

## **Membranes**

### **Synthesis and Properties of Polyhydrazides and Polyoxadiazoles Containing Pyridine Rings in the Polymer Backbone**

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#### Summary

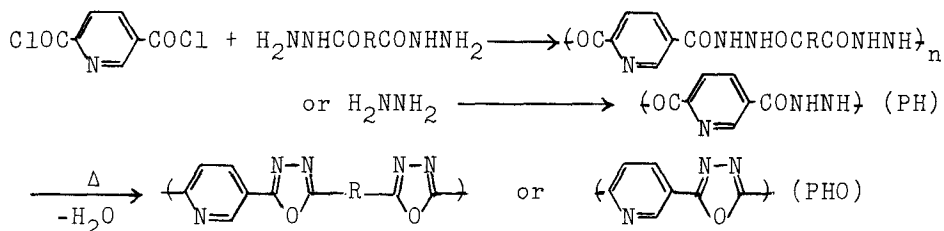
Polyhydrazides containing pyridine rings in the backbone were synthesized by interfacial or solution polycondensation from 2,5-pyridine dicarboxylic acid and three dihydrazides or hydrazine. Heating conditions suitable for the formation of polyoxadiazoles by dehydration of the polyhydrazides were studied by infrared analysis. The polyoxadiazoles formed were thermally stable but poorly soluble. The polyhydrazides were soluble and could take up cobalt (II) ions. The potential applicability of the polyhydrazides to a reverse osmosis membrane was demonstrated.

#### Introduction

In the course of our studies on reverse osmotic behaviors of the membranes prepared from 4-vinylpyridine copolymers it was demonstrated that pyridine rings in the membrane matrix contributed to the enhancement of salt rejection retaining a fair water permeability (1). Therefore, it is of interest to prepare the polymers which contain pyridine rings in the backbone and to employ the polymers as reverse osmosis membranes, since such polymers may improve reverse osmosis performance in view of their rigid backbone and polarity of pyridine rings (2).

Of various conceivable types of pyridine ring-containing polymers polyhydrazide and polyoxadiazole are dealt in this article. The purpose of the present study is to prepare polyhydrazides by condensing 2,5-pyridine dicarboxylic acid chloride (PDCC) with a dihydrazide, deriving polyoxadiazoles by heat treatment of the polyhydrazides, and to investigate their properties including film forming properties, heat resistance

and other features.



R = CH<sub>2</sub>: PM, PMO; (CH<sub>2</sub>)<sub>4</sub>: PA, PAO; p-C<sub>6</sub>H<sub>4</sub>: PT, PTO.

O denotes oxadiazole.

### Experimental

Materials PDCC (3) was prepared from 2,5-pyridine dicarboxylic acid and thionyl chloride in 92% yield, mp 55-57°C. The dihydrazides used were commercially available malonyl dihydrazide, adipic dihydrazide and terephthalic dihydrazide. They were recrystallized from ethanol, methanol and water, respectively. In addition to them, hydrazine hydrate was used. Chloroform and hexamethylphosphoramide (HMPA) were distilled before use.

Polycondensation Interfacial method: a chloroform solution of PDCC was added to a water solution of hydrazide and acid acceptor (sodium hydroxide or potassium carbonate) and the mixture was mechanically stirred vigorously for a required time. The precipitated polymer was separated by a centrifuge, washed successively with dilute hydrochloric acid solution (pH 5~6), water, hot water and methanol, and dried under reduced pressure. Solution method: an HMPA solution of PDCC was added to an HMPA solution of hydrazide in a nitrogen atmosphere. The mixture was mechanically stirred for 2 or 4 hr. After the addition of a small amount of potassium carbonate the solution was poured into acetone or methanol and the mixture was stirred overnight. The precipitated polymer was collected by a centrifuge, washed and dried similarly as in the interfacial method.

Cyclization by dehydration Polyhydrazides obtained were heated in a glass boat which was hung from the rubber stopper in a glass tube under reduced pressure of 8 mmHg or atmospheric pressure. A thermometer was put by the boat through the rubber stopper. A small amount of the heated polymer was taken out

at a determined time interval and subjected to infrared analysis. Infrared absorption spectra were recorded in KBr pellet method by using a Hitachi 215 spectrophotometer.

Thermogravimetric analysis was carried out in air with a Tokyo Koki SE-52 thermobalance and temperature increase of 2.5°C/min.

### Results and Discussion

The results of polycondensation by dehydrochlorination are summarized in Table 1. Hydrazine was more reactive than hydrazides and brought a higher yield and viscosity in interfacial method. Terephthalic dihydrazide was hardly soluble in water and needed a larger volume of solvent to obtain a given amount of the polymer (PT2). However, the solution method was advantageous since it gave quantitative yield and the highest viscosity in this study (PT6). The results of PM showed no substantial difference between interfacial and solution method, but the former was more favorable because no strict equivalence between the two reagents was necessary. As for the reaction

Table 1 Results of polycondensations

Interfacial <sup>a)</sup>	PDCC in CHCl <sub>3</sub> , M	Hydrazide in H <sub>2</sub> O, M	Temp. °C	Time min.	Yield %	$\eta_i$ b)
PM8	0.30	0.15	25	120	63.8	0.23
PM11	0.29	0.29	21	30	72.5	0.47
PA5	0.30	0.15	19	120	72.6	0.30
PH2	0.30	0.30 <sup>c)</sup>	21	30	97.4	0.61
PT2	0.10	0.02	24	120	69.8	0.34
Solution <sup>d)</sup>	PDCC in HMPA, M	Hydrazide in HMPA, M	Temp. °C	Time min.	Yield %	$\eta_i$ b)
PM9	0.69	0.20	20	120	67.7	0.28
PT4	0.38	0.25	25	120	74.8	0.28
PT5	0.50	0.21	26	120	74.2	0.28
PT6	0.96	0.17	25	120	100	0.77
PT71	0.57	0.20	80	110	99.2	0.68
PT72	0.57	0.20	80	240	94.4	0.67

a) Acid acceptor: NaOH (K<sub>2</sub>CO<sub>3</sub> for PT2). b) Inherent viscosity for 0.5 g/dl in DMSO+5%LiCl at 30°C. c) Hydrazine hydrate.

d) The same molar amount of PDCC and hydrazide was used.

Total concentration: 0.30 M.

time 30 min. for interfacial method and 120 min. for solution method were sufficient and a longer reaction time did not improve the results. A high temperature of 80°C did not make any difference either (PT6 and PT71).

The polymers were ivory white to pale yellow and soluble in aprotic solvents and sulfuric acid, and insoluble in other common organic solvents.

The conditions suitable for the dehydration of the polymers were investigated by base line method in infrared analysis. Since thermogravimetric analysis of the polymers revealed that a continuous weight loss began at 250~290°C, the change in the absorbance at 1080  $\text{cm}^{-1}$  due to oxadiazole (4) and at 1700  $\text{cm}^{-1}$  due to carbonyl relative to that at 1480  $\text{cm}^{-1}$  due to pyridine was followed for PM polymers at three different temperatures as shown in Figure 1a. The absorbance ratios for oxadiazole increased with time up to 5 hr and concurrently that for

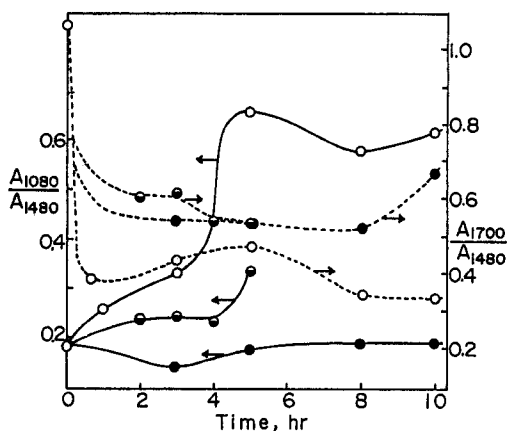


Figure 1a

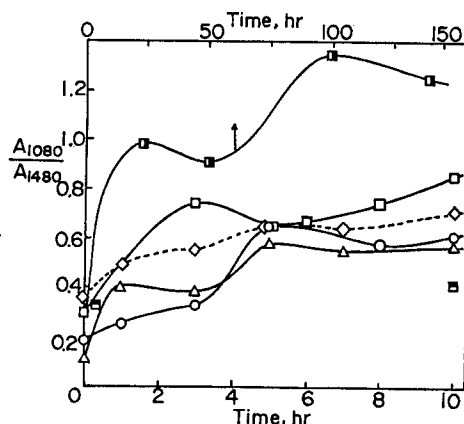


Figure 1b

Figure 1 The change in the ratio of absorbance of oxadiazole  $A_{1080}$  and carbonyl  $A_{1700}$  to that of pyridine  $A_{1480}$  with heating time

○: PM8(300°C/r.p.), ●: PM8(250°C/r.p.), ◐: PM6(270°C/a.p.) prepared similarly as PM8 except for reaction time of 240 min.  $\eta_i=0.23$ . □: PT4(300°C/r.p.). ◑: PT4(200°C in polyphosphoric acid), ◒: PT5(300°C/a.p.), △: PA5(250°C/r.p.), ◇: PH1(300°C/r.p.) prepared similarly as PH2 except for reaction time of 120 min.,  $\eta_i=0.29$ . r.p.: reduced pressure, a.p.: atmospheric pressure.

carbonyl decreased. Apparently, the heating at 300°C was most effective to the oxadiazole formation. The change in the relative absorbance at 960  $\text{cm}^{-1}$  which is another characteristic absorption due to oxadiazole (4) also showed a very similar trend. The absorbance ratios for other polymers in different conditions are illustrated in Figure 1b. The heating in air was conducted at 300°C except for PA5. PA polymers readily changed their color to dark brown to black and 250°C was the highest temperature with no significant degradation. Although the ratios obtained from the dehydration of PT4 in polyphosphoric acid were higher than those for other air-heated samples, the spectrum itself was quite different from that of others and the absorption at 1480  $\text{cm}^{-1}$  decreased to a greater degree, indicating the loss of pyridine rings by degradation. The heating together with dicyclohexylcarbodiimide which was an effective dehydrating agent for a totally aromatic polyhydrazide (5) did not improve the absorbance ratio at all and the resulting polyoxadiazole started to degrade at 280°C, a temperature lower than that for the samples which were air-heated without the imide.

The air-heated samples in Figure 1b show a general tendency to increase initially up to 3 to 5 hr, followed by a slight decrease and a subsequent increase. The initial increase corresponds to the gradual formation of oxadiazole rings, and the slight decrease may indicate the decrease in oxadiazole rings by thermal scission of N-N bonds. The subsequent increase in the absorbance ratio suggests the decrease in pyridine ring by thermal degradation in a long heating period. The weight loss amounted from 15% (PT4) to 30% (PH1) at 8 hr. Consequently, 3 to 5 hr appears to be the appropriate time for the dehydration. The difference in the ratio between PT4 and PT5 at 10 hr indicates that the reduced pressure facilitates the dehydration. This coincides with the fact that PT4 lost 18% of its weight under reduced pressure while it lost 13% under atmospheric pressure when heated at 300°C for 5 hr.

The elemental composition is tabulated in Table 2. The relative composition of each element can be compared with the calculated one in the parentheses. The observed relative val-

Table 2 Elemental analysis of the polyoxadiazoles<sup>a)</sup>

	PA05		PM08		PH02		PT05	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
H	4.12 (83.23)	4.34 (85.43)	2.22 (64.35)	2.24 (65.88)	2.08 (67.31)	2.74 (76.51)	2.44 (71.55)	2.76 (81.18)
C	57.99 (113.4)	56.68 (117.9)	52.87 (115.9)	55.54 (118.1)	57.94 (112.4)	53.43 (111.8)	62.29 (112.4)	58.66 (111.1)
N	26.01 (113.4)	25.63 (123.3)	30.83 (115.9)	26.66 (119.3)	28.96 (112.4)	25.82 (114.1)	24.21 (112.4)	22.03 (112.9)

a) Heated at 300°C under reduced pressure for 5 hr except for PA05 (250°C). Values in parentheses are 100X(% after heating) divided by (% before heating).

ues for PM08 and PA05 are close to the calculated ones, but PH02 and PT05 still have hydrogen to be eliminated by dehydration, though C and N content do not greatly differ between the observed and calculated values.

The thermal stability of the polyoxadiazoles was enhanced compared with the corresponding polyhydrazides. The thermogravimetric curves are depicted in Figure 2, which shows that the initiating temperature for thermal degradation is 390°C for PT04, 375°C for PH02, 350°C for PM08 and 330°C for PA05; i.e.,

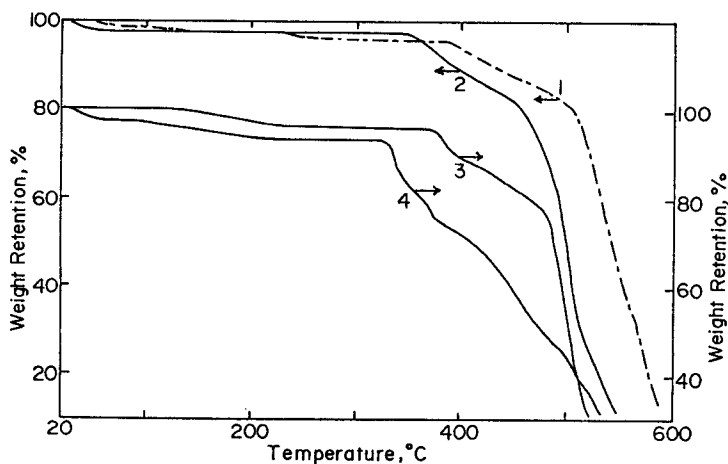


Figure 2. Thermogravimetric curves in air with temperature increase of 2.5°C/min.

1: PT04, 2: PM08, 3: PH02, 4: PA05.

Prepared at 300°C/r.p. for 5 hr except for PA05 (250°C).

an aromatic polymer is thermally stabler than an aliphatic one.

The polyoxadiazoles obtained in this study were soluble in sulfuric acid but insoluble in organic solvents. Therefore, their application to membranes seems difficult. Polyhydrazides, on the other hand, were soluble in an aprotic solvent, but their films were weak. They could take up a fair amount of cobalt (II) ion unlike the corresponding polyoxadiazoles as shown in Table 3. Since the metal-coordinating ability of a

Table 3 Adsorption of cobalt(II) ion<sup>a)</sup>

Code	mM/g	Code <sup>b)</sup>	mM/g
PM10 <sup>c)</sup>	0.170	PM08	0.000
PT71	0.055	PT071	0.001
PH2	0.176	PH03 <sup>c)</sup>	0.003
PA3 <sup>d)</sup>	0.159	PA05	0.004

a) 0.1 g of 200 mesh samples was stirred in 2 mM  $\text{CoCl}_2$  at room temperature for 24 hr, and the concentration difference was obtained by chlate titration. b) Heated at 300°C under reduced pressure for 5 hr, except for PA05 (250°C). c) Prepared similarly as PM11 and PH2, respectively.  $\eta_1$ : 0.36 for PM10, 0.54 for PH3. d) Prepared similarly as PA5 except for the reaction time of 30 min.  $\eta_1=0.25$ .

membrane material is favorable for the rejection of the metal ions in reverse osmosis (6), the polyhydrazides may be applicable to practical use for the membrane if they are reinforced by crosslinking. Preliminary experiments in reverse osmosis gave the following results; a PM11 membrane of 60  $\mu\text{m}$  in thickness was formed by casting ca. 16% DMSO solution mixed with 24 wt% (based on PM11) of hexamethylene diisocyanate as a crosslinking agent and drying at 80°C for 2 hr. The membrane had a tensile strength comparable to that of cellulose acetate (relative strength 0.97), 73% rejection for 0.06 M (0.35%) NaCl feed, 80% for 0.06 M  $\text{CoCl}_2$  feed, and water permeability of  $1.6 \times 10^{-9}$  cm/s·atm and  $0.62 \times 10^{-9}$  cm/s·atm, respectively.

The detailed membrane performance of PM and other polyhydrazides will be revealed by further studies.

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