A Polymerization of Isophthalonitrile Di-*N*-oxide by 1, 3-Dipolar Cycloaddition Reaction

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We wish to report a novel polymerization of isophthalonitrile di-*N*-oxide with diolefins, *m*-phenylenebismaleimide, ethylene dimethacryllate and biallyl. The polymerization proceeded by the repetition of the so-called 1, 3-dipolar cycloaddition between a nitrile *N*-oxide and a carbon-carbon double bond, forming a 4*H*-isoxazoline ring.1) The 1, 3-dipolar cycloaddition resembles the Diels-Alder reaction in many respects ;2) on the other hand, it has been shown that polymerizations by the Diels-Alder reaction produce high-molecular-weight polymers.3,4)

Isophthalonitrile di-*N*-oxide (m. p. 92—94°C decomp.) was prepared by the same method as was terephthalonitrile di-*N*-oxide.5) The conditions of the polymerizations and the properties of the polymers obtained are presented in Tables I and II.

A typical polymerization is as follows: Into a solution of 0.402 g. (0.002 mol.) of *m*-phenylenebismaleimide (m. p. 201°C) in 4.0 ml. of dimethylformamide, 0.320 g. (0.002 mol.) of isophthalonitrile di-*N*-oxide was added portion

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1) R. Huisgen, *Proc. Chem. Soc.*, **1961**, 357; *Angew. Chem.*, **75**, 604 (1963).

2) R. Huisgen, ibid., **75**, 742 (1963).

3) W. J. Bailey and J. Economy, Abstracts of papers presented at the 126th Meeting of the Ammerican Chemical Society, (1954), p. 195.

4) J. K. Stille, *Fortschr. Hochpolym. Forsch.*, 3, 48 (1961); J. K. Stille and J. Anoys, *J. Polymer Sci.*, **A2**, 1487 (1964).

5) Y. Iwakura, M. Akiyama and K. Nagakubo, This Bulletin, 37, 767 (1964).

TABLE I. POLYMERIZATION OF ISOPHTHALONITRILE DI-*N*-OXIDE WITH DIOLEFINS
In each run, 0.002 mol. of the di-*N*-oxide and 0.002 mol. of a diolefin were used.

Polymer	Diolefin	Solvent ml.	Temp. °C	Time hr.	Yield %	Polymer melt temp. °C	η_{inh}[1]	Analysis, % Found C			Calcd. C		
								C	H	N	C	H	N
I	*m*-Phenylene bismaleimide	26[2]	25	24	77	400	0.17						
I	*m*-Phenylene bismaleimide	4.0[3]	25	2.5	92		0.19	59.06	3.40	12.09	61.68	2.82	13.08
I	*m*-Phenylene bismaleimide	4.0[3]	75	2.5	93		0.26	60.03	3.45	11.29			
II	Ethylene dimethacrylate	2.6[2]	20	24	55	170	0.21	60.25	5.17	8.09	60.33	5.06	7.82
III	Biallyl	2.0[3]	20	24	86	200	0.10	67.55	5.79	10.24	69.40	5.83	11.56

[1] Measured at a concentration of 0.5 g./100 ml. of dimethylformamide at 30°C.
[2] Dioxane
[3] Dimethylformamide

TABLE II. INFRARED ABSORPTTION MAXIMA OF POLYMERS
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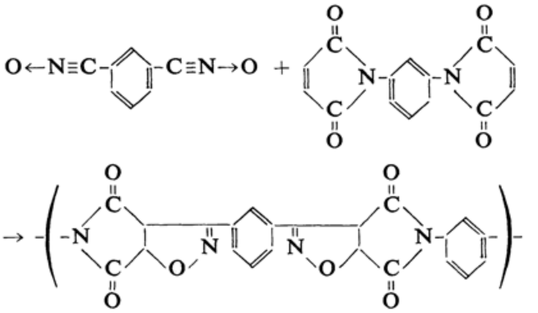
Polymer	Absorption maxima, cm^{-1}
I	1790, 1725(s), 1605, 1490, 1375, 1310(w), 1180(s) 905, 795 and 685.
II	1740(s), 1600(w), 1340, 1300, 1175, 910, 795 and 685.
III	1640(w), 1580(s), 1440, 1335, 910, 795 and 685.

by portion, over a period of 30 min. at room temperature. The mixture was then stirred for an additional two hours and poured into methanol. The polymer separated was washed with hot dioxane and hot methanol and dried under vacuum at 110°C, to give an almost colorless powder (90% yield) which did not melt up to 400°C. The polymer showed the infrared absorptions at 1790 and 1725 cm^{-1} characteristic of an imide group, those at 1605 and 1490 cm^{-1} characteristic of a phenyl group, and those at 795 and 685 cm^{-1} characteristic of an *m*-phenylene group. It also gave at 905 cm^{-1} the strong band which was common to all the other polymers obtained in these experiments and which was assigned tentatively to the isoxazoline ring. Absorptions of isophthalonitrile di-*N*-oxide at 2320, 1350 and 1080 cm^{-1}, and those of *m*-phenylenebismaleimide at 1150, 830 and 700 cm^{-1}, disappeared in the polymer. The infrared spectral data and the high yield of the product strongly support the theory that the polymerization of isophthalonitrile di-*N*-oxide with *m*-phenylenebismaleimide takes place according to Eq. 1.



(1)

Further detailed studies are now in progress.

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