Effect of Solvent on Anthraquinone-Sensitized Photopolymerization of Methyl Methacrylate

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Synopsis

Photopolymerization of methyl methacrylate was carried out in the system containing anthraquinone (AQ) sensitizer and solvent under nitrogen at 30°C. Hydrocarbons, alcohols, and mixtures of both, for example, cyclohexane and isopropanol, were used as solvents. The maimum yield of polymerization was observed at a certain concentration of alcohol in hydrocarbon, a phenomenon which is discussed from measurements of polymer molecular weight and the UV spectrum of irradiated AQ.

INTRODUCTION

The authors[1] have observed that vinyl monomers are effectively introduced in polyolefin films using sensitizer-coated samples with benzophenone and anthraquinone (AQ) by photografting in a vapor phase system. AQ was especially effective in grafting methyl methacrylate (MMA), affording a percent grafting of more than 1000% on the film. With such a high percent grafting, the interaction between sensitizer and polymer is of great importance. This study deals with photopolymerizations of MMA using AQ sensitizer in various solvents to provide insight into the initiation reaction of the polymerization.

AQ and its derivatives affect the photo-oxidation of alcohols of low molecular weight[2-5] and the photodecomposition of polymers.[6-8] The initiation of these reactions originates from the abstraction of hydrogen atoms from the substrates. On the other hand, AQ and its derivatives have sensitizing abilities to initiate photopolymerization[9-12] as well as photografting.[13,14] Ledwith et al.[12] reported AQ-sensitized polymerization of MMA in tetrahydrofuran, in which the polymerization is initiated with the tetrahydrofuran radicals formed by the abstraction of hydrogen atoms by photoexcited AQ.

In this investigation, hydrocarbons, alcohols, and mixtures of both were used as solvents. The photopolymerization shows a maximum yield of polymerization at a certain concentration of alcohol in hydrocarbon.

EXPERIMENTAL

The alcohols methanol, ethanol, *n*-propanol, isopropanol(iso-PrOH), *n*-butanol, isobutanol, and *tert*-butanol; and hydrocarbons cyclohexane *n*-hexane, and isooctane were used as polymerization solvents. These solvents were purified by distillation before use. MMA monomer was washed with a saturated aqueous solution of sodium sulfate (pH 3) and then with water, and was finally distilled under reduced pressure. AQ and benzoyl peroxide (BPO) were of reagent grade of commercial origin.

A Pyrex glass tube containing 10 ml AQ solution with a known concentration and 1 ml MMA was flushed with nitrogen, and polymerization was carried out by irradiating with light at 30°C for 60 min. Irradiations with a high-pressure mercury lamp (400 W) were conducted in a Riko rotary photochemical reactor RH400-10 W. Polymerization products were poured into a large amount of methanol, filtered, and washed with methanol. After drying under reduced pressure, polymer yields were measured gravimetrically.

The number-average molecular weight of poly(MMA) was determined by means of gel permeation chromatography (Toyo Soda HLC-802) using tetrahydrofuran as solvent. The UV spectrum of AQ was recorded with a Hitachi spectrophotometer 124 type under nitrogen atmosphere.

RESULTS AND DISCUSSION

Photopolymerzations of MMA were carried out in various solvent systems. The AQ-sensitized system, prepared as described in the experimental section, was irradiated in a Pyrex glass tube. The polymer yields ranged from 0 to 50% according to the kind of solvent, suggesting a great effect of sovent on the polymerization reaction in the system (Table I). Alcohols are more effective solvents for polymerization than hydrocarbons, which are dependent on the readiness to release hydrogen atom from the solvent.

Figure 1 shows the results of polymerization in solvent systems with mixtures of cyclohexane and alcohols in various concentrations. The yield of polymer in the cyclohexane system increased sharply when a small quantity of alcohol was added, reached a maximum value, and then decreased on further addition of alcohol. Almost the same phenomenon was observed in alcohols other than ethanol and iso-PrOH.

Figure 2 compares polymerizations with three different initiation systems in solvent mixtures of cyclohexane and iso-PrOH. Although photopolymerization of the AQ-sensitized system gave a sharp peak of polymer yield at a certain concentration of alcohol, neither photopolymerization employing BPO as initiator nor thermal polymerization with BPO afforded a maximum yield through all iso-PrOH concentrations. In the latter two systems, polymerization is probably initiated directly from the fragment radicals of the initiator by either

TABLE I
AQ-Sensitized Photopolymerization of MMA in Various Solvents[a]

Solvent	Conversion, %
Methanol	7.5
Ethanol	13.3
n-Propanol	40.3
Isopropanol	22.0
n-Butanol	49.0
Isobutanol	51.3
tert-Butanol	16.3
Cyclohexane	8.6
n-Hexane	3.5
Isooctane	3.2
Benzene	0

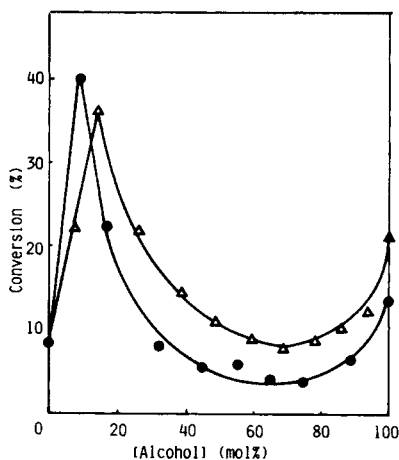[a] Irradiation time, 60 min; temperature, 30°C; [AQ] = 3×10^{-4} mol/L; [MMA] = 0.94 mol/L.

Fig. 1. AQ-sensitized photopolymerizations of MMA in (●) ethanol–cyclohexane and (△) iso-PrOH–cyclohexane. Temperature, 30°C; time, 60 min; [AQ] = 3 × 10^{-4} mol/L; [MMA] = 0.94 mol/L.

photochemical or thermal reaction. Photosensitizer AQ does not initiate polymerization directly, but abstracts hydrogen atom from the neighboring molecule, resulting in the formation of an active radical capable of initiating polymerization. Accordingly, the maximum peak which appeared in the conversion curve is closely related to the reaction of photoexcited AQ abstracting hydrogen atom from the solvent. Why the magnitude of conversion is not proportional to the concentration of alcohol is now the question.

Some measurements of poly(MMA) samples, were prepared with solvents of different alcohol concentrations (Table II). As the alcohol concentration increased, the number-average molecular weight of the sample gradually became larger. On the other hand, a sharp drop in the absorption at 254 nm was observed with the addition of alcohol as solvent in the polymerization system. A strong absorption at 254 nm for polymer prepared in 100% cyclohexane may be assigned to the anthrahydroquinone residues, which can be introduced at the polymer chain ends. Ledwith et al.[12] reported that semianthrahydroquinone radical
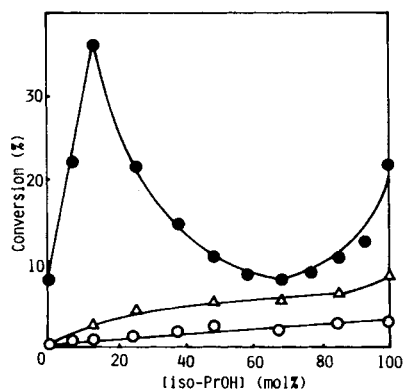

Fig. 2. Polymerization of MMA with various sensitizers in iso-PrOH–cyclohexane system: (●) [AQ] = 3 × 10^{-4} mol/L, 30°C; irradiation time, 60 min; (△) [BPO] = 3 × 10^{-4} mol/L, 30°C; irradiation time, 60 min; (○) [BPO] = 3 × 10^{-4} mol/L, 60°C; time, 60 min.

TABLE II
Measurements of Poly(MMA)[a]

iso-PrOH content (mol-%)	$\overline{M}_n \times 10^{-4}$	Relative absorption at 254 nm
0	3.2	5.3
13.6	4.3	1.0
68.0	4.8	1.3
100	7.7	1.0

[a] Irradiation time, 60 min; temperature, 30°C; [AQ] = 3 × 10⁻⁴ mol/L; [MMA] = 0.94 mol/L.

(AQH·) participates in the termination of the growing poly(MMA) radical. The fact that the polymer obtained in the system with solvent containing iso-PrOH shows a markedly lower level of 254 nm absorption, as compared to the polymer with 100% cyclohexane suggests a poorer introduction of anthrahydroquinone residue into the polymer. This indicates a suppresion of termination reactions for growing polymer with AQH· radical due to alcohol.

Figure 3 shows spectrum changes of AQ solutions due to UV irradiation at 30°C under nitrogen atmosphere. By photolysis in cyclohexane solvent, AQ decreased in absorbance at 322 nm unilaterally, which is characteristic of the AQ molecule.[5,12] On the other hand, in iso-PrOH, a new absorption appeared at 383 nm, instead of the decrease at 322 nm absorption, which recorded a maximum magnitude in the early stages of irradiation and decreased slowly. This peak was assigned to the anthrahydroquinone (AQH₂) molecule.[5,12] The above experiment suggests that AQH_2 can easily be formed in iso-PrOH solution, but hardly in cyclohexane.

Changes of two absorbances at 322 and 383 nm are compared in Figure 4. The horizontal axis shows the concentration of iso-PrOH in cyclohexane. As the alcohol concentration became higher, the curve of the AQ absorption tended to decrease, while that of AQH_2 increased. The alcohol concentration giving the maximum polymer yield corresponds roughly to the point at which the two curves intersect.

Based on the above investigations, the reactions of AQ-sensitized photo-polymerization of MMA were estimated as follows:
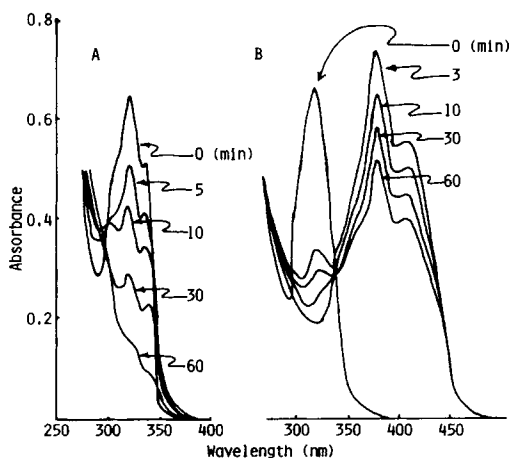

Fig. 3. Changes in UV spectra in AQ solutions with UV irradiation at 30°C under nitrogen atmosphere. Solvent: A, cyclohexane; B, iso-PrOH; [AQ] = 3 × 10⁻⁴ mol/L.
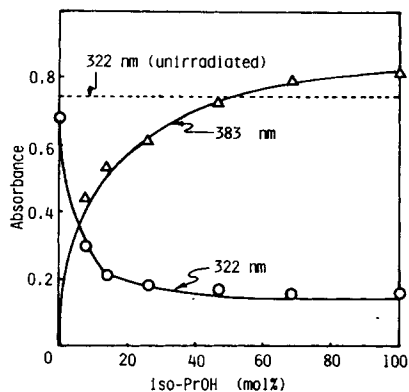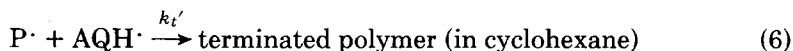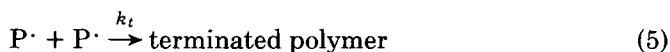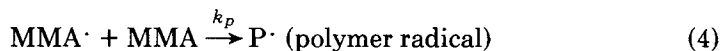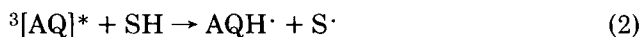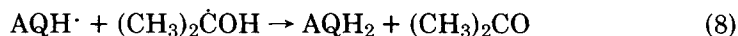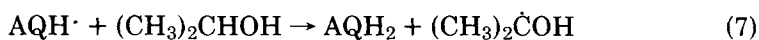
Fig. 4. Changes in absorbances at 322 and 383 nm in cyclohexane–iso-PrOH system with UV irradiation at 30°C under nitrogen atmosphere. Irradiation time, 5 min; [AQ] = 3×10^{-4} mol/L.

Photopolymerization of MMA:

$$AQ \xrightarrow{h\nu} {}^{1}[AQ]^* \rightarrow {}^{3}[AQ]^* \tag{1}$$

$$^{3}[AQ]^* + SH \rightarrow AQH^{\cdot} + S^{\cdot} \tag{2}$$

$$S^{\cdot} + MMA \xrightarrow{k_i} MMA^{\cdot} \tag{3}$$

$$MMA^{\cdot} + MMA \xrightarrow{k_p} P^{\cdot} \ (\text{polymer radical}) \tag{4}$$

$$P^{\cdot} + P^{\cdot} \xrightarrow{k_t} \text{terminated polymer} \tag{5}$$

$$P^{\cdot} + AQH^{\cdot} \xrightarrow{k_t{}'} \text{terminated polymer (in cyclohexane)} \tag{6}$$

Formation of AQH_2 in iso-PrOH:

$$AQH^{\cdot} + (CH_3)_2CHOH \rightarrow AQH_2 + (CH_3)_2\dot{C}OH \tag{7}$$

$$AQH^{\cdot} + (CH_3)_2\dot{C}OH \rightarrow AQH_2 + (CH_3)_2CO \tag{8}$$

where SH denotes solvent molecule.

In the system with cyclohexane solvent, the excited AQ molecule abstracts a hydrogen atom from the solvent to form $AQH^{\cdot}$ and solvent radical ($S^{\cdot}$) as in eq. (2). The solvent radical initiates polymerization as in eq. (3). Termination occurs mostly by eq. (5). However, from the measurements of molecular weight and the UV spectrum, the termination by eq. (6) is a reaction which cannot be overlooked in the cyclohexane solvent system. On the other hand, if iso-PrOH exists in the system, the reactions of eqs. (7) and (8) proceed extensively, as noted by the spectrometric determination of AQH_2.

The alcohol radical as well as AQH_2 are formed following eq. (7) in the system with diluted alcohol. However, if the alcohol concentration exceeds a certain level, the consumption of alcohol radical by eq. (8) may become considerable, leading to a decrease in alcohol radical concentration. This is the major reason for the maximum polymer yield when the alcohol concentration is changed. For

a complete discussion of the phenomena, however, more detailed investigations are required.

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