

SHORT COMMUNICATIONS

**Photopolymerization of Methyl Methacrylate in the Presence of a Charge-Transfer Complex of an Ether with Oxygen**

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Oxygen usually inhibits the radical polymerization of vinyl monomers; however, we previously reported that the rate of photopolymerization of *N*-vinylpyrrolidone is enhanced by oxygen after an induction period.<sup>1</sup> More recently we have reported that the photopolymerization of methyl methacrylate (MMA) in the presence of amides such as *N*-methyl-2-pyrrolidone is accelerated by oxygen, in which the charge-transfer complexes of oxygen with the amide produce initiating radicals.<sup>2</sup>

This communication shows a new finding that the charge-transfer complex composed of oxygen and dibenzyl ether initiates the photopolymerization of MMA.

EXPERIMENTAL

*Materials*

MMA was purified by distillation under reduced pressure after the usual treatment. Dibenzyl ether and diphenyl ether were distilled under reduced pressure in a stream of nitrogen, and diethyl ether was dried over sodium under reflux over night and distilled.

*Photopolymerization*

Photopolymerization was carried out in a

Pyrex or quartz ampule by the same method as described previously.<sup>2</sup> The preirradiation effect was examined with dibenzyl ether by following method: after the ether was preirradiated for a given time under oxygen, MMA was introduced from a branch sealed under nitrogen and the solution was irradiated successively or allowed to stand in the dark. After a given time the polymerization mixture was poured into a large excess of methanol to precipitate the polymer. The conversion was calculated gravimetrically.

*Measurement of UV Absorption Spectra*

The absorption spectra of ethers saturated with nitrogen or oxygen were measured by the method of Tsubomura and Mulliken<sup>3</sup> with Hitachi 100-60 spectrophotometer.

*Measurement of Molecular Weight*

The molecular weight of poly(MMA) was determined by viscometry in benzene at 30°C.<sup>4</sup>

RESULTS AND DISCUSSION

The results of photopolymerization of MMA in the presence of ethers are presented in Table I. Under nitrogen, diethyl ether enhanced the conversion (Run 1 and 3), though the monomer

**Table I.** Photopolymerization of MMA in the presence of ethers<sup>a</sup>

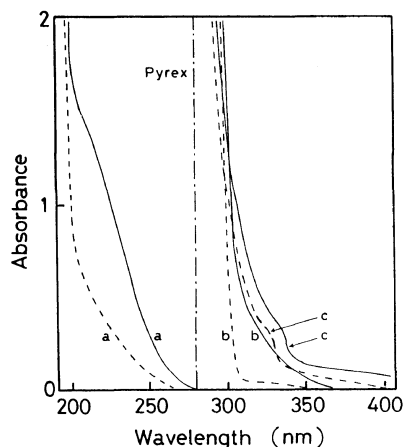
Run	Ether	Atmosphere	Conversion
			%
1	— <sup>b</sup>	N <sub>2</sub>	4.0
2	— <sup>b</sup>	O <sub>2</sub>	0
3	Diethyl ether	N <sub>2</sub>	5.3
4	Diethyl ether	O <sub>2</sub>	0
5	Dibenzyl ether	N <sub>2</sub>	18.4
6	Dibenzyl ether	O <sub>2</sub>	24.9
7	Diphenyl ether	N <sub>2</sub>	0.5
8	Diphenyl ether	O <sub>2</sub>	0

<sup>a</sup> The mixture of MMA (3 ml) and ether (2 ml) in a Pyrex ampule was irradiated for 4 h at 14°C.

<sup>b</sup> MMA (5 ml) was photopolymerized in bulk.

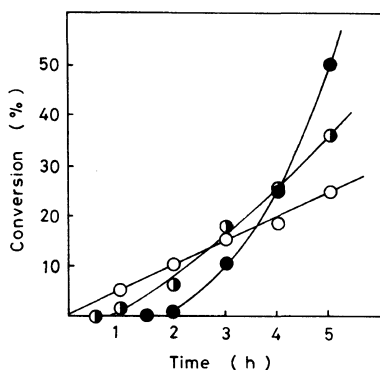
was diluted with the ether; this indicates the generation of some initiating radicals. In the case of triethylamine, whose electronic structure is similar to that of the ether, the complex of excited MMA with the amine has been reported to initiate the polymerization, in which the initiating radicals are formed by the electron transfer in the exciplex.<sup>5</sup> Since Pyrex glass does not transmit the light of wavelengths shorter than 280 nm, diethyl ether is not excited in the ampule used; hence, the MMA molecules excited by the irradiation seem to complex with the ether to form exciplexes which generate free radicals through an electron transfer from the ether to the monomer. The larger enhancement with dibenzyl ether can be ascribed to the unstable properties of the excited complex of the ether with MMA, where the formation of initiating radicals would be easy due to the reactive benzylic hydrogen as shown below. Diphenyl ether, on the contrary, retarded the polymerization probably because the excited complex of the monomer with the ether is not so unstable to form free radicals easily, therefore the complexation leads to stabilization of the excited monomer.

Oxygen usually inhibits radical polymerization of vinyl monomers, whereas, in some cases, a little amount of oxygen is incorporated in the



**Figure 1.** UV absorption spectra of ethers under N<sub>2</sub> (---) and O<sub>2</sub> (—). (a) diethyl ether; (b) diphenyl ether; (c) dibenzyl ether.

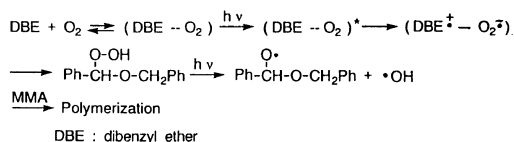
backbones of the polymers by copolymerization forming a hydroperoxide structure. As seen in Table I, the polymerization of MMA was effectively inhibited by oxygen; however, the conversion in the presence of dibenzyl ether is greater under oxygen than under nitrogen (Run 5 and 6). Oxygen as a charge acceptor forms complexes with organic charge donors, and we have reported a rate enhancement effect arising from the complex formation between oxygen and amides on the photopolymerization of MMA.<sup>2</sup> We have also reported a similar rate enhancement effect in the polymerization of MMA with a complex of oxygen-*N,N*-dimethylbenzylamine which decomposes photochemically to form initiating radicals.<sup>6</sup> The similarity in the electronic structure between the amine and dibenzyl ether suggests that the greater conversion under oxygen come from the complex formation of oxygen with the ether. Hence, the UV spectra of the ethers were measured under oxygen to examine this complex. First, after nitrogen was bubbled into the ether in a quartz cell the UV absorption spectrum was recorded. Then oxygen was bubbled into the ether to see the change in the absorption. As shown in Figure 1, extra absorption was observed for each ether as was



**Figure 2.** Photopolymerization of MMA in the presence of dibenzyl ether under N<sub>2</sub> (○), air (●), and O<sub>2</sub> (●). The reaction condition was the same as described in Table II.

reported by Stenberg *et al.*<sup>7</sup> These extra absorption bands due to charge-transfer interaction disappeared reversibly on bubbling nitrogen again; the complex formation can be ascribed to contact or collisional interaction.<sup>3</sup>

Figure 2 shows the effect of oxygen on the photopolymerization of MMA in the presence of dibenzyl ether. The induction period was prolonged by the presence of oxygen and after that, however, the rate of polymerization in the ampule sealed under oxygen was greater than that under nitrogen. This time-conversion profile with dibenzyl ether is very similar to that we got previously using amides,<sup>2</sup> suggesting a mechanistic similarity. The induction period caused by oxygen is due to the usual inhibition. The charge-transfer complex of the ether with oxygen converts into an unstable intermediate, which seems most likely to be a hydroperoxide as has been reported.<sup>7-10</sup> After the oxygen in the atmosphere had been consumed to form the intermediate, the free radicals produced by the decomposition of the photochemically unstable intermediate initiate the polymerization at a relatively higher rate:



**Table II.** Effect of oxygen on the molecular weight of Poly(MMA)<sup>a</sup>

Run	Atmosphere	Irradiation time	Conversion	
		h	%	$M_n \times 10^{-4b}$
1	N <sub>2</sub>	2	10.2	14.7
2	Air	1.5	5.7	5.11
3	O <sub>2</sub>	3	10.5	3.45

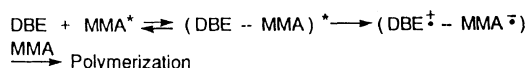
<sup>a</sup> The solution of MMA (3 ml) and dibenzyl ether (2 ml) in a Pyrex ampule was irradiated at 14°C.

<sup>b</sup> The number-average molecular weight was calculated on the basis of viscometry.<sup>4</sup>

The accumulation of the intermediate postulated in the above mechanism is compatible with the features of this polymerization, that is, the long induction periods and the subsequent enhanced rates after that. When the ether was preirradiated for 2 h under oxygen before the monomer was introduced, the induction period was shortened to 30 min, and a prolonged preirradiation of the ether under oxygen did not lead to further shortening of the induction period but a decrease in the rate of polymerization after that. These results also support the assumed mechanism, because the preirradiation of the complex of the ether with oxygen promotes the formation of the intermediate which consumes oxygen and shortens the induction period, and a prolonged preirradiation wastes the hydroperoxide intermediate by the photochemical decomposition before the monomer is introduced, which results in the reduction of the rate of polymerization after the induction period. The fact that the polymerization after the preirradiation did not proceed in the dark indicates that the hydroperoxide intermediate is rather stable around 14°C. The molecular weights of the polymers obtained in the presence of oxygen were lower than those obtained under nitrogen (Table II), suggesting an increase in the number of the initiating radicals and also supporting the mechanism.

As seen in Table I and Figure 2, under

nitrogen the rates of polymerization were greater in the presence of dibenzyl ether than those in its absence. These results indicate that the free radicals formed by the electron transfer in the exciplex of MMA with the ether can also initiate the polymerization as mentioned first. The kinetics would, therefore, be much more complex; however, the mechanism assumed above is still applicable because the formation of the exciplex only leads to an increase in the number of free radicals and brings about no change in the fundamental mechanism.



The lack of  $\alpha$ -hydrogen in diphenyl ether makes the complex of the ether with oxygen unable to form a hydroperoxide; hence, only the inhibition was observed. In the case of diethyl ether, the complex is not excited in the Pyrex ampule because of the shorter wavelengths of its absorption bands; however, in a quartz ampule the polymerization took place after an induction period; this can be explained on the basis of the same mechanism as shown above.<sup>7-9</sup> Since the polymerization is initiated easily by the excited MMA itself in the quartz

ampule, the effect of the complex formation is sometimes difficult to distinguish. The results obtained with various ethers suggest that in general the formation of an oxygen-ether complex brings about an acceleration of radical polymerization of vinyl monomers.

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