Polymerization of Methyl Methacrylate Initiated by N-Nitrosophenylurea

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N-Nitrosophenylurea has been prepared by Huisgen[1] by the following reaction of nitrous fumes (a mixture of NO and NO_2) and phenylurea:

$$2C_6H_5NHCONH_2+N_2O_3$$
$$=2C_6H_5N(NO)CONH_2+H_2O$$

N-Nitrosoacylarylamines which are related to *N*-nitrosophenylurea have been noted as sources of free radicals by many investigators[2]. Blomquist[3] has reported polymerizations of methyl methacrylate, styrene and acrylonitrile initiated by several *N*-nitrosoacylarylamines, and suggested that the polymerizations were initiated by aryl radicals which were produced through the decomposition of the *N*-nitrosoacylarylamines. Although *N*-nitrosoacylarylamines were frequently used as initiators during the early period of studies on radical polymerization, they have never since been employed, owing to the facts that they were not efficient as polymerization-initiators and too labile, i. e. they decomposed spontaneously at room temperature. *N*-Nitrosophenylurea is much more stable than *N*-nitrosoacylarylamines, e. g. the half-value periods of *N*-nitrosoacetanilide and *N*-nitrosophenylurea are respectively 99.5 min. at 20°C and 140 min. at 40°C[1].

It has been found by the present author that *N*-nitrosophenylurea is an efficient initiator of the polymerization of methyl methacrylate. In the present paper, results of experiments on the dependence of the initial rate of polymerization upon the concentration of *N*-nitrosophenylurea and methyl methacrylate are given.

The polymerization was carried out in an atmosphere of nitrogen. In Table I, the conversion versus time and average degree of polymerization of polymethyl methacrylate in the bulk polymerization of methyl methacrylate initiated by *N*-nitrosophenylurea 1.21×10^{-2} mol./l. at 60°C are shown. The conversion in the bulk polymerization initiated by benzoyl peroxide 1.30×10^{-2} mol./l. is also shown in Table I. As an initiator of the polymerization of methyl methacrylate, *N*-nitrosophenylurea is more efficient than benzoyl peroxide.

Dependences of the initial rate of polymerization (R) upon the concentration of *N*-nitrosophenylurea ([NPU]) in solution-polymerization in benzene (methyl methacrylate 50%) at temperatures of 40, 50, 60 and 70°C are shown in Fig. 1. It is evident that the square root dependence holds for each case, i. e. the initial rate of polymerization is linearly proportional to the square root of the concentration of *N*-nitrosophenylurea. The relationship between the initial rate of polymerization and the concentration of methyl methacrylate ([MMA]) in benzene (*N*-nitrosophenylurea 1.24×10^{-2} mol./l.) was studied at 60°C. It is clear that the initial rate

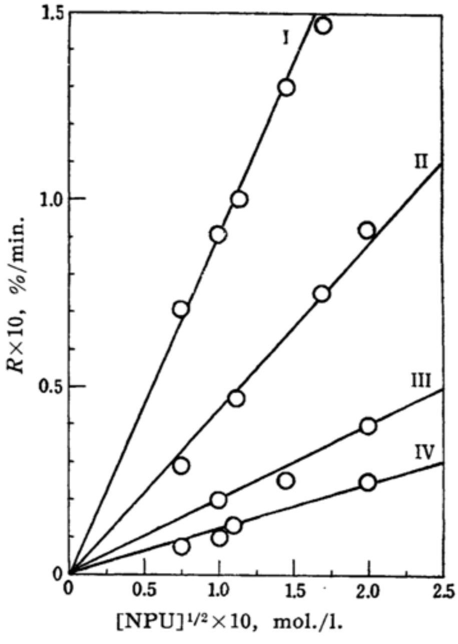

Fig. 1. Correlations of the initial rate of polymerization with the concentration of *N*-nitrosophenylurea (methyl methacrylate 50% in benzene) at 70 (I), 60 (II), 50 (III) and 40°C (IV).

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[1] R. Huisgen and L. Krause, *Ann.*, **157**, 5474 (1951).

[2] See, e. g. W. S. Grieve and D. H. Hey, *J. Chem. Soc.*, **1934**, 1797.

[3] A. T. Blomquist et al., *J. Am. Chem. Soc.*, **65**, 2446 (1943).

TABLE I. CONVERSIONS AND AVERAGE DEGREES OF POLYMERIZATION IN THE BULK POLYMERIZATION AT 60°C BY MEANS OF *N*-NITROSOPHENYLUREA 1.21×10^{-2} mol./l.

Time min.	Conversion, % by NPU	Conversion, % by BPO	Average degree of polymerization*
30	3.8	3.1	2820
60	5.5	4.2	4300
90	8.1	6.9	4210
120	11.1	9.3	4330
150	15.1	13.4	4560
180	22.5	17.8	6020
210	33.4	25.9	6300
240	53.0	45.5	7720
270	74.0	65.0	7900
300	87.1	76.2	7800
330	93.0	82.1	6950
360	95.4	85.5	6300

* Polymethyl methacrylate produced by NPU.

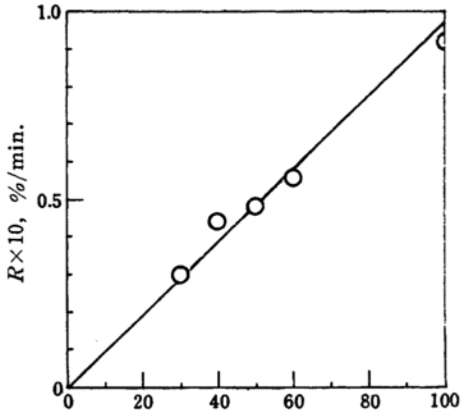

Fig. 2. Correlation of the initial rate of polymerization with the concentration of methyl methacrylate (at 60°C, NPU 1.24×10^{-2} mol./l.)

was linearly proportional to the concentration of methyl methacrylate.

These rate-concentration relationships are quite similar to those which are observed in the polymerizations of vinyl monomers initiated by benzoyl peroxide or α, α'-azo-bis-iso-butylonitrile in which unimolecular first order decompositions of the initiators are considered as the initiating reactions by many investigators[4]. Consequently, it is very probable that the polymerization of methyl methacrylate by means of *N*-nitrosophenylurea is initiated by radicals which are produced through the unimolecular first order decomposition of *N*-nitrosophenylurea. The nature of the initiating reaction will be studied in future.

When logarithms of the initial rates of polymerization (methyl methacrylate in benzene 50% and *N*-nitrosophenylurea 1.24×10^{-2} mol./l.) were plotted against reciprocals of temperatures ($1/T$), a good straight line was obtained (Fig. 3). The overall activation energy calculated from the slope in Fig. 3 was found to be 12.8 kcal./mol.

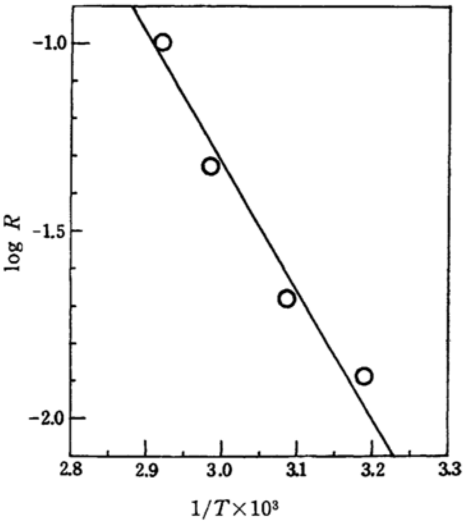

Fig. 3. Correlation of $\log R$ with $1/T$ (MMA 50%, NPU 1.24×10^{-2} mol./l.).

Experimental

Materials.—Purification of methyl methacrylate and benzene was carried out as mentioned in a previous paper[5]. *N*-Nitrosophenylurea was prepared through the reaction of nitrous fumes upon phenylurea. Phenylurea (6.8 g.) was suspended in a mixture of glacial acetic acid and acetic anhydride (3 : 1 by volume, 40 cc.) and cooled to 0°C. Nitrous fumes which were produced from arsenious oxide and nitric acid[6] were passed into the suspension until 20 g. of them were absorbed. The crude product was precipitated by pouring the suspension into ice water (200 cc.). The crude product was washed with water (400 cc.) and recrystallized twice from ether, giving pure *N*-nitrosophenylurea (3.1 g.), m. p. 89°C with decomposition. The pure product could be stored in an ice bath for several weeks without any appreciable decomposition.

Polymerization.—Details of the procedures of polymerization and the determination of the initial rate of polymerization were given previously[5]. In solution-polymerization, *N*-nitrosophenylurea was dissolved in benzene. Measured amounts of the benzene solution and methyl

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[4] P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N. Y. (1953), p. 116.

[5] R. Uehara, This Bulletin., 31, 685 (1958).

[6] A. W. Dox, "Organic Syntheses", Col. Vol. 1, John Wiley & Sons, Inc., New York (1941), p. 266.

methacrylate were placed in a test tube and mixed. The test tube was cooled in a dry ice-methanol bath, flashed with nitrogen, evacuated and sealed. Conversions of the polymerization were measured by precipitating and weighing polymethyl methacrylate formed. Degrees of polymerization of polymethyl methacrylate were estimated from their intrinsic viscosities in chloroform according to Sakurada[7].

Summary

N-Nitrosophenylurea is an efficient initiator of the polymerization of methyl methacrylate. The initial rate of polymerization of methyl methacrylate was linearly dependent upon the concentration of methyl methacrylate and the square root of the concentration of *N*-nitrosophenylurea. These facts suggest that the polymerization is initiated by radicals which are produced through a unimolecular first order decomposition of *N*-nitrosophenylurea.

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[7] I. Sakurada, *Chem. High Polymers* (*Kobunshi Kagaku*), 2, 253 (1945).