Polymerizations by 1, 3-Dipolar Cycloaddition Reactions. II. α, α'-(*p*-Phenylene)bis(*N*-phenylnitrone)

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In a previous communication,[1] a 1, 3-dipolar cycloaddition polymerization of isophthalonitrile di-*N*-oxide with diolefins was reported. Hitherto extensive studies have been made on the chemistry of nitrones,[2-4] and some bisnitrones have been prepared for dialdehyde syntheses.[3,5] This communication will describe a new polymerization of α, α'-(*p*-phenylene)-bis(*N*-phenylnitrone) (I) with diolefins, *m*-phenylenebismaleimide and ethylene dimethacrylate, by the 1,3-dipolar cycloaddition reaction.

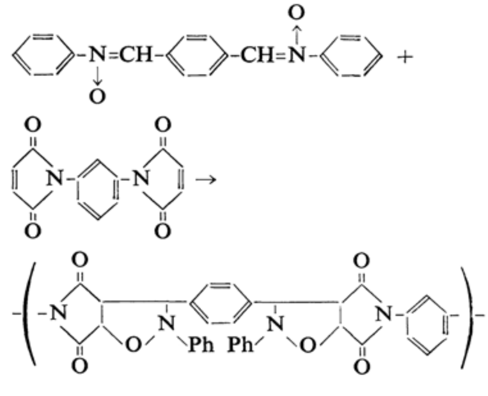
A new bisnitrone, I, was obtained by the reaction of terephthalaldehyde with phenylhydroxylamine[6] (yield, 66%), and recrystallized from dimethylformamide; m. p. 227—228°C (decomp.). Found: C, 75.71; H, 4.97; N, 9.11. Calcd. for $C_{20}H_{16}O_2N_2$: C, 75.93; H, 5.10; N, 8.86%.

I gave an infrared spectrum similar to that of α, *N*-diphenylnitrone.

Two bisadducts of I were prepared as model compounds. I (0.414 g.) was refluxed in methyl methacrylate to yield 1, 4-bis(2'-phenyl-5'-methyl-5'-methoxycarbonyl-3'-isoxazolidinyl)-benzene (II) as colorless needles (0.186 g.); m. p. 188—190°C (from ethylacetate). Found: C, 69.67; H, 6.26; N, 5.38. Calcd. for $C_{30}H_{32}O_6N_2$: C, 69.75: H, 6.24; N, 5.42%.

By the addition reaction of I (0.316 g.) with *N*-phenylmaleimide (0.346 g.) in dimethylformamide at 120°C for 3 hr., 3, 3'-(*p*-phenylene)-bis(2-phenylisoxazolidine-4, 5-dicarboxyphenylimide) (III) was obtained (0.620 g.); m. p. 228—229°C (from benzene), (Found: C, 72.35; H, 4.69; N, 8.25. Calcd. for $C_{40}H_{30}O_6N_4$: C, 72.49; H, 4.56; N, 8.46%).

A typical polymerization of I with *m*-phenylenebismaleimide is as follows. 0.473 g. (0.0015 mol.) of I, 0.402 g. (0.0015 mol.) of *m*-phenylenebismaleimide, 0.005 g. of phenyl-β-naphthylamine and 8.0 ml. of dimethylformamide were placed in a glass ampule; the mixture was then sealed under an atmosphere of nitrogen, heated for 30 hr. at 95°C, and poured into diethyl ether. The polymer (IV) which separated was washed with ether, dried under vacuum (yield, 90%), and reprecipitated from dimethylformamide with ether. The inherent viscosity was 0.19 (0.5 g./100 ml. of dimethylformamide at 30°C). IV did not melt up to 300°C. Found: C, 69.88; H, 4.37; N, 9.32. Calcd. for $C_{34}H_{24}O_6N_4$: C, 69.85; H, 4.14; N, 9.59%. The infrared spectrum of IV exhibited the following absorption bands: 1790(w), 1720(s), 1600, 1490, 1450, 1365(broad), 1180(broad), 1020(w), 755 and 688 cm^{-1} (KBr disk), and showed good agreement with that of III. These data strongly suggest that the polymerization proceeds by a repetition of the 1, 3-dipolar cycloaddition reaction, as in the equation below:



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[1] Y. Iwakura, M. Akiyama and S. Shiraishi, This Bulletin, 38, 335 (1965).

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[3] J. Hamer and A. Macaluso, ibid., 64, 473 (1964).

[4] R. Huisgen, *Angew. Chem.*, 75, 604 (1963).

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[6] O. H. Wheeler and P. H. Gore, *J. Am. Chem. Soc.*, 78, 3363 (1956).

A similar polymerization of I with ethylene dimethacrylate was carried out in hexamethylphosphoramide at 140°C for 4 hr. The yield of the polymer (V), obtained as an ether-insoluble fraction, was 11%; m. p. 100—107°C, and the inherent viscosity, 0.09. Found: C, 69.89; H, 5.76; N, 5.43. Calcd. for $C_{30}H_{30}O_6N_2$: C, 70.02; H, 5.88; N, 5.44%. The infrared spectrum of V displayed the following maxima: 2940, 2850(w), 1735(s), 1600, 1490, 1453, 1375 (w), 1280(broad), 1175(s), 1125—1095, 1030(w), 753 and 690 cm^{-1} (KBr disk), and was essentially identical with that of II.

Further investigations are now in progress.

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