

## Synthesis of Polyphenylene-1, 2, 4-Oxadiazoles and Quinone Polymer by the Reactions of Tere- and Iso-phthalohydroxamoyl Chlorides with Bisdipolarophiles

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**Abstract:** Tere- and isophthalohydroxamoyl chlorides were condensed with 1, 4-benzoquinone to afford quinone type polymer with the oxidation of the ring structure. Similarly, tere- and isophthalohydroxamoyl chlorides were condensed with tere- and isophthaldioximes and terephthalonitrile to give crystalline polyphenylene-1, 2, 4-oxadiazoles, among which the reaction product of terephthalohydroxamoyl chloride with terephthalonitrile in xylene afforded the highest crystallinity.

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### Introduction

Since Huisgen and his coworkers<sup>1</sup> have generalized the concept of 1, 3-dipolar cycloadditions, these reactions have been utilized to synthesize a number of 5-membered heterocyclic compounds. The recent investigations of the synthesis of the polymers with heterocyclic rings have been promoted by these reactions. Among the 1, 3-dipolar polycycloadditions, special interests were given to the reaction of terephthalonitrile di-N-oxide with bisdipolarophiles<sup>2</sup> for the preparation of polyisoxazolines, this reaction proceeded by successive 1, 3-dipolar cycloadditions. But the polymer yields were lowered because di-N-oxide was highly reactive and easily dimerized to furoxan in the course of polymerization. In a previous paper<sup>3</sup> we have found that the same polyisoxazolines and polyisoxazole as routine 1, 3-polycycloadducts were prepared in excellent yields by direct reaction of terephtha-

lohydroxamoyl chloride, di-N-oxide precursor, with bisdipolarophiles through the multicentered transition state favoring simultaneous dehydrochlorination reaction. Accordingly, the condensation reaction of TPHC with bifunctional compounds would lead to yield a broad class of polymeric products with heterocyclic rings in the main chains.

The present paper deals with further polymerization results performed on several bisdipolarophiles, with a view of extending synthetic potentials of the precursor method. Reactions of tere- and isophthalohydroxamoyl chlorides with terephthalonitrile, tere- and isophthaldioximes, and 1, 4-benzoquinone were carried out in polar and non-polar solvents to yield the corresponding polymers with heterocyclic rings.

### Experimental

**Measurement.** The infrared spectra were measured on a Hitachi EPI-S-II spectrometer.

The NMR spectra were measured on a Varian 60 MHz spectrometer using about 10% solution of sample in trifluoroacetate with tetramethylsilane as an internal standard.

The X-ray diffraction diagrams were obtained by powder method with use of nickel-filtered Cu-K $\alpha$  radiation, by use of Shimazu-VD-I diffractometer.

Solvents used were purified by the conventional method. Xylene of 138-40°C fraction of boiling points was used for the reaction medium.

**Monomers.** According the usual way, TPHC and iso-TPHC were prepared by the chlorination of the corresponding dioximes, which were obtained by the reaction of dialdehydes with hydroxylamine hydrochloride<sup>9</sup>.

**Polymerization procedure.** A typical example of polymerization procedure is as follows: 0.466 grams of TPHC(0.002 mole) and 0.216 grams of 1,4-benzoquinone(0.002 mole) were refluxed in 10ml. of toluene until the evolution of hydrogen chloride ceased completely. After the reaction completed, the reaction mixture was

filtered, purified by the reprecipitation with DMF-MeOH, then dried under a vacuum to afford 0.44 grams of deep brown colored powder.

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### Results and Discussion

The reactions of terephthalohydroxamoyl chloride(TPHC) and isophthalohydroxamoyl chloride(iso-TPHC) with bisdipolarophiles were carried out in toluene or anisole, xylene at their refluxing temperatures until the evolution of hydrogen chloride ceased. The end points of the polymerization reactions were determined by the Beilstein test. After the reaction completed, the resulting polymer precipitates were purified by the reprecipitation, when possible, then dried under a vacuum, and their viscosities were measured in an Ubbelohde viscometer.

Table 1. summarizes the results of the polymerization reactions of TPHC and iso-TPHC

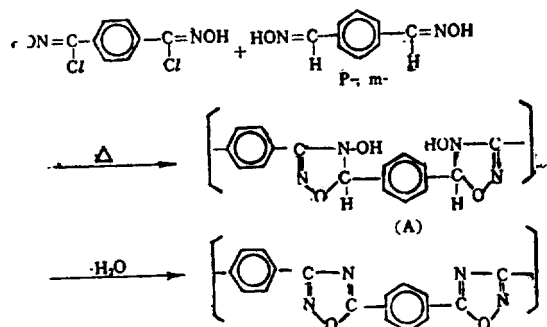
Table 1. The Results of the Polymerizations of TPHC and Iso-TPHC with Bisdipolarophiles

Dipolarophiles	Reaction medium	Reflux time(hr)	Yield (%)	$\eta_{sp}/C^{*1)}$	IR <sup>*2)</sup> (cm <sup>-1</sup> )	PMT <sup>*3)</sup> (°C)	Anal.			
							Found	(Calcd.)		
							C	H	N	
TPHC Terephthaldioxime	Toluene	70	65	0.26 <sup>*4)</sup>	$\nu_{C=N}$ , 1600	>250	64.90 (66.66)	3.48 (2.80)	18.95 (19.44)	
TPHC isophthaldioxime	"	53	60	0.20 <sup>*4)</sup>	$\nu_{C=N}$ , 1590	>250	—	—	18.60 (19.44)	
TPHC Terephthalonitrile	Xylene	38.5	70	0.10 <sup>*4)</sup>	$\nu_{C=N}$ , 1600	>250	—	—	18.40 (19.44)	
Iso-TPHC	"	Anisole	35	70	0.20 <sup>*4)</sup>	$\nu_{C=N}$ , 1595	>250	—	—	18.72 (19.44)
Iso-TPHC	"	Xylene	40	87	0.08 <sup>*4)</sup>	$\nu_{C=N}$ , 1600	>250	—	—	—
TPHC 1,4-benzoquinone	Toluene	35	83	0.14 <sup>*4)</sup>	$\nu_{C=N}$ , 1610 $\nu_{C=O}$ , 1700	>200	61.80 (63.63)	2.35 (1.51)	9.70 (10.60)	
Iso-TPHC	"	"	35	75	0.10 <sup>*4)</sup>	"	—	—	—	

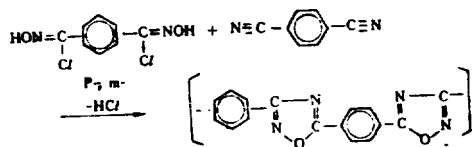
\*1) at 30°C \*2) by nujol mull \*3) capillary method, uncorrected, the melting points were not clear  
\*4) 0.2g/dl of 98%-sulfuric acid \*5) 0.1 g/dl-98%-sulfuric acid \*6) 0.2 g/dl-DMF

with several bisdipolarophiles.

Phenylhydroxamoyl chloride has been known to react with phenyloxime<sup>4</sup> and benzonitrile<sup>5</sup> to afford 1,2,4-oxadiazoles. Utilizing these model reactions, polyphenylene-1,2,4-oxadiazoles were synthesized by the reaction of TPHC with tere- and isophthaldioximes and terephthalonitrile. The reaction of TPHC with tere- and isophthaldioximes, as an extended reaction of monofunctional hydroxamoyl chloride<sup>4</sup> would proceed slowly through transition state(A) formed by dehydrochlorination, followed by simultaneous dehydration, to polymers.



Terephthalonitrile reacted with TPHC and iso-TPHC to afford the corresponding polyphenylene-1,2,4-oxadiazoles.

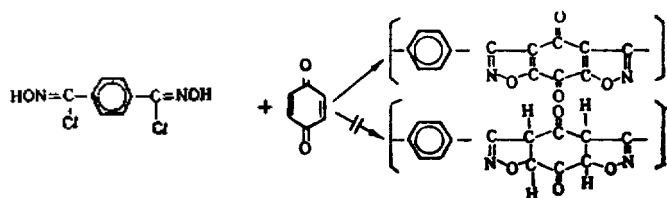


As shown in table 1, terephthalonitrile afforded higher polymer yield than tere- and isoph-

thaldioximes. Such results might be due to the higher reactivity of terephthalonitrile, caused from higher polarity of cyano group, toward tere- and isophthalohydroxamoyl chlorides. In the case of the reaction of iso-TPHC with terephthalonitrile, when anisole, polar solvent, used as a reaction medium, higher degree of polymerization was attained. However, polymer yield was lowered than in the case of xylene, such facts would be presumably caused from that lower molecular weight portions of the polymers obtained were dissolved in the polar solvent. While terephthaldioxime reacted slowly with TPHC than isophthaldioxime, the higher degree of polymerization was attained. All the polyphenylene-1,2,4-oxadiazoles obtained did not dissolve in ordinary organic solvents tested, but only in 98%-sulfuric acid.

Quilico<sup>6</sup> demonstrated that 1,4-benzoquinone reacted with benzonitrile to afford 1:1 adduct, with subsequent oxidation to quinone having condensed benzene-isoxazole nuclei, and using hydroxamoyl chloride<sup>5b</sup> the same result was obtained. This model reaction was applied for the polymer formation.

The polymer obtained was purified by the reprecipitation with DMF-MeOH to give deep brown colored powder. The NMR spectra of the polymer in trifluoroacetate, showing no methyne protons but aromatics (near  $\tau=2.5$ ), indicated the oxidation of the ring structures of the polymer, which would be resulted from the oxidation by benzoquinone, itself, and oxygen



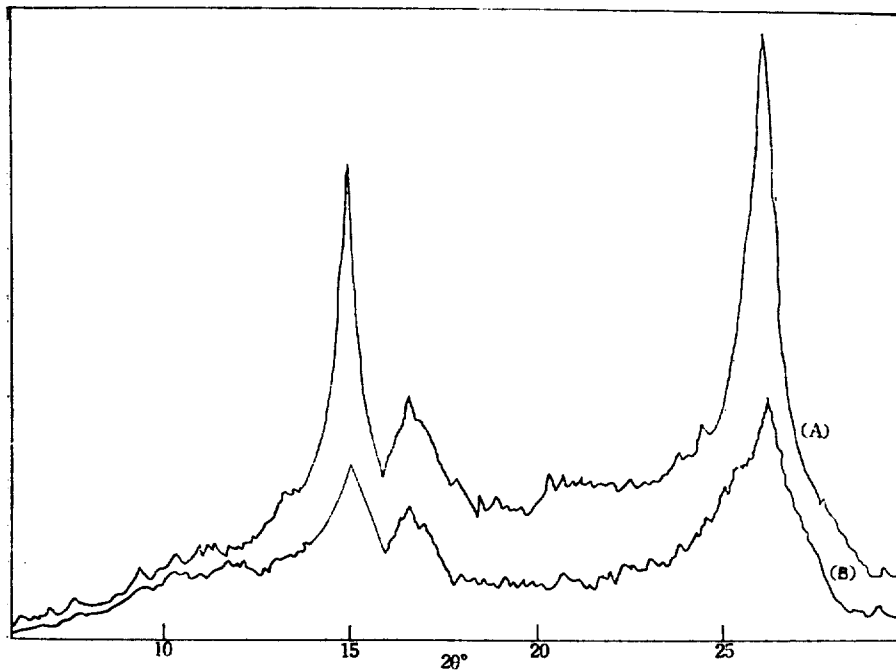


Fig. 1. The X-ray diffraction diagrams of polyphenylene-1, 2, 4-oxadiazoles:  
 (A)—from TPHC-terephthalonitrile in xylene,  
 (B)—from TPHC-isophthaldioxime in toluene.

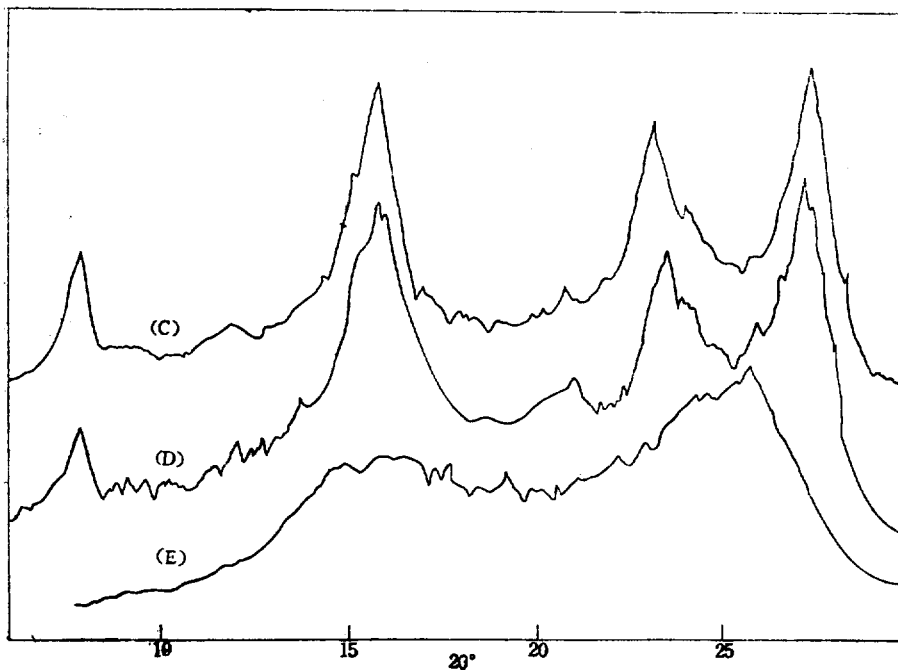


Fig. 2. The X-ray diffraction diagrams of polyphenylene-1, 2, 4-oxadiazoles from the reaction of iso-TPHC with terephthalonitrile:  
 (C)—in xylene, (D)—in anisole, (E)—the recovered polymer originated from (C).

existed in the reaction system under the present reaction conditions.

All the polyphenylene-1,2,4-oxadiazoles obtained were purified by washing thoroughly with hot methanol, dried under a vacuum, then submitted to take the X-ray diffraction diagrams, as shown in Fig. 1 and 2. The diagrams indicate that both polyphenylene-1,2,4-oxadiazoles from oximes and terephthalonitrile are crystalline, but the latter has a high degree of crystallinity, presumably due to the more regular alignment of the polymer chains. Polyphenylene-1,2,4-oxadiazole from the reaction of terephthalonitrile di-N-oxide with terephthalonitrile has been synthesized already<sup>7</sup>. However, the detailed results of the polymerization could not be found. In the present work, highly crystalline polyphenylene-1,2,4-oxadiazoles were prepared from the reaction of TPhC and iso-TPhC with terephthalonitrile.

Polyphenylene-1,2,4-oxadiazole from the reaction of TPhC with terephthalonitrile in xylene (A) affords higher degree of crystallinity than in the case of iso-TPhC because of the more symmetrical polymer structure. The polymer obtained from the reaction of iso-TPhC with terephthalonitrile in xylene (C) dissolved in 98% sulfuric acid and reprecipitated in water. The recovered polymer (E) gave amorphous XRD pattern as shown in Fig. 2. This is attributed to the increase of random alignment of the polymer chain resulted from the instantaneous precipitation in the course of polymer recovery. It

can be said from these results that the insolubility and crystallinity of the polyphenylene-1,2,4-oxadiazoles would be due to the rigidity of the polymer chain similar to those of polyphenylene-1,3,4-oxadiazole<sup>8</sup>. As indicated in Fig. 2, polyphenylene-1,2,4-oxadiazole, (C) in xylene, (D) in anisole, show almost same crystallinity. Accordingly, the polarity of the reaction medium did not affect to the crystallinity of the polyphenylene-1,2,4-oxadiazoles.

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