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OXYGEN-ACCELERATED PHOTOPOLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF AMIDES

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ABSTRACT

The photopolymerization of methyl methacrylate (MMA) was accelerated by amides such as *N*-methylpyrrolidone (NMP), pyrrolidone (PD), and dimethylacetamide (DMA) in the following order: NMP > PD > DMA. The rates of photopolymerization of styrene and vinyl acetate were also increased by NMP. The results suggest that the free radicals produced by the photodecomposition of these amides initiate the polymerization. Moreover, the rate of photopolymerization of MMA in the presence of the amides was enhanced by oxygen after an induction period. The UV absorption spectra of these amides were measured under nitrogen and oxygen; the extra absorptions observed under oxygen were ascribed to charge-transfer complexes between oxygen and the amides. The reaction mechanism is discussed on the basis of the photoreaction of the complexes.

INTRODUCTION

Oxygen usually inhibits the radical polymerization of vinyl monomers. However, Kodaira et al. reported that the photopolymerization of styrene (St) is accelerated by oxygen, in which a charge-transfer complex between St and oxygen is speculated to participate in the initiation [1]. We recently found that the rate of photopolymerization of *N*-vinylpyrrolidone is enhanced by oxygen after an induction period [2], and then found that the photopolymerization of methyl methacrylate (MMA) is accelerated by oxygen in the presence of amides. Oxygen as a charge acceptor forms complexes with charge-donating aromatic molecules [3] and amides [4]. Therefore, the rate enhancement of the photopolymerization of MMA by oxygen seems to come from complex formation between oxygen and the amides in the reaction mixture.

In the present work we investigated the accelerating effect of oxygen on the photopolymerization of MMA in the presence of the amides in order to elucidate the reaction mechanism.

EXPERIMENTAL

Materials

Vinyl monomers were purified by distillation under reduced pressure after the usual treatment. Reagent-grade amides were used without further purification.

Polymerization

A magnetic stirring bar and the monomer were sealed in a Pyrex ampule, with or without the amide, under vacuum, air, or oxygen after the contents had been degassed by repeated freezing and thawing. The ampule was placed vertically in a Pyrex cooling jacket thermostated at 18°C by circulating water. The polymerization was carried out by irradiating with a 400-W high-pressure mercury lamp (Riko UVL-400HA). The distance from the jacket to the lamp was 5 cm. After the desired time, the reaction mixture was poured into an excess of nonsolvent: MMA and St into methanol, vinyl acetate (VAc) into diethyl ether. The precipitated polymer was filtered and dried *in vacuo* at 60°C to constant weight.

UV Spectra

UV spectra were obtained on a Hitachi 100-60 spectrophotometer. The procedure was similar to that reported earlier [1].

Measurement of Molecular Weight

The molecular weight of polyMMA was determined by viscometry in acetone at 30°C [5].

RESULTS AND DISCUSSION

Figure 1 shows the acceleration effect of *N*-methylpyrrolidone (NMP), pyrrolidone (PD), and dimethylacetamide (DMA) on the photopolymerization of MMA in the absence of oxygen. These three amides enhance the rate of the polymerization in the following order: NMP > PD > DMA. As seen in Table 1, the rate of the polymerization increased with the amount of NMP, in spite of the accompanying lowered monomer concen-

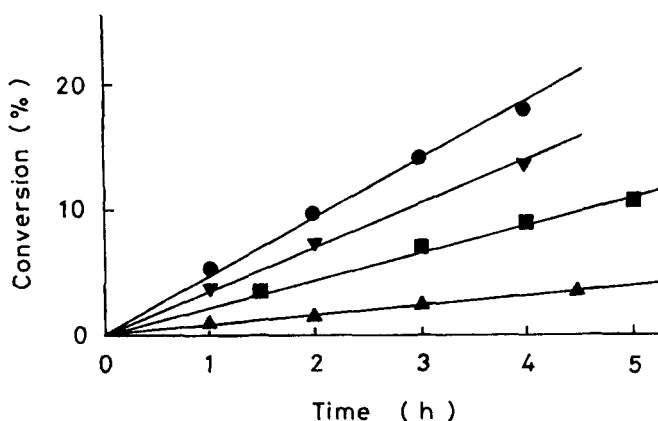


FIG. 1. Effect of amides on the photopolymerization of MMA in the absence of oxygen. MMA, 3 mL; amide, 2 mL; (●) NMP; (▼) PD; (■) DMA; (▲) bulk (MMA, 5 mL).

TABLE 1. Effect of *N*-Methylpyrrolidone on the Photopolymerization of Methyl Methacrylate

MMA, mL	NMP, mL	Conversion in 3 h, %
5	0	2.2
3	0.1	5.7
3	0.3	8.5
3	0.5	10.5
3	1	12.4
3	2	14.1
2	3	24.0
1	4	29.2

tration. The effect of NMP on the photopolymerization of St and VAc is presented in Table 2. The acceleration effect is considerable in the case of VAc: the conversion reaches nearly 20% in 4 h in the presence of NMP, whereas no polymerization occurs in its absence. Accordingly, the effect of the amide is considered to be general for the photopolymerization of the common vinyl monomers. This acceleration can be ascribed to the formation of free-radical species generated by the photodecomposition of the amides.

The photochemical decomposition of amides has been studied [6, 7], and primary and secondary amides have been reported to decompose on irradiation with light of shorter wavelengths ($\lambda < 250$ nm) [8]. Although Pyrex glass transmits only light of longer wavelengths ($\lambda > 280$ nm), the effect of the amides used for the present photopolymerization is obvious as

TABLE 2. Effect of *N*-Methylpyrrolidone on the Photopolymerization of Styrene and Vinyl Acetate

Monomer, mL	NMP, mL	Time, h	Conversion, %
St 5	0	12	2.8
St, 3	2	4	2.9
St, 3	2	8	6.1
St, 3	2	12	8.8
VAc, 5	0	5	0
VAc, 3	2	4	18.4

described above. In fact, these secondary and tertiary amides absorb light above 280 nm. On the other hand, amides as charge donors form complexes with organic charge acceptors [9]. However, the UV spectral data gave no evidence for complex formation between the above amides and MMA as a weak charge acceptor. Some loose-contact charge-transfer complexes are sometimes difficult to detect spectrophotometrically because the charge-transfer absorption bands overlap the original strong absorption bands. Therefore, the possibility of formation of such complexes and their participation in the polymerization cannot be excluded.

Since oxygen as a charge acceptor forms complexes with organic charge donors [3], the effect of complex formation between oxygen and the amides was then investigated. Figure 2 shows the effect of oxygen on the photopolymerization of MMA in the presence of NMP. The rate of polymerization under oxygen after an induction period was greater than

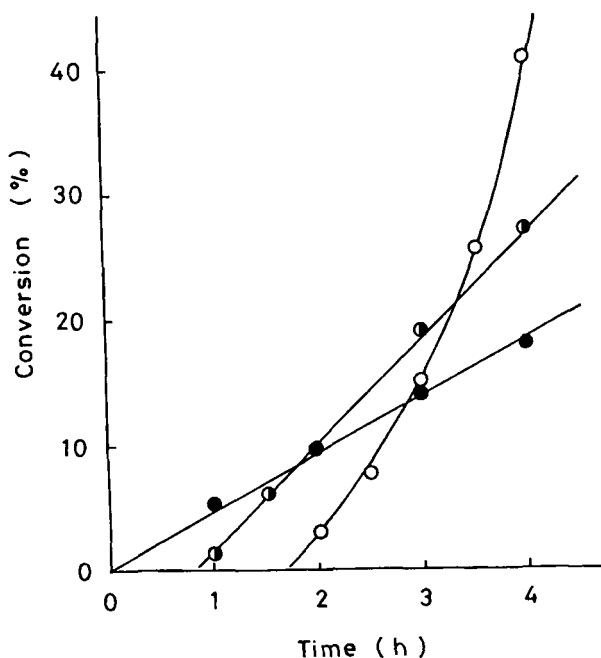


FIG. 2. Effect of oxygen on the photopolymerization of MMA in NMP. MMA, 3 mL; NMP, 2 mL; (●) in the absence of oxygen (from Fig. 1); (◐) under air; (○) under oxygen.

that in its absence, and the effect depends on the oxygen content in the initial atmosphere, i.e., the rate under oxygen was larger than that under air. The results of the photopolymerization of MMA in the above three amides under oxygen are shown in Fig. 3. After the induction periods, the rates were higher than those in the absence of oxygen (Fig. 1). The concave curves in Fig. 3 can be ascribed partially to a gel effect observed for bulk polymerization, since the reaction solutions were too viscous to stir with a magnetic stirring bar at conversions above 40%. This gel effect leads to an increase in the molecular weight of the polymer with increasing conversion, as shown below.

Oxygen inhibits the usual radical polymerization of vinyl monomers, and indeed the photopolymerization of MMA was inhibited by oxygen in the absence of the amide. Nevertheless, an oxygen-accelerated vinyl polymerization has been reported for the photopolymerization of St, in which a charge-transfer complex between oxygen and St participates as a light-absorbing species [1].

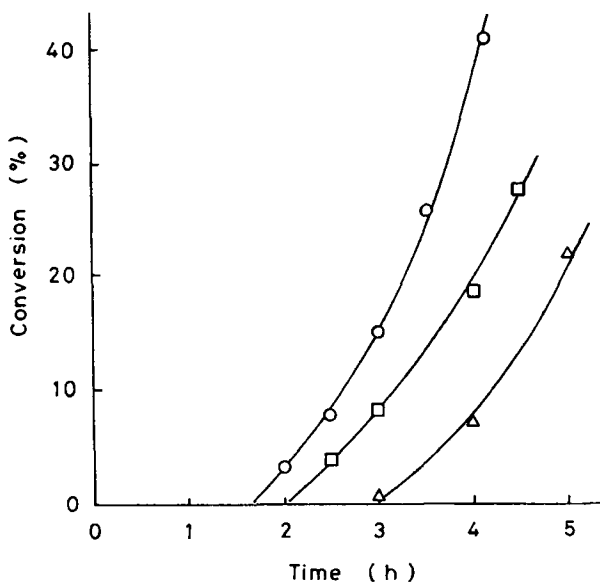


FIG. 3. Photopolymerization of MMA in various amides under oxygen. (○) NMP (from Fig. 2); (□) PD; (△) DMA.

The acceleration by oxygen in the present polymerization suggests that complexes between oxygen and the amides cause the rate enhancement. Hence, the UV spectra of the amides were measured under oxygen to investigate this complex formation. First, nitrogen was bubbled into the amide in a quartz cell, and after the cell was stoppered the UV absorption spectrum was recorded. Then oxygen was bubbled into the amide to note changes in the absorption. As seen in Fig. 4, extra absorption bands were observed for the three amides, as was reported by Tsubomura and Mulliken [10]. These extra absorption bands due to the charge-transfer complex disappeared reversibly on bubbling nitrogen again. The oxygen-enhanced absorbance is directly proportional to the partial pressure of oxygen, and the complex formation is ascribed solely to contact or collisional interaction [11].

Accordingly, one possible mechanism for the acceleration by oxygen in the photopolymerization of MMA in the presence of the amides is as

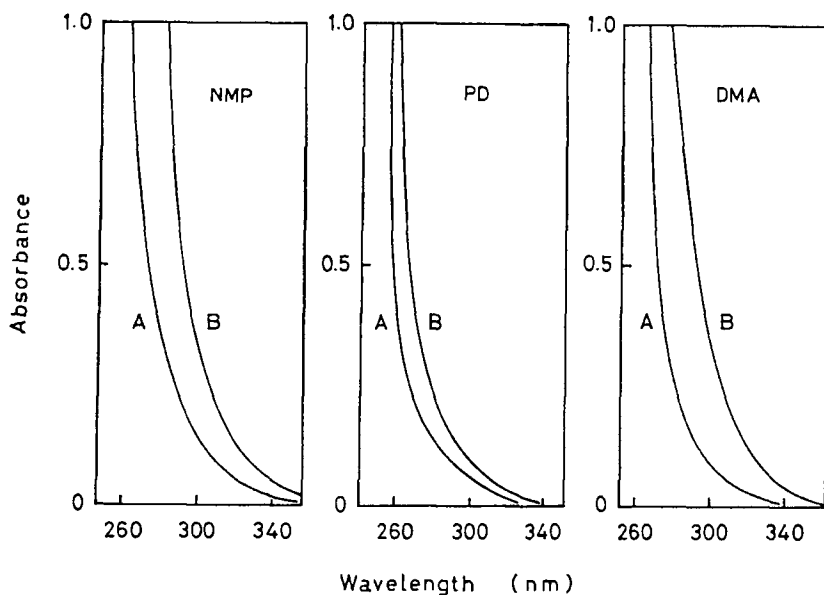
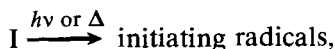
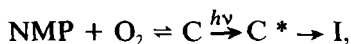
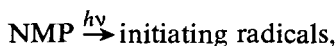


FIG. 4. Ultraviolet absorption spectra of amides. (A) Saturated with nitrogen; (B) saturated with oxygen.

follows:



where C and I are the charge-transfer complex and an unstable intermediate, respectively. The induction period observed in the presence of oxygen can be attributed to the well-known inhibition of radical polymerization. Therefore, after the oxygen in the atmosphere had been consumed to form the intermediate, the free radicals produced by the decomposition of the photochemically and/or the thermally unstable intermediated initiated the polymerization at a relatively higher rate. The radicals generated by the direct photodecomposition of the amides can also initiate the polymerization. The kinetics would, therefore, be more complicated. The accumulation of the intermediate postulated in the above mechanism is compatible with the features of this photopolymerization, i.e., the rather long induction period and the enhanced rate after that. However, the structure of the intermediate has still not been determined.

The IR spectral data of the polyMMA obtained showed that no oxygen molecule was combined in the polymer chain, in contrast to the photopolymerization of St [1]. The concave curves of the time-conversion plots (Fig. 3) can be ascribed to the gel effect usually observed for bulk polymerization.

The molecular weights of the polyMMA, listed in Table 3, were lower in the presence of NMP, suggesting that the concentration of initiating species increases on photodecomposition of the amide. Moreover, the presence of oxygen resulted in the formation of shorter polymer chains. This can also be explained by an increase in the initiating species. That is to say, the unstable intermediate formed by the photoreaction of the charge-transfer complex composed of oxygen and the amide decomposes easily to yield the initiating species. Our results support this mechanism.

TABLE 3. Effect of Oxygen on the Molecular Weight of PolyMMA

Conditions	Time, h	Conversion, %	$\bar{M}_w \times 10^{-4}$ ^a
Degassed, bulk ^b	2	1.5	184
Degassed, bulk	3	2.2	205
Degassed, bulk	4.5	3.0	214
Degassed, in NMP ^c	2	9.8	27.8
Degassed, in NMP	3	14.1	27.9
Degassed, in NMP	4	16.8	35.7
Air, in NMP	3	19.7	8.0
Air, in NMP	4	27.3	8.4
Oxygen, in NMP	2.5	7.7	4.3
Oxygen, in NMP	3	14.5	4.3
Oxygen, in NMP	3.5	25.8	4.4
Oxygen, in NMP	4	41.0	5.8

^aThe weight-average molecular weight was calculated from viscometry data [5].

^bMMA, 5 mL.

^cMMA, 3 mL; NMP, 2 mL.

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