

폴리아미드옥심의 합성

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Synthesis of Polyamidoximes

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In the earlier work, the addition reactions of nitrile oxides has centered mainly on the 1,3-dipolar cycloadditions with unsaturated systems¹. The results of such reactions have been extensively utilized to synthesize various polymers with heterocycles^{2,3}. And hydroxamoyl chloride, a precursor of nitrile oxide, reacted also with olefinic systems to give the same 1,3-dipolar cycloadducts⁴. This reaction has been successively utilized to the formation of polymers, polyisoxazolines and polyisoxazole⁴.

Recently, the formation of benzamidoxime by the reaction of benzonitrile with aniline and cyclohexylamine has been reported by Grundmann^{6,7}. It is expected to obtain polymers by extending this reaction to the bifunctional systems. Thus, the present paper deals with the reactions of terephthalohydroxamoyl chloride (TPHC), precursor of dinitrile oxide, with aromatic diamines and alicyclic diamine in the presence of triethylamine, affording the corresponding polyamidoximes.

Experimental

Instrumentations. The IR spectra were measured on a Perkin—Elmer spectrophotometer.

The X-ray diffraction diagrams of polymers were obtained by the powder method with use of nickel filtered $\text{CuK}\alpha$ radiation, using a Shimadzu VD—1 diffractometer.

Reagents. Terephthalohydroxamoyl chloride was prepared by the conventional method⁵. The other reagents(reagent grade) were used without any further purification.

Reaction of TPHC with Diamine. A typical reaction of TPHC with diamine is as follows: In 50 ml of tetrahydrofuran(THF), 4.66 g of TPHC (0.02 mole) and *p*-phenylenediamine (0.02 mole) were dissolved. Then this mixture was kept with stirring at below 5°C for 30 min under gentle nitrogen stream. Into this mixture 8 g of triethylamine in 20 ml of THF was added slowly through a dropping funnel. After additional 30 min stirring at below 5°C, the resultant mixture was stirred for two hours at room temperature, allowed to stand for over night under an inert atmosphere. The reaction mixture was poured into 200 ml of methanol. The polymer(I) was gathered by filtration, washed thoroughly with water and boiling methanol, and dried at 50°C in a vacuum oven for 24 hours to give 3.3 g of yellowish powdered poly-

amidoxime(I) (m. p; 218~222 °C, yield: 50 %).

The polymers obtained were characterized by the IR spectra and elemental analysis. The results of polymerizations are summarized in Table 1.

On the other hand, polyaddition reaction of terephthal di-*N*-oxide isolated from TPHC by the action of triethylamine, with *p*-phenylenediamine was also carried out in THF under nitrogen flow at room temperature.

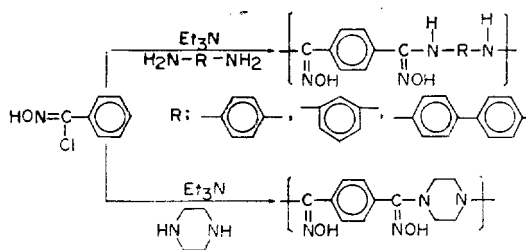
Then this addition product was purified as the above, and was found to be identical with polymer(I) from the reaction of TPHC with *p*-phenylenediamine.

Results and Discussion

The reactions of TPHC with aromatic diamines and piperadine were conducted at low temperature under the presence of triethylamine to give the corresponding polyamidoximes.

The results of the reactions of TPHC with diamines are summarized in Table 1.

As indicated in experimental section, in the reaction system dehydrochlorination from TPHC might occur smoothly by the action of triethyl-



amine to give stable di-*N*-oxide, which undertook addition reaction with diamine. Accordingly such synthetic method for the preparation of polyamidoxime might deserve novelty. However, comparatively lower polymer yields might result from the solubility of lower molecular weight portion of polymer in polar solvent.

Viscosities of obtained polymers were comparatively low as shown in Table 1. However, polyamidoxime(III) derived from benzidine showed the highest values of polymer yield and reduced viscosity among the polymers obtained.

The qualitative solubility of the polymers obtained was tested. All of the polymers were soluble in boiling dimethyl acetamide, and completely soluble in 98 % sulfuric acid at room

Table 1. The reactions of TPHC with various diamines.

Polymer No.	Diamine	Yield (%)	η_{sp}/C^b	m. p (°C)	IR (KBr) ^c (cm ⁻¹)	Anal. (Calc.)		
						C	H	N
I ^{a)}	H ₂ N--NH ₂	50	0.15	218~222	3360, 3160, 1600.	60.8	4.53	19.5
II	H ₂ N--NH ₂	55	0.17	220~227	3370, 3150, 1585.	61.5 (62.2)	4.51 4.57	20.1 20.9
III	H ₂ N--NH ₂	65	0.25	218~223	3370, 3180, 1590.	—	—	16.4 (1.63)
IV	HNNH	60	0.19	245 (decomp.)	3430, 3150, 1590.	56.9 (57.9)	5.45 5.69	22.4 22.8

a) For the addition product of terephthal di-*N*-oxide with *p*-phenylenediamine; Yield, 50 %, m. p. 217~222 °C, N % 20.5, η_{sp}/C 0.17.

b) 0.2 g/dl of 68 % sulfuric acid at 30 °C, measured in an Ubbelohde viscometer.

c) The addition product of terephthal di-*N*-oxide with *p*-phenylenediamine showed similar characteristic infrared absorption bands as those of polymer(I) ($\nu_{C=N}$ 1600 cm⁻¹ etc.).

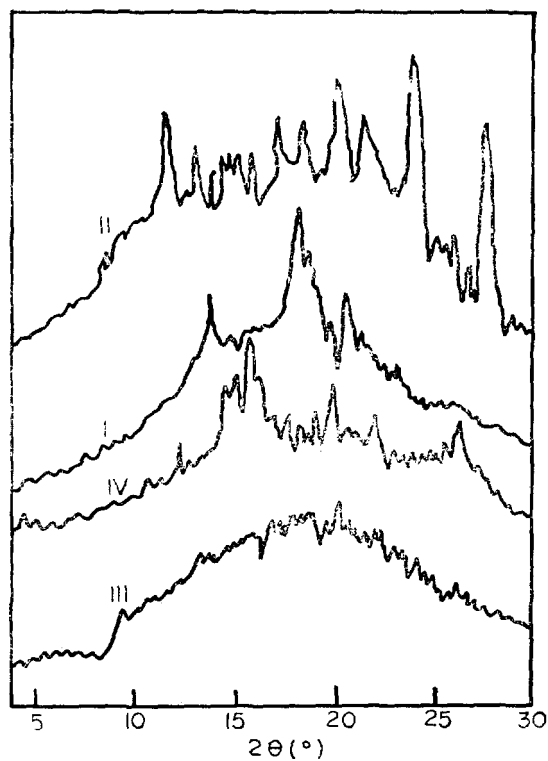


Fig. 1. X-ray diffraction diagrams of polyamidoximes.

temperature.

The information on the crystallinity of polymers was obtained by X-ray diffractions as shown in Fig. 1.

These polymers showed some degree of crystallinity as indicated in Fig. 1. Polymer(I) and (II) revealed higher degree of crystallinity. Such facts might be due to the stronger hydrogen bonding interaction resulted from $-NOH$ groups.

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