Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Yano, Haruhiko , Takemoto, Kiichi and Imoto, Minoru(1968) 'Vinyl Polymerization. CLXVII. Vinyl Polymerization Initiated with p-Methoxy p'-nitrobenzoyl Peroxide', Journal of Macromolecular Science, Part A, 2: 1, 81 — 91

To link to this Article: DOI: 10.1080/00222336808053349

URL: http://dx.doi.org/10.1080/00222336808053349

J. MACROMOL. SCI.—CHEM., A2(1), pp. 81-91, Jan.,1968

Vinyl Polymerization. CLXVII. Vinyl Polymerization Initiated with p-Methoxy-p'-nitrobenzoyl Peroxide

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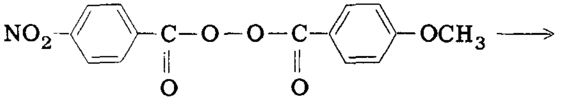
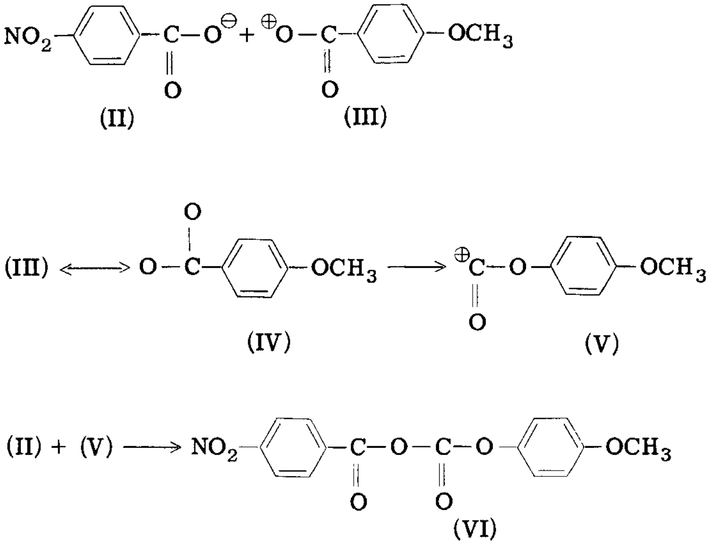
Summary

It was described in the literature that p-methoxy-p'-nitrobenzoyl peroxide decomposed homolytically in benzene, but heterolytically in acetone. However, in the present study the polymerizations of styrene and acrylonitrile were found to proceed always through radical mechanism in benzene, dimethylformamide, or acetone. And in the above various solvents, the rate of polymerization was found to be almost equal.

The decomposition of benzoyl peroxide and its symmetrically substituted derivatives and the vinyl polymerization with them have been studied earlier in our laboratory [1]. The decomposition of unsymmetrically disubstituted benzoyl peroxides, however, seems not to have been thoroughly investigated, with the exception of Leffler's and Denney's papers, which are concerned with the decomposition of p-methoxy-p'-nitrobenzoyl peroxide. Leffler [2] concluded that when benzene was used, the decomposition proceeded through homolysis, but when nitrobenzene, acetone, and methanol were used, decomposition proceeded through heterolysis. The scheme of Leffler is shown by scheme A (I-VI).



(I)



SCHEME A. Ionic decomposition of p-methoxy-p′-nitrobenzoyl peroxide by Leffler.

Denney and Denny [3, 4] have studied the decomposition of p-methoxy-p′-nitrobenzoyl peroxide labeled with O^{18} at the carbonyl of the p-methoxybenzoyl or p-nitrobenzoyl group, and show that the decomposition of p-methoxy-p′-nitrobenzoyl peroxide was assumed to proceed by ionic process. Furthermore, Leffler and Petropropoulos [5] have shown that 4-methoxy-3′ · 5′-dinitrobenzoyl peroxide also decomposed heterolytically.

It is interesting to see whether p-methoxy-p′-nitrobenzoyl peroxide can act as an initiator in ionic polymerization or not. In this paper, the mechanism of the decomposition of p-methoxy-p′-nitrobenzoyl peroxide is discussed from the kinetics of vinyl polymerization initiated with p-methoxy-p′-nitrobenzoyl peroxide.

EXPERIMENTAL

Preparation of p-Methoxy-p′-nitrobenzoyl Peroxide

p-Methoxy-p′-nitrobenzoyl peroxide was prepared by the reaction of p-nitrobenzoyl chloride with sodium per (p-methoxy) benzoate aqueous solution obtained from the reaction of p, p′-dimethoxybenzoyl peroxide, which was prepared by the reaction of anisoyl chloride with Na_2O_2, with sodium methoxide, according to the modification of the preparation of sodium perbenzoate [6]. Product was reprecipitated with ethyl alcohol and chloroform and further with petroleum ether and chloroform, m.p. 114°C (dec.):

	C	H	N
Calcd.	56.78	3.50	4.42
Found	56.79	3.48	4.42

Polymerization Procedures

Styrene and acrylonitrile were purified in the usual manner and distilled in a nitrogen stream before use. Benzene, acetone, and dimethylformamide (DMF), which were used as solvents, were purified by the usual method [7]. After charging all reagents and solvent, the glass tube was cooled in a dry ice–methanol bath, flushed several times with oxygen-free nitrogen, and sealed under vacuum. Polymerization was carried out in a thermostat under shaking. The tubes were taken out at definite intervals and the content was poured into an excess of methyl alcohol to isolate the polymer formed. The polymer was dried thoroughly in vacuum. From the amount of polymer formed, time-conversion curve was drawn.

RESULTS

Polymerization of Styrene in Benzene

Polymerization of styrene was carried out at 60°C in the presence of p-methoxy-p′-nitrobenzoyl peroxide. As can be seen from Fig. 1, the initial rate of polymerization was proportional to the square root of the initial concentration of the initiator.

Polymerization was also carried out, varying the temperature between 50 and 70°C, with constant concentrations of monomer and initiator. The plot of the rate of polymerization against 1/T gave a straight line, as shown in Fig. 2. From the slope over-all activation energy was calculated to be 22.0 kcal/mole, using the Arrhenius equation. From this value the activation energy of initiation, E_i, was estimated as 31.2 kcal/mole, using the value of E_p (7.8 kcal/mole) and E_t (2.4 kcal/mole) given by Matheson et al. [8] for the polymerization of styrene. This value of E_i showed a close resemblance to the values which was obtained for benzoyl peroxide ($E_i = 30.7$ or 29.9 kcal/mole) and other substituted benzoyl peroxides.

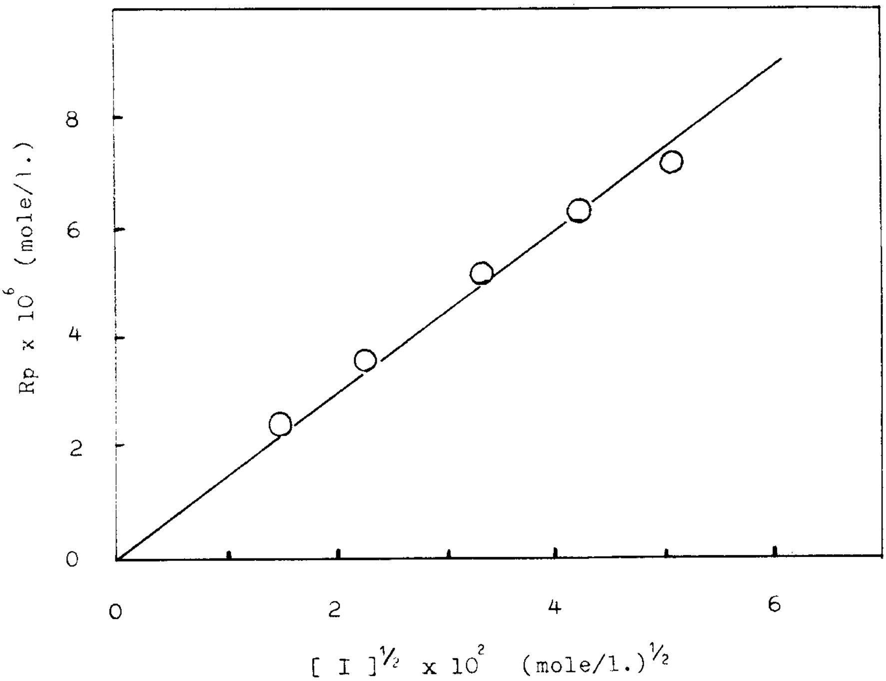


FIG. 1. Relationship between the initial rate of polymerization and the concentration of p-methoxy-p′-nitrobenzoyl peroxide in benzene at 60°C; [styrene] = 4.364 moles/liter.

It was found further that the addition of picric acid as a radical scavenger in the polymerization system inhibited the polymerization of styrene.

Polymerization of Styrene in Dimethylformamide

Polymerization of styrene initiated with p-methoxy-p′-nitrobenzoyl peroxide was carried out in DMF. The relationship between the initial rate of polymerization and the initial concentration of initiator is shown in Fig. 3. The initial rate of polymerization, R_p, was found to be proportional to the square root of the initial concentration of initiator as well as in the case where the polymerization of styrene was carried out in benzene solution.

Polymerization of Styrene in Acetone

Polymerization of styrene initiated with p-methoxy-p′-nitrobenzoyl peroxide was carried out at 60°C in acetone. The relationship

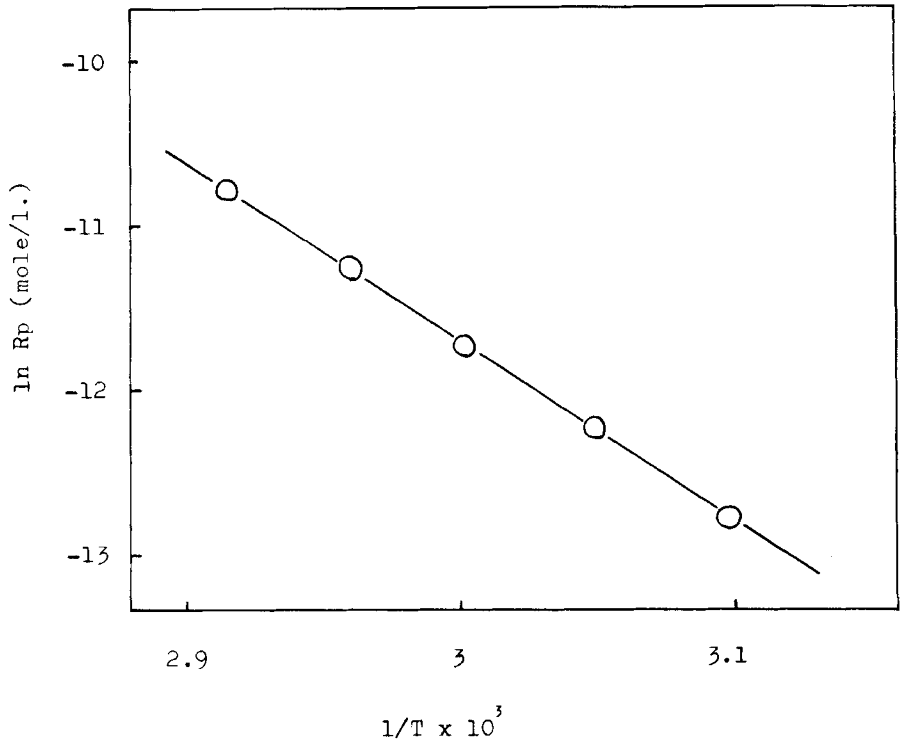


FIG. 2. Relationship between ln R_p and 1/T in benzene; [p-methoxy-p′-nitrobenzoyl peroxide] = 2.962 × 10^{-3} mole/liter; [styrene] = 4.364 moles/liter.

between the initial rate of polymerization and the initial concentration of initiator is shown in Fig. 4. The initial rate of polymerization, R_p, was found to be proportional to the square root of the initial concentration of initiator as well as in the case where the polymerization of styrene was carried out in benzene and DMF solution.

Polymerization of Acrylonitrile in Dimethylformamide

Polymerization of acrylonitrile was examined in the same way as in the case of styrene. The relationship between the initial rate of polymerization and the initial concentration of initiator is shown in Fig. 5.

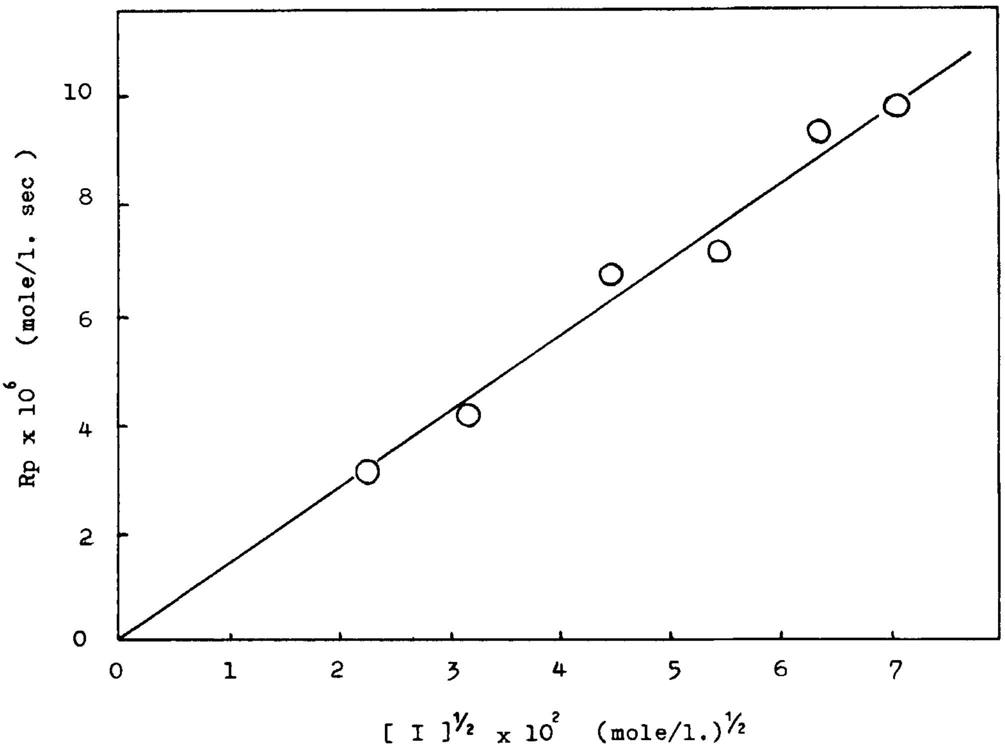


FIG. 3. Relationship between the initial rate of polymerization and the concentration of p-methoxy-p′-nitrobenzoyl peroxide in DMF at 60°C; [styrene] = 4.364 moles/liter.

Copolymerization of Styrene with Acrylonitrile in Dimethylformamide

Copolymerization of styrene with acrylonitrile was carried out also in DMF at 60°C, where the concentration of initiator was kept at 5.02×10^{-3} mole/liter. The composition curve of the copolymer formed is given in Fig. 6, which was characteristic of radical copolymerization. This observation, together with the results for the square root dependence and the value of activation energy, suggests that the polymerization with p-methoxy-p′-nitrobenzoyl peroxide proceeds by radical mechanism.

Polymerization of Styrene with the p-Methoxy-p′-nitrobenzoyl Peroxide–Dimethylaniline System

Polymerization of styrene was next carried out with p-methoxy-

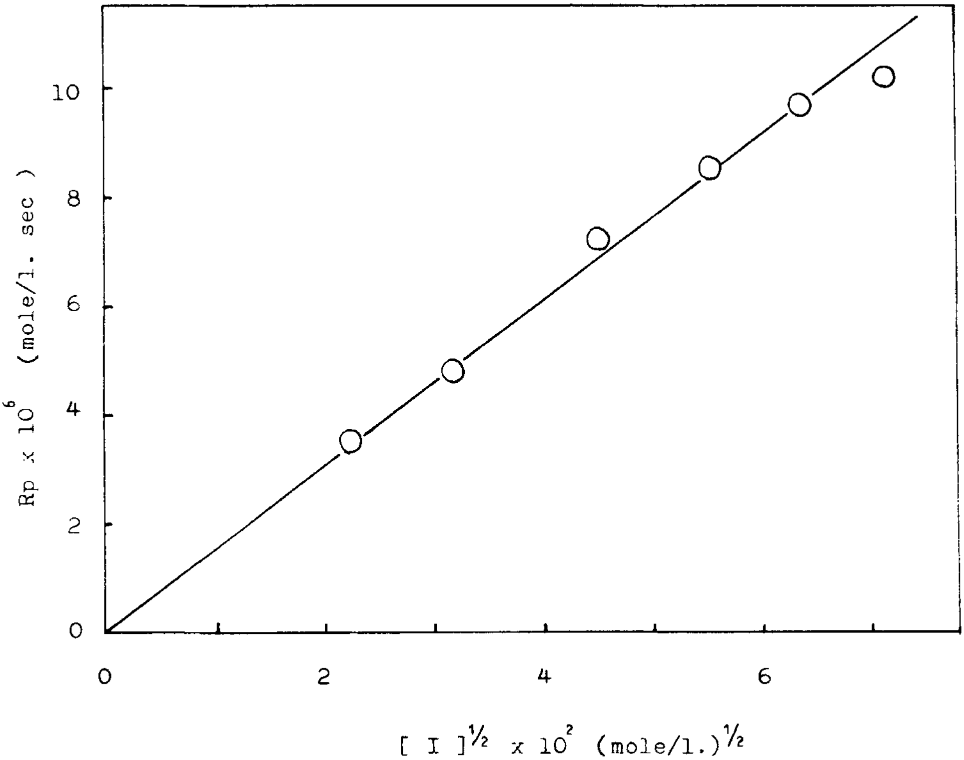


FIG. 4. Relationship between the initial rate of polymerization and the concentration of p-methoxy-p′-nitrobenzoyl peroxide in acetone at 60°C; [styrene] = 4.364 moles/liter.

p′-nitrobenzoyl peroxide and DMA as an initiator system. The relationship between the initial rate of polymerization and the initial concentration of DMA is shown in Fig. 7. As can be seen from the Fig. 7, the initial rate of polymerization was proportional to the square root of the initial concentration of dimethylaniline.

Polymerization of n-Butyl Vinyl Ether in Benzene

Polymerization of n-butyl vinyl ether initiated with p-methoxy-p′-nitrobenzoyl peroxide was carried out in benzene at 30° C. The polymerization was not observed after 5 hr.

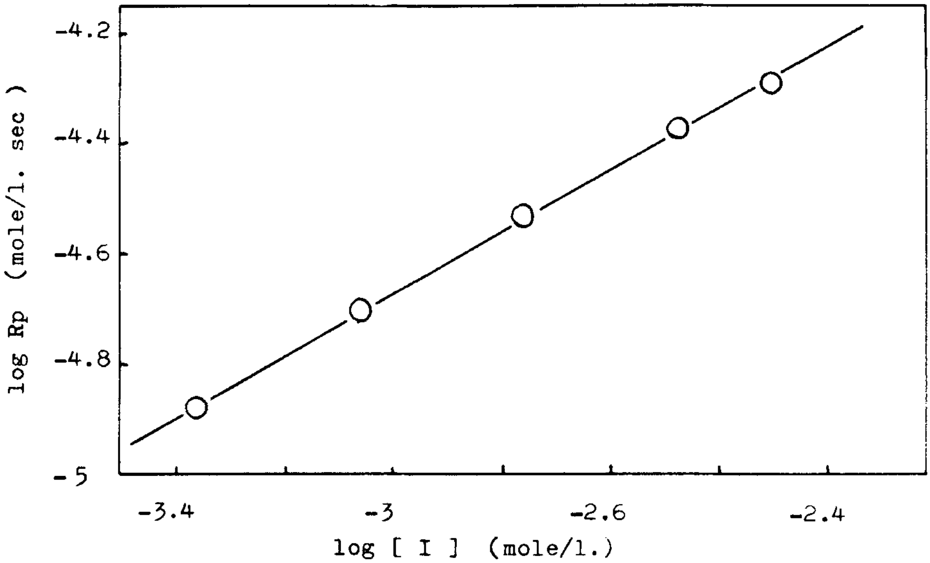


FIG. 5. Relationship between the initial rate of polymerization and the concentration of p-methoxy-p′-nitrobenzoyl peroxide in DMF at 60°C; [acrylonitrile] = 3.038 moles/liter.

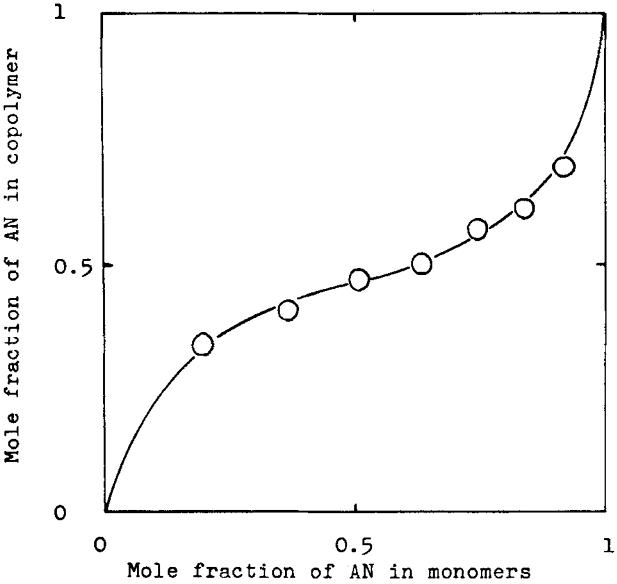


FIG. 6. Composition curve of styrene and acrylonitrile copolymer formed with p-methoxy-p′-nitrobenzoyl peroxide in DMF at 60°C; [p-methoxy-p′-nitrobenzoyl peroxide] = 5.02×10^{-3} mole/liter.

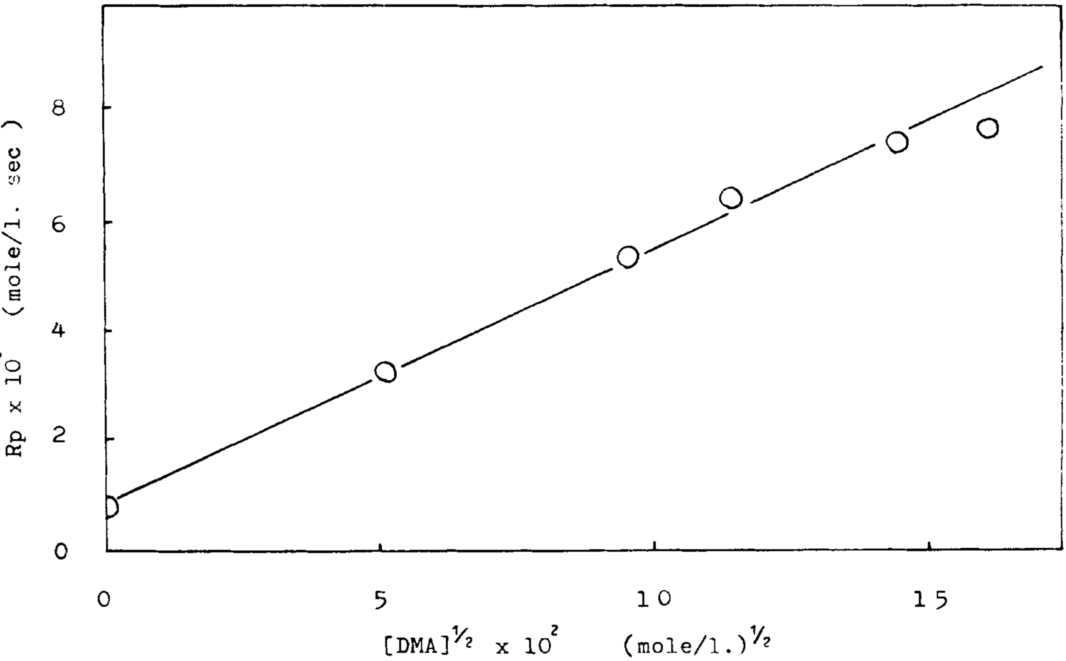


FIG. 7. Relationship between the initial rate of polymerization and the concentration of dimethylaniline in benzene at 30°C; [p-methoxy-p′-nitrobenzoyl peroxide] = 1.326 × 10^{-2} mole/liter; [styrene] = 4.364 moles/liter.

DISCUSSION

As can be seen from the results here described, p-methoxy-p′-nitrobenzoyl peroxide cleaved itself homolytically to initiate vinyl polymerization. The initial rates of polymerization of styrene in dimethylformamide, benzene, and acetone showed the same dependence upon the concentration of p-methoxy-p′-nitrobenzoyl peroxide. Accordingly if, as shown by Leffler [2], the feature of the cleavage of p-methoxy-p′-nitrobenzoyl peroxide changed by the kinds of solvents, the initial rate of polymerization of styrene should be also changed by the kinds of solvents used. But, as shown in Table 1, the values of R_p obtained from Fig. 1, 3, and 4 were nearly constant in dimethylformamide, acetone, and benzene.

TABLE 1. Initial Rate of Polymerization of Styrene Initiated with p-Methoxy-p'-nitrobenzoyl Peroxide in Different Solvents at 60°C[a]

Solvent	$R_p \times 10^6$, moles/liter sec
Benzene	6.8
DMF	6.7
Acetone	7.2

[a] [p-Methoxy-p'-nitrobenzoyl peroxide] = 2.0×10^{-3} mole/liter; [styrene] = 4.364 moles/liter.

As a conclusion, p-methoxy-p'-nitrobenzoyl peroxide was always a radical initiator in the polymerizations of styrene and acrylonitrile in benzene, DMF, or acetone.

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Accepted by editor July 28, 1967
Submitted for publication December 6, 1967

Zusammenfassung

In der Literatur wurde beschrieben, dass p-Methoxyl-p′-nitrobenzoylperoxid homolytisch in Benzol zerfällt, während heterolytischer Zerfall in Aceton auftritt. In der gegenwärtigen Arbeit wurde jedoch gefunden, dass Polymerisationen von Styrol und Acrylnitril in Benzol, Dimethylformamid oder Aceton immer radikalisch verlaufen. Die Polymerisationsgeschwindigkeit in den oben erwähnten Lösungsmitteln wurde als fast gleich gefunden.

Résumé

La décomposition du p-méthoxy-p′-nitrobenzoyl peroxyde a été décrite dans la littérature comme processus homolytique dans le benzène, mais héterolytique dans l'acétone. Cependant, les auteurs ont trouvé dans la présente étude, que la polymérisation du styrène avec l'acrylonitrile procède toujours par un mécanisme radicalaire dans le benzène, le diméthylformamide ou l'acétone. On a aussi trouvé que la vitesse de polymérisation dans ces solvants est presque identique.