S. no. | Sample no. | $\eta_{inh}$ (dl/g) | Moisture regain % | Elemental composition % (observed) C | H | N | O | (calculated) C | H | N | O |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | I | 0.25 | 4.84 | 61.75 | 4.19 | 13.78 | 20.28 | 63.86 | 4.21 | 14.90 | 17.03 |
| 2 | II | 0.35 | 4.78 | 62.43 | 4.84 | 13.17 | 19.56 | 63.86 | 4.21 | 14.90 | 17.03 |
| 3 | III | 0.62 | 4.97 | 64.57 | 4.56 | 12.97 | 17.90 | 63.86 | 4.21 | 14.90 | 17.03 |
| 4 | IV | 0.67 | 4.98 | 63.14 | 4.09 | 13.97 | 17.80 | 63.86 | 4.21 | 14.90 | 17.03 |

pointed out that polymers showing very poor % moisture regain are reported to be unsuitable as membrane barrier for reverse osmosis separation application. It is reported[7] that polymers having moisture regain of more than 4% have been successfully fabricated into reverse osmosis membranes with adequate water and solute permeabilities.

The observed elemental composition of the polymer samples are compared with the calculated elemental composition and a good agreement between the two is noticeable.

*3.2.2. IR spectra* The infrared spectra of the three polymer samples are shown in Figures 1 and 2. The IR spectra of polymer samples show a characteristic absorption peak in the range of 3200–3400 cm$^{-1}$ due to N—H stretching vibration. Several other characteristic absorption bands due to —C=O stretching at 1650 cm$^{-1}$, C—N stretching vibration at 1575 cm$^{-1}$, N—H bending vibration in the range of 1390 cm$^{-1}$ are also observed in the spectra.

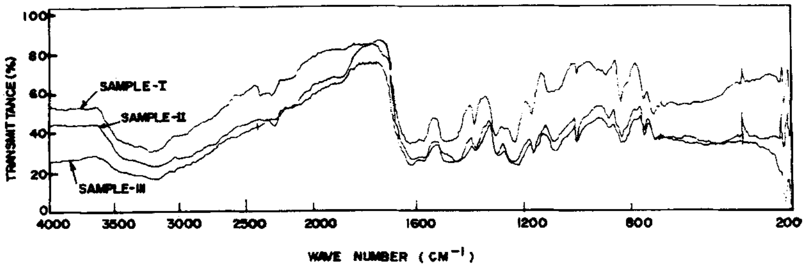

FIGURE 1 IR spectra of polymer samples

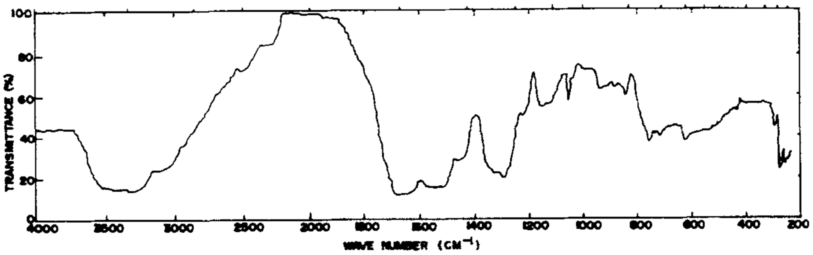

FIGURE 2 IR spectra of polymer sample IV

In addition to the above, absorption peaks characteristic of the presence of aromatic ring are also seen in the spectra.

*3.2.3. Thermal stability* The polymer samples were also characterised in terms of their thermal stability. The thermogravimetric (TGA) and differential thermal analysis (DRA) profiles of polyamide hydrazide samples are shown in Figures 3 and 4 respectively. It is well known that wholly aromatic polyamides and polyamide hydrazides because of strong hydrogen bonding and chain stiffness possess high thermal stability. It can be seen from the figures that all polymers showed characteristic thermal stability behaviour which has previously been reported.[21,22] Polymer I exhibits an endothermic peak of 420°C and a broad exothermic peak begins at 490°C with the peak maximum at 570°C. The endothermic peak at 425°C is followed by a rapid weight loss in the sample. This is ascribed[21] to the thermally induced cyclodehydration reaction of polymer hydrazine bonds forming oxadiazole rings in the structure. Similar rapid weight loss is noticeable beyond 490°C matching with the exothermic peak indicating the pyrolitic decomposition of the oxadiazoles formed. The initial weight loss noticeable below 120°C could be due to the escape of adsorbed moisture and solvents.

Polymer II also exhibits a similar sharp endothermic peak characteristic of polymer fusion at 480°C which is followed by rapid weight loss in sample. The sharp endothermic peak noticed in this case could be ascribed to the possibility of increased crystallinity of the sample due to closer packing of the polymer chains for all para substituted monomer units. A broad exothermic peak is noticeable beyond 500°C with a peak maximum at 620°C. This peak is also

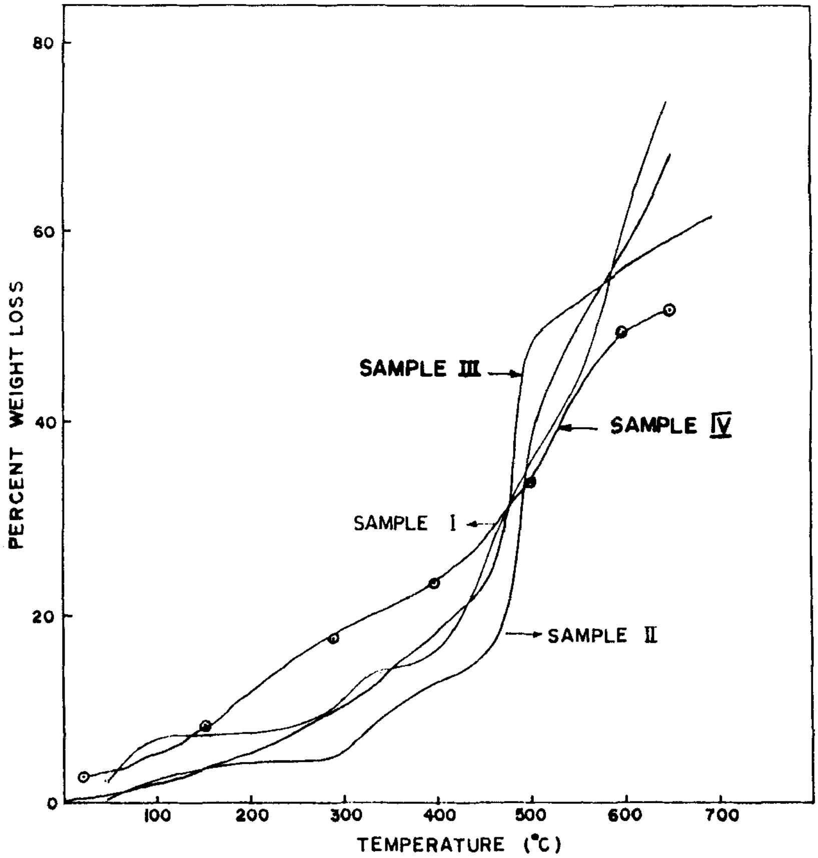

FIGURE 3 TGA spectra of polymer samples

accompanied by rapid weight loss and is indicative of pyrolitic decomposition. Thermal degradation temperature are both higher by nearly 50°C for the polymer II obtained from terephthaloyl chloride compared to polymer I obtained from isophthaloyl chloride. The thermal degradation temperature is taken in this case as the temperature at which exothermic peak maximum is noticed. The % weight loss for all para substituted polymer sample is also lower compared to para- meta- substituted polymer. These results suggest that the thermal stability of polyamide hydrazide polymer is

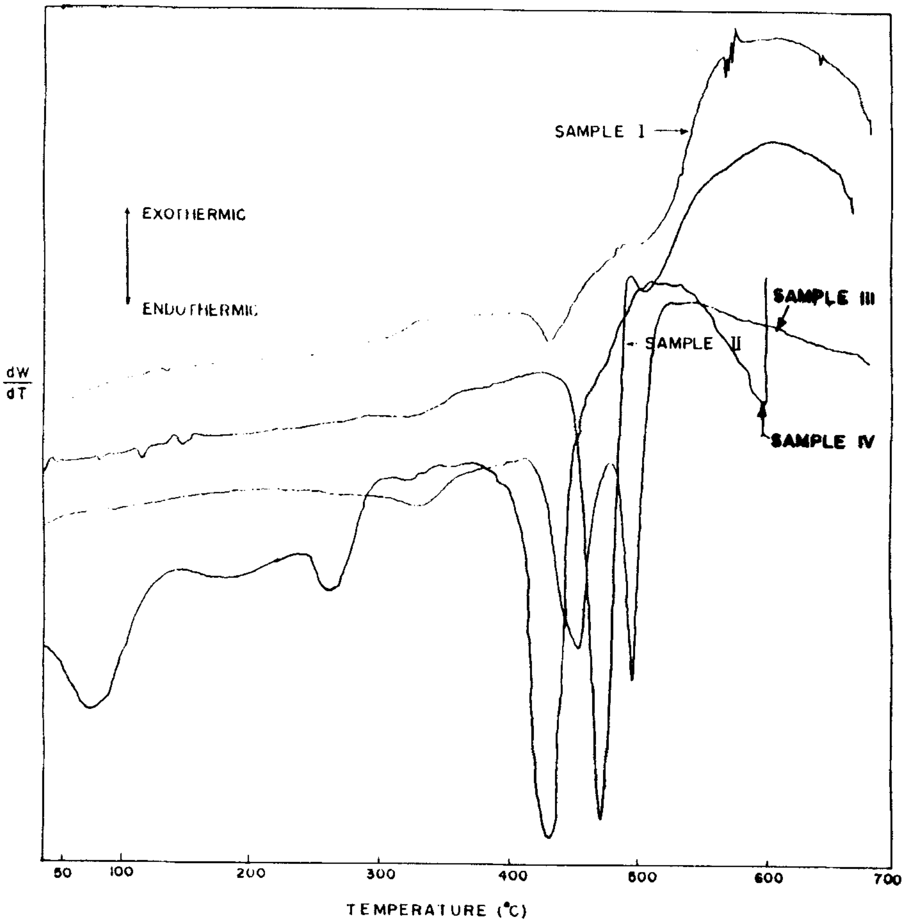

FIGURE DTA spectra of polymer samples

greatly influenced by the variation of isomeric form of the acid chloride.

Polymer III exhibits two sharp endothermic peaks at 450°C and 495°C characteristic of polymer fusion. Polymer IC similarly exhibits a sharp endothermic peak around 480°C and a small peak around 280°C. The presence of two endothermic peaks is indicative of two types of crystalline regions showing the presence of some

TABLE V

Reverse osmosis performance of polyamide hydrazide films

| S. no. | Applied pressure $Kg/cm^2$ | Water flux gfd | %SR |
|---|---|---|---|
| 1 | 40 | 18.1 | 95.5 |
| 2 | 50 | 21.0 | 96.9 |

feed = 3000 ppm sodium chloride.
gfd = gallons of permeating water per square feet area of membrane per day.
%SR = solute retention percentage.

sort of sequential order rather than a random structure. The polymer III and IV also exhibits a broad exothermic peak with rapid loss in weight which is indicative of thermal decomposition.

*3.2.4. Reverse osmosis performance* The use of four monomer reacting systems resulted in a film forming polymer which could be useful as a separation barrier under reverse osmosis conditions. The films obtained from Polymer IV were tested in a reverse osmosis test cell[23] using sodium chloride solution as feed. The results obtained are shown in Table V. The reverse osmosis performance obtained are shown in terms of water flux across the membrane and percent solute separation. The films showed good performance characteristics, under reverse osmosis. The detailed studies involving separation of various organic and inorganic solutes across the films will form part of our subsequent communication.

## SUMMARY

The studies on the synthesis of aromatic polyamide hydrazide polymer were carried out. The effect of reaction control, stoichiometric equivalence and use of multimonomer systems were looked into. The use of four monomer reacting systems resulted in a film forming polymer capable of giving good reverse osmotic separations. The polymer samples were characterised in terms of IR spectra and thermal analysis.

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## References

1. S. Loeb and S. Sourirajan, *Advan. Chem. Series,* **38,** 117 (1962).
2. P. Blais, *Polyamide Membranes,* Chap. IX, in *Reverse Osmosis and Synthetic Membranes-Theory-Engineering-Technology* ed: S. Sourirajan National Research Council, Canada (1977).
3. V. Ramachandhran, V. K. Agrawal, B. M. Misra and M. P. S. Ramani, *J. Sci. Ind. Research.* **46,** 350 (1987).
4. P. J. Flory, "Principles of Polymer Chemistry", Cornel University Press, Ithaca, N.Y. (1953).
5. R. McKinney Jr. and J. H. Rhodes, *Macromolecules,* **4,** 633 (1971).
6. R. McKinney, Jr., *Sep. Purif. Methods,* **1,** 31 (1972).
7. F. S. Model and L. A. Lee, "PBI Reverse Osmosis Desalination Membrane – An Initial Survey" in "Reverse Osmosis Membrane Research", eds., H. K. Lonsdale and H. E. Podall, Plenum, New York (1972).
8. R. McKinney Jr., "Properties of Aromatic Polyamide and Polyamide Hydrazide Membranes", chap. in "Reverse Osmosis Membrane Research" eds., H. K. Lonsdale and H. E. Podall, Plenum, New York (1972).
9. J. H. Dickson, T. Matsura, P. Blais and S. Sourirajan, *J. Appl. Polym. Sci.,* **19,** 801 (1975).
10. J. S. Shukla and Harish Dwivedi, *Intern. J. Polymeric Mater.,* **9,** 63 (1981).
11. J. S. Shukla and Harish Dwivedi, *J. Macromolecular Science-Chem.,* **A16,** 681 (1981).
12. J. S. Shukla and P. K. Misra, *ibid,* **A21,** 69 (1984).
13. J. S. Shukla, R. Rastegi, S. Saxena and P. K. Misra, *ibid,* **A21,** 445 (1984).
14. J. S. Shukla and P. K. Misra, *J. polym. Sci-Polymer chem.,* **22,** 3401 (1984).
15. Peter R. Dvovnic, *J. Polym. Sci., Part A: Polymer Chem.,* **24,** 1133 (1986).
16. Peter R. Dvovnic, *Macromolecules,* **17,** 1348 (1984).
17. Peter R. Dvovnic, *J. Appl. Polym. Sci.,* **28,** 2729 (1983).
18. P. W. Morgan, "Condensation Polymerisation," Wiley Interscience, New York (1965).
19. P. W. Morgan, *J. Polym. Sci.,* **12,** 1075 (1963).
20. B. Sivaramireddy, Ganga Radhakrishnan and M. Santappa, *Curr. Sci.,* **48,** 437 (1979).
21. B. M. Culbertson and R. Murphy, *J. Polym. Sci. Polym. Lett. Ed.,* **5,** 807 (1967).
22. J. Preston, W. B. Black and W. L. Hefferbert, Jr., *J. Macromol. Sci. Chem.,* **A7,** 67 (1973).
23. V. Ramachandhran and B. M. Misra, *J. Appl. Polym. Sci.,* **28,** 1641 (1983).