The Dye-sensitized Photopolymerization of Vinyl Acetate in the Presence of Benzoyl Peroxide

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(Received July 21, 1964)

Oster1) reported that the dye-sensitized photopolymerization of vinyl monomers can easily occur in the presence of oxygen when a suitable combination of a dye and a reducing agent is used. Since then, many studies have been made concerning polymerization by means of such sensitizing systems.2-8) One of the present authors previously found4) that the riboflavin-sensitized photopolymerization of acrylamide in an aqueous solution was initiated by free radicals arising from the photoredox process between the photoreduced dye and the peroxidic compound produced during an induction period, and, furthermore, that this polymerization readily occurred at or below room temperature, even in the complete absence of oxygen, when a small amount of a peroxide, such as hydrogen peroxide or potassium persulfate, was added to the monomer mixture.

These sensitizing systems, including peroxide, seem to be superior to the previous one in that there is no induction period and polymerization can be easily controlled by varying the amounts of the peroxide added. For this reason, the present work was undertaken.

Experimental

The sample solution, a mixture of the monomer and methanol (80 : 20 by volume), was deaerated by flushing it with purified nitrogen. Then the solution was irradiated with a 500-W. tungsten projector lamp through a color filter which removed the light of wavelengths shorter than 3000 Å.

Results and Discussion

Table I shows the effects of several organic peroxides on the photopolymerization sensitized by riboflavin and acriflavine at 24°C. The polymerization was markedly accelerated by the addition of small amounts of such peroxides. The polymerization in the dark scarcely occurred under identical conditions, however. The rates of photopolymerization induced by the reaction between BPO and acetamide and by BPO itself are of an order of magnitude lower than that in the presence of both the dye and BPO. In all cases, the fading of the dye commenced immediately on irradiation, and then polymerization occurred. The conversion was increased with the increase in BPO concentration, whereas the polymerization

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1) G. Oster, *Nature*, **173**, 300 (1954).

2) K. Nakatsuka, *Chemistry* (*Kagaku*), **11**, 218 (1956).

3) H. Oba and I. Fujita, *Chem. High Polymers, Japan* (*Kobunshi Kagaku*), **15**, 445 (1958).

4) Y. Nishijima, K. Takakura, T. Hayahara and Y. Ohno, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959; K. Takakura, Master Thesis, Dept. of Polymer Chem., Kyoto University, March, 1959.

5) G. Takayama, *Chem. High Polymers, Japan* (*Kobunshi Kagaku*), **17**, 644 (1960).

6) G. Delzenne, S. Toppet and G. Smets, *J. Polymer Sci.*, **48**, 347 (1960).

7) G. Delzenne, W. Dewinter, S. Toppet and G. Smets, *J. Polymer Sci.*, **A2**, 1069 (1964).

8) Y. Nishijima, T. Fujimoto and K. Shimabayashi, presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

TABLE I. EFFECT OF BPO AND ITS DERIVATIVES ON THE DYE-SENSITIZED PHOTOPOLYMERIZATION OF VAc

Dye-sensitizer mol./l. × 10^5		Peroxide mol./l. × 10^4		Acetamide[a] mol./l.	Conversion %	DP[b]
RF[c]	4		0	0.34	1.7	3440
	4	BPO	8.3	0.42	14.6	4000
	40	BPO	8.3	0.42	4.7	1270
	4	BPO	8.3	0	10.7	3860
AF[d]	2	BPO	2.1	0	9.6	4060
	2	BPO	4.2	0	13.7	3650
	2	BPO	8.3	0	15.2	3650
	4	BPO	8.3	0	23.4	4020
	2	Bis(*p*-ClB)PO[f]	8.3	0	16.6	4450
	2	Bis(*o*-methoxyB)PO[g]	8.3	0	21.7	4300
	4	LPO[e]	10.0	0	30.0	3860
	0	BPO	8.3	0.25	2.7	4640
	0	Bis(*o*-methoxyB)PO[g]	8.3	0	3.0	5200

a) Mild reducing agent. b) Degree of polymerization of PVAc determined viscometrically.
c) Riboflavin-5′-phosphate sodium salt. d) Acriflavine. e) Lauroyl peroxide. f) Bis-(*p*-chlorobenzoyl)peroxide. g) Bis(*p*-methoxybenzoyl)peroxide.
Irradiation time, 2 hr.; temp., 24°C

TABLE II. EFFECT OF BPO ON THE DYE-SENSITIZED PHOTOPOLYMERIZATION OF SEVERAL MONOMERS IN ORGANIC SOLUTIONS

Monomer	Dye-sensitizer mol./l. × 10^5		BPO mol./l. × 10^4	Irradiation time hr.	Conversion %
MMA	AF	2	0	8	2.9
	AF	2	8.3	8	13.0
	AF	2	8.3	8	15.7
		0	8.3	8	4.2
AN	RF	2	8.3	2	10.5
	AF	2	0	2	0.5
AAm	RF	2	0	3/4	2.0
	RF	2	8.3	3/4	41.5
		0	8.3	3/4	5.0

MMA, methyl methacrylate : benzene : methanol = 40 : 40 : 20 (by vol.)
AN, acrylonitrile : DMSO : methanol = 20 : 60 : 20 (by vol.)
AAm, acrylamide in methanol, 5 g./dl.
Temp., 24°C in nitrogen

was markedly retarded at higher dye concentrations. The BPO-catalyzed polymerization of VAc at 60°C in the dark was almost entirely inhibited when riboflavin was present.

Figure 1 shows the course of the polymerization performed at three different temperatures. The overall activation energy was calculated to be 7.4±0.5 kcal./mol., a value which was in good agreement with that of a previous study.[5)]

On irradiation the absorption spectra of the reaction mixture in the visible regions began to disappear. The original color of the dye could no longer be recovered by admitting air into the irradiated system. It should be noted that such a spectral change in the polymerizing system was not observed in the dark, even at a high temperature. Therefore, it may be suggested that the photo-excited dyes or some derived species would react with BPO and undergo irreversible decomposition to produce some active free radicals.

Among the dyes examined, fluorescein sodium, acriflavine, rhodamin B and riboflavin

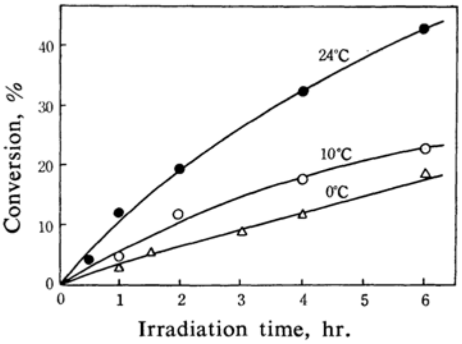

Fig. 1. Time-conversion curve for the photopolymerization of VAc sensitized by acriflavine-BPO: (Acriflavine) $=2.4\times10^{-5}$ mol./l., (BPO) $=8.3\times10^{-4}$ mol./l., (Acetamide) $=0.68$ mol./l.; VAc : methanol $=80:20$ (by vol.), under nitrogen.

are particularly effective. All of them are photoreducible dyes and are characterized by their fluorescence.[9]

This sensitizing system has been successfully applied to the photopolymerization of other vinyl monomers in organic solutions. The preliminary results are summarized in Table II. The effect of BPO is pronounced here also, and the polymerization is always accompanied by the photobleaching of the dye.

The results obtained may be explained in terms of a photo-redox mechanism by which the photoreduced dye is irreversibly oxidized with BPO to produce active initiating radicals.

The authors wish to thank Dr. Masakazu Matsumoto and Dr. Junji Ukida of our laboratory for their helpful discussions during this work.

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[9] For example, M. Koizumi, "An Introduction to Photochemistry" (Kokagaku Gairon), Asakura Shoten, Tokyo (1963), p. 346.