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# Synthesis and Study of the Polyhydrazides for Semipermeable Membrane for Desalination

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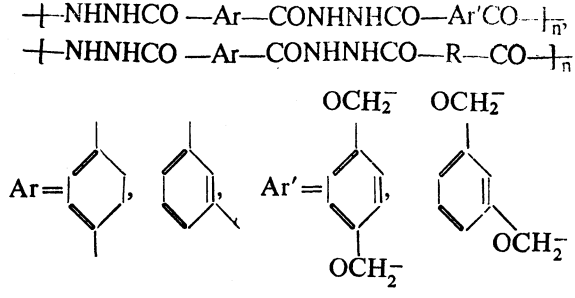
A series of some newer polyhydrazides was synthesized in order to study the structure-property relationship for membranes. The properties studied under the influence of chain variation between two aromatic rings were chain flexibility, hydrogen bonding, solubility, inherent viscosity, thermogravimetric and differential thermal analysis etc. The polyhydrazides were prepared by low temperature solution polycondensation of terephthalic/isophthalic acid hydrazides with different aromatic and aliphatic diacid chlorides. The inherent viscosities varied from 0.09–0.24 dL/g. The normal region of weight loss was 300–465°C. The polymer melt temperature (Tm) and glass transition temperature (Tg) were found in the range of 110–310°C and 73.3–206.6°C respectively.

## INTROUCTION

The structure of polyhydrazides in which the repeating unit contains CONHNHCOC– and –CONHNHCOH$_2$O– type linkages are represented by the following structures.




A large number of synthetic semipermeable membranes have been developed for use in desalination as well as in water waste treatment. V. Ramchandran and B. M. Misra[1] have reported the application of charged membranes in electrodialysis process. Development of suitable membranes for a variety of industrial applications is the need of the time. The significance of polyamidohydrazides, polymides, polyhydrazides as important polymeric materials for membranes in the field of reverse osmosis has been well established[2–6].

In our earlier communication[7] we have reported some newer polyamides with excellent properties of membranes for desalination. The present work deals with the synthesis and study of newer polyhydrazides by the condensation of dihydrazide molecules with diacid chloride molecules under appropriate conditions.

## EXPERIMENTAL

### Synthesis of Diacid Chlorides

1,4/1,3 phenylene dioxy diacetyl chlorides were prepared by the method reported earlier[8]. Aliphatic diacid chlorides were prepared with thionyl chloride.

### Synthesis of Terephthalic Acid Hydrazide

A solution of ethyl terephthalate 20 gm (0.09 mole) and hydrazine hydrate 99–100% (0.27 moles) in absolute ethanol was refluxed for 6 hrs. Excess of solvent was distilled off under reduce pressure. Solid mass so obtained was recrystallised with ethanol (m.pt. $> 300°C$; yield 70%) Similarly isophthalic acid hydrazide was prepared (m.pt. 220°C, yied 90%).

### Low Temperature Solution Polymerization

Dihydrazide 10 gm (0.05 mole) and 100 ml dry N,N-DMAC were placed in a three-necked polymerization tube equipped with a stirring unit, dropping funnel and a thermometer. The reaction mixture was cooled to—20°C and a solution of diacid chloride (0.1 mole) in dry N,N-DMAC was added dropwise with stirring. After addition of diacid chloride the reaction mixture was well stirred for 6 hrs, after which the temperature was allowed to rise to room temperature. It was then neutralized by the addition of lithium hydroxide needed to neutralize HCl formed during the reaction. The viscous solution was further stirred for 8 hrs, then it was poured into 10% aqueous methanol. Solid mass thus obtained was filtered and dried below 50°C.

## RESULTS AND DISCUSSION

### Infrared Spectra

The infrared spectra were obtained by the use of KBr disk method on a Jasco Model A-1 IR Spectrophotometer. It was assumed that the polyhydrazides will exhibit free hydrogen bonding sites, which is very essential requirement for altering structure of permeating water in reverse osmosis. These assumptions were confirmed by I.R. spectra as it was observed that adsorption bands due to –NH and C=O groups have been shifted to lower wave numbers (Table 1).

TABLE 1

INFRARED ABSORPTION BANDS OF POLYHYDRAZIDES

| 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 | 1670(s) | 3380(b) | 1550(s) | 1490(m) | 1220(m) |
| IV | 1610(s) | 3220(b) | — | 1480(m) | 1260(m) |
| V | 1625(s) | 3400(b) | 1520(w) | 1490(w) | 1220(m) |
| VIII | 1690(s) | 3420(b) | 1510(w) | 1480(m) | 1240(m) |

s = sharp, m = medium, b = broad, w = weak
st. = stretching vibration, Ben. = Bending vibration.

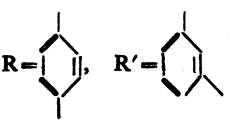
## Inherent Viscosity

The inherent viscosities of the polyhydrazides are summarized in Table 2. The inherent viscosities were observed by measuring flow time

TABLE 2

STRUCTURE OF POLYHYDRAZIDES AND THEIR INHERENT VISCOSITY

| Polymer code | Repeating unit | Yield | Inherent viscosity at 25 ± 5°C dL/g |
|---|---|---|---|
| I | $-\{-NHNHCO-R-CONHNHCOCH_2O-R-OCH_2CO-\}_n$ | 90 | 0.24 |
| II | $-\{-NHNHCO-R-CONHNHCOCH_2O-R'-OCH_2CO-\}_n$ | 86 | 0.19 |
| III | $-\{-NHNHCO-R-CONHNHCO-(CH_2-)_4CO-\}_n$ | 90 | 0.17 |
| IV | $-\{-NHNHCO-R-CONHNHCO-(CH_2-)_8CO-\}_n$ | 90 | 0.15 |
| V | $-\{-NHNHCO-R'-CONHNHCOCH_2O-R-OCH_2CO-\}_n$ | 82 | 0.12 |
| VI | $-\{-NHNHCO-R'-CONHNHCOCH_2O-R'-OCH_2CO-\}_n$ | 60 | 0.10 |
| VII | $-\{-NHNHCO-R'-CONHNHCO-(CH_2-)_4CO-\}_n$ | 72 | 0.09 |
| VIII | $-\{-NHNHCO-R'-CONHNHCO-(CH_2-)_8CO-\}_n$ | 70 | 0.09 |



of the polyhydrazide solution in conc. sulphuric acid (0.5 gm/100 ml.) at 25 ± 5°C. It is clear from Table 2 that the wholly aromatic polyhydrazides (I, II, V, VI) have higher inherent viscosity than those of III,

IV, VII, VIII. Also the para substituted polyhydrazides have higher inherent viscosity in comparison to meta substituted. The polymerization completion time for wholly aromatic polyhydrazide was 3 to 5 hrs (Fig.1). For polyhydrazides III, IV, VII and VIII it was 4 to 6 hrs.

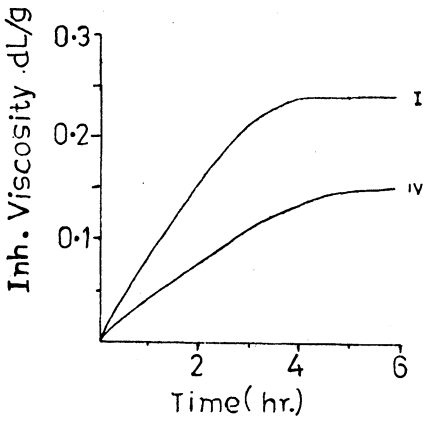



Fig. 1

## Solubility

Solution casting techniques for membranes primarily depend on the solubility of the polymers in water miscible, volatile polar organic solvents. Keeping this point in mind the polyhydrazides were screened against for solubility in many polar and non-polar organic solvents. The solubilities of polyhydrazides are recorded in Table 3.

TABLE 3

SOLUBILITY OF POLYHYDRAZIDES AT 25 ± 2°C

| Sl. No. | Polymer Code → / Solvents ↓ | Solubility | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | I | II | III | IV | V | VI | VII | VIII |
| I. | $H_2SO_4$ (Conc.) | S | S | S | S | S | S | S | S |
| II. | N,N-DMF | S | S | SH | PS | S | S | S | S |
| III. | N,N-DMAC | S | S | S | S | S | S | S | S |
| IV. | DMSO | SH | S | S | S | S | S | PS | PS |
| V. | Ethanol | Ins | Ins | Ins | Ins | Ins | Ins | Ins | Ins |
| VI. | Acetone | Ins | Ins | Ins | Ins | Ins | Ins | Ins | Ins |
| VII. | Dioxane | Ins | PS | Ins | Ins | Ins | Ins | Ins | Ins |
| VIII. | Benzene | Ins | PS | PS | PS | Ins | Ins | Ins | Ins |

(S) = soluble at room temperature, (SH) = soluble on heating
(PS) = Partially soluble, (Ins.) = Insoluble.

The polyhydrazides were readily soluble in conc. sulphuric acid. The solubility in polar organic solvent like DMAC, DMF, DMSO etc. were quite good. On the order hand the non-polar organic solvents like benzene was ineffective. The para substituted polyhydrazides were readily soluble in organic solvents in comparison to the meta-substituted polyhydrazides, with these results, the polyhydrazides are expected to have application in membrane technology.

**Moisture Uptake**

The presence of judicious combination of hydrophobic and hydrophilic characters in a polymer are noted for requisite water permeation as well as solute rejection.[9] The polyhydrazides were found to have such type of combinations, so they are expected to have good moisture uptake property.

**Thermal Properties**

The data obtained from differential thermal and thermogravimetric analysis are reported in Table 4. The thermogravimetric analysis curves

TABLE 4

TGA and DTA ANALYSIS OF POLYHYDRAZIDES I, V AND VII

| Polymer Code | IDT[a] °C | SWLR[b] °C | MWL[c] at 600°C % | $T_m$[d] °C | $T_g$[e] °C |
|---|---|---|---|---|---|
| I | 250 | 450–600 | 68 | 310 | 206.6 |
| V | 255 | 400–550 | 72 | 240 | 160 |
| VII | 200 | 350–550 | 69 | 110 | 73.3 |

a = Initial decomposition temperature.
b = Steep weight loss region.
c = Maximum weight loss at 600°C.
d = Polymer melt temperature.
e = Glass transition temperature.

were obtained by heating the polyhydrazides in static air at the heating rate of 5°C/min and chart speed was 5 cm/h. The polyhydrazides were started to decompose at 200°C. It was assumed that the weight loss (2 to 10%) below 200°C was due to loss of moisture and solvent.

In general the steep weight loss was observed in the range of 400–600°C. The wholly aromatic polyhydrazides I, II, V, VI showed the high range of temperature for steep weight loss in comparison to the polyhydrazides III, IV, VII and VIII. At 600°C the maximum weight loss ranged from 65–72%. It was observed that the polyhydrazides obtained

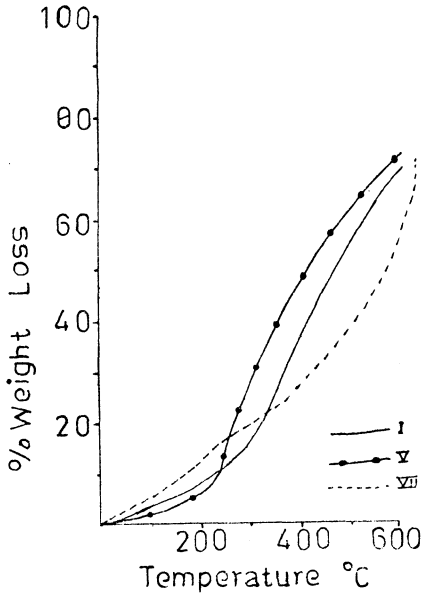



Fig. 2

by the condensation, of dihydrazide molecules with 1,4/1,3 phenylene dioxy/diacetyl chloride molecules showed quite high thermal stability, than those formed by the condensation of dihydrazide molecules with diacid chlorides of adipic and sebacic acids. The endothermic and exothermic peaks of polyhydrazides I, V and VII were in the range of 110–310°C and 250–500°C respectively.

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