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Some Factors Affecting the Photosensitized Polymerization of Methyl Methacrylate

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ABSTRACT

The effects of sensitizer, alcohol, and reaction temperature on the photosensitized polymerization of methyl methacrylate in cyclohexane-alcohol mixtures were investigated. A maximum conversion was indicated at a certain concentration of alcohol in the mixture for the systems sensitized with quinones such as anthraquinone, 2-tert-butylanthraquinone, and α-naphthoquinone, while it was not observed for the benzophenone-sensitized system. The concentration of alcohol corresponding to the maximum conversion increased in the order methanol < ethanol < n-propanol < n-butanol, and shifted to the lower side by raising the reaction temperature from 20 to 40°C. Based on the absorption and ESR spectra of irradiated solution of quinones, reasons for maximum conversion at an optimum concentration of alcohol are discussed.

INTRODUCTION

In a previous paper [1] the solvent effect on the photopolymerization of methyl methacrylate (MMA) sensitized with anthraquinone (AQ) was examined. A peak of monomer conversion was reported at a certain concentration of a hydrocarbon-alcohol combination as the polymerization solvent. This article deals with the kinds of sensitizer and solvent and the polymerization temperature affecting the monomer conversion of MMA with UV irradiation to provide the mechanism for initiating the photosensitized polymerization.

EXPERIMENTAL

AQ, 2-tert-butylanthraquinone (TBAQ), α-naphthoquinone (NQ), p-benzoquinone (BQ), and benzophenone (BP) were all of reagent grades and used without further purification. MMA was distilled under reduced pressure according to a usual method. Cyclohexane, methanol (MeOH), ethanol (EtOH), n-propanol (PrOH), iso-propanol (iso-PrOH), n-butanol (BuOH), iso-butanol, and tert-butanol were used as polymerization solvents which were purified by distillation.

A Pyrex glass tube containing 10 mL of solution, in which known concentrations of sensitizer and MMA were dissolved, was filled with nitrogen. Polymerization was then carried out by keeping the system at a given temperature for 60 min under irradiation. The irradiation was conducted in a Riko rotary photochemical reactor RH400-10W with a high-pressure mercury lamp (400 W). The polymerization products were poured into excess MeOH, filtered, washed with MeOH, and then dried under reduced pressure. The polymer yields were measured gravimetrically.

Absorption spectra were recorded with a Hitachi spectrophotometer 124 under nitrogen atmosphere.

A quartz glass tube (3 mm diameter) filled with TBAQ solution and degassed by the freeze-thaw technique was exposed at 77 K for 60 min to an Ushio super high-pressure mercury lamp 250D ($\lambda > 300$ nm). ESR measurements were made at 77 K with a Japan Electron Optics Laboratory JES-ME-X. Resonance spectra were observed with the X band and 100-kc field modulation.

RESULTS AND DISCUSSION

Figure 1 shows the results of photopolymerization with the cyclohexane-iso-PrOH mixture and employing sensitizers of various quinones and BP. All quinones with the exception of BQ recorded a peak in each conversion-iso-PrOH concentration curve, whereas no peak was observed in the curve for BP. These results suggest that such peaks in the curves of conversion-alcohol concentration are peculiar to quinones.

In Fig. 2 the effect of sensitizer concentration on the photopolymerization of the cyclohexane-iso-PrOH system employing TBAQ is shown. It is shown in the figure that the concentration of alcohol corresponding to each maximum conversion is not affected by the

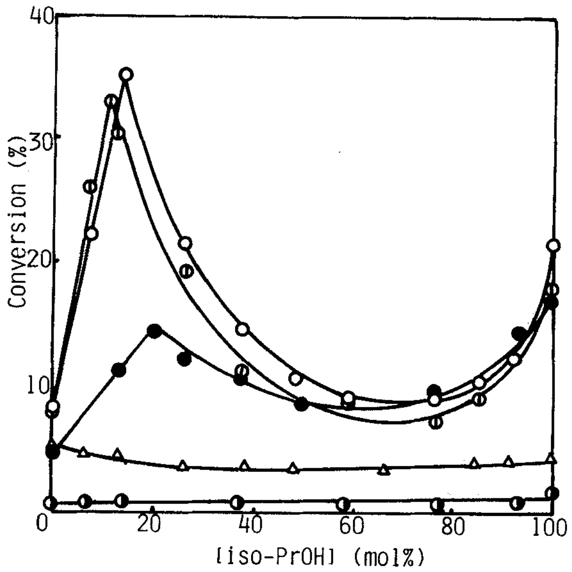


FIG. 1. Photopolymerization of MMA sensitized with various quinones and BP in cyclohexane-iso-PrOH at 30°C for 60 min. (○) AQ, (⦶) TBAQ, (●) NQ, (◑) BQ, (△) BP. [Sensitizer] = 3 × 10^{-4} mol/L, [MMA] = 0.94 mol/L.

concentration of TBAQ. However, the extent of conversion changes with the sensitizer concentration as shown in Fig. 3. As the TBAQ concentration rose, the conversion increased sharply. However, in the region higher than 0.7 × 10^{-3} mol/L TBAQ, the curve decreased in the cyclohexane-EtOH and cyclohexane-iso-PrOH solvent systems. This suggests that the radical capable of initiating polymerization tends to diminish in the high concentration region of TBAQ.

In Table 1 the alcohols are compared in terms of the concentration yielding the maximum conversion. The concentration corresponding to the maximum conversion for each alcohol increased in the order MeOH < EtOH < PrOH < BuOH. Thus the initiation reaction seems to be affected by the carbon number and the side chain of the alcohol, while the magnitude of conversion shows about the same level for each alcohol.

As described above, a maximum conversion was indicated for each cyclohexane-alcohol system. However, in the case of the system in which cyclohexane was replaced by another solvent, for example by MeOH, no maximum conversion appeared as shown in Fig. 4. The solution of AQ in MeOH-iso-PrOH mixture was irradiated at 30°C for 2 min under nitrogen atmosphere, and the absorption spectrum was recorded as in Fig. 4. The absorptions [2, 3] of AQ and anthrahydroquinone (AQH_2) are known to appear at 322 and 383 nm in the spectrum,

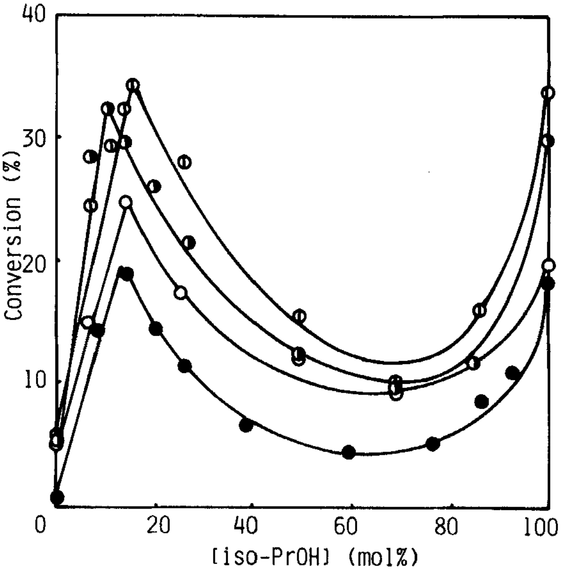


FIG. 2. TBAQ-sensitized photopolymerization of MMA in cyclohexane-iso-PrOH at 30°C for 60 min. [TBAQ] (mol/L): (○) 0.1 × 10^{-3}, (⦶) 0.5 × 10^{-3}, (◑) 1.0 × 10^{-3}, (●) 3.0 × 10^{-3}. [MMA] = 0.94 mol/L.

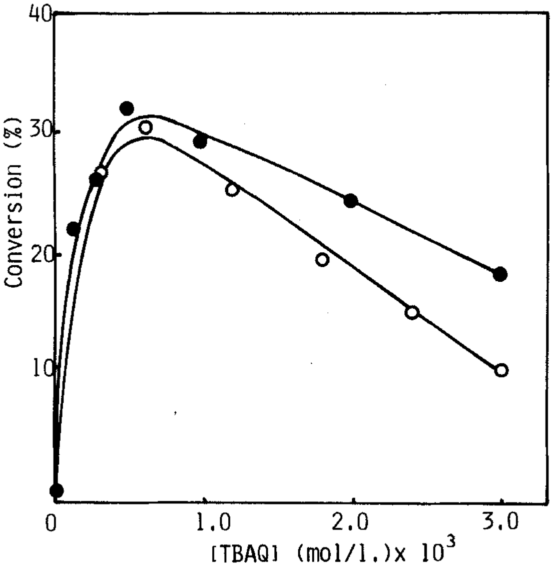


FIG. 3. Relationship between conversion and TBAQ concentration in (○) cyclohexane-EtOH and (●) cyclohexane-iso-PrOH systems. Irradiation was carried out at 30°C for 60 min. [Alcohol] = 13.5 mol%, [MMA] = 0.94 mol/L.

TABLE 1. Anthraquinone-Sensitized Photopolymerization of Methyl Methacrylate in Cyclohexane-Alcohol Solvents[a]

Alcohol	Alcohol content at maximum conversion (mol%)	Maximum conversion (%)
Methanol	4.1	34.0
Ethanol	7.4	40.1
n-Propanol	10.5	36.5
iso-Propanol	13.5	35.8
n-Butanol	17.5	38.2
iso-Butanol	17.4	31.5
sec-Butanol	17.5	30.2
tert-Butanol	33.4	27.0

[a] Photopolymerization was carried out at 30°C for 60 min. Concentrations of AQ and MMA were 3×10^{-4} mol/L and 0.94 mol/L, respectively.

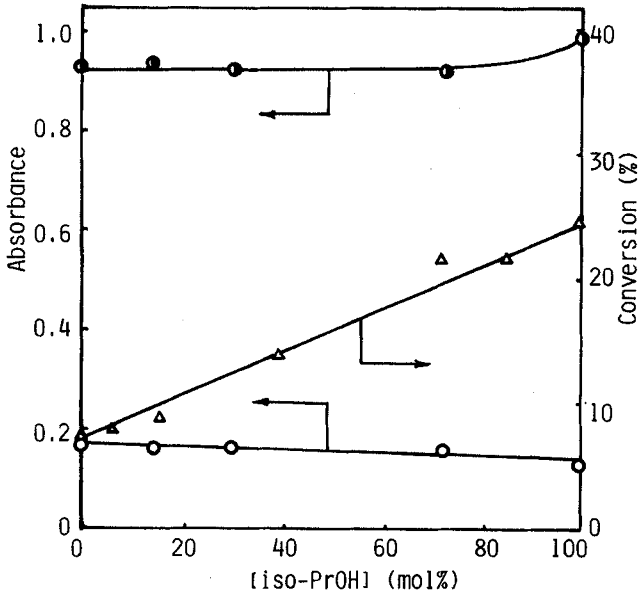


FIG. 4. Changes of absorbances at (○) 322 nm (AQ) and (◑) 383 nm (AQH_2) in MeOH-iso-PrOH system with irradiation at 30°C for 2 min under nitrogen atmosphere. AQ-sensitized photopolymerization was carried out at 30°C for 60 min. [AQ] = 3×10^{-4} mol/L, [MMA] = 0.94 mol/L.

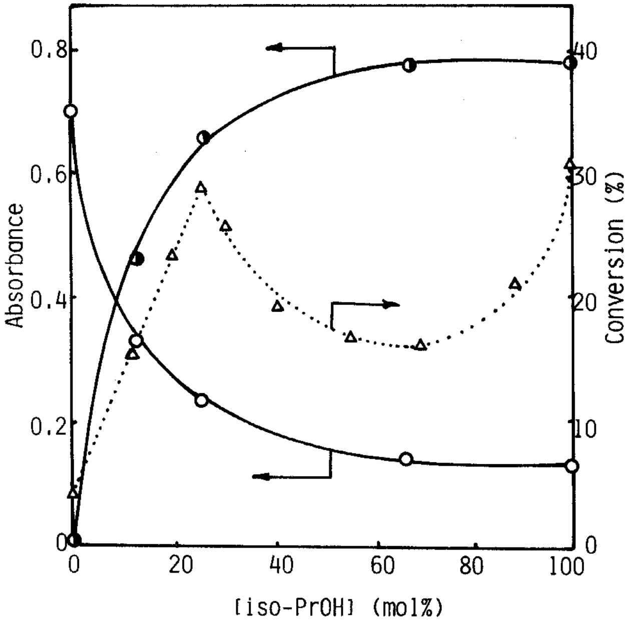


FIG. 5. Changes of absorbances at (○) 322 nm (AQ) and (◑) 383 nm (AQH_2) in cyclohexane-iso-PrOH system with irradiation at 20° C for 2 min under nitrogen atmosphere. AQ-sensitized photopolymerization was carried out at 20° C for 60 min. [AQ] = 3×10^{-4} mol/L, [MMA] = 0.94 mol/L.

respectively. It is noted that the other compound, AQH_2, is produced in the solution instead of the disappearance of AQ by the irradiation. This change seemed indifferent to the ratio of the two alcohols in the solution. Therefore the feasibilities of abstracting hydrogen atom by excited AQ from MeOH and iso-PrOH are estimated as being almost at the same level. On the other hand, conversion was found to increase linearly with the iso-PrOH content in the mixture. Consequently, it is believed that the ability of alcohol radicals to initiate polymerization is less active for MeOH than for iso-PrOH.

The same experiment was performed for the system using a cyclohexane-iso-PrOH mixture, shown in Fig. 5. As the concentration of alcohol increased, the absorbance of AQ decreased one-sidedly. On the other hand, the absorbance of AQH_2 was observed to increase with the concentration of alcohol. The two curves seem to level off roughly at the concentration of alcohol yielding the maximum conversion of polymerization.

The reactions recorded in Fig. 6 were performed at 30° C. In the

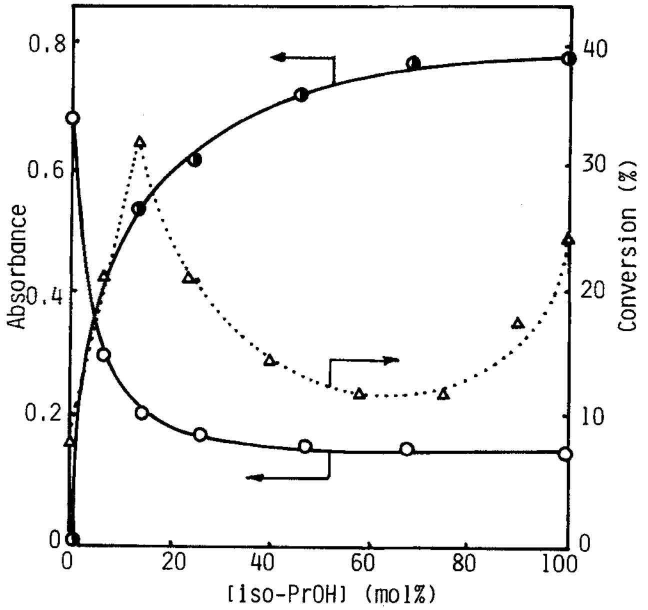


FIG. 6. Changes of absorbances at (○) 322 nm (AQ) and (◑) 383 nm (AQH_2) in cyclohexane-iso-PrOH system with irradiation at 30°C for 2 min under nitrogen atmosphere. AQ-sensitized photopolymerization was carried out at 30°C for 60 min. $[AQ] = 3 \times 10^{-4}$ mol/L, $[MMA] = 0.94$ mol/L.

other experiment the alcohol concentration yielding the maximum conversion had been observed to shift to the lower side by elevating the reaction temperature, which is clear by comparing the dotted curves of Figs. 5 and 6. As the peak moved to the left side, the shoulders of two curves of AQ and AQH_2 were also observed to transfer to the same side, indicating a close relationship among AQ, AQH_2, and the maximum conversion. In the system at 40°C, larger shifts of the maximum conversion and the shoulders of two curves of AQ and AQH_2 to a lower concentration were observed.

The ESR spectra of irradiated TBAQ in the cyclohexane-iso-PrOH mixture were measured, and the intensity is shown in Fig. 7. A maximum value was indicated at a certain concentration of alcohol, which seems to have good correspondence with that yielding the maximum conversion of polymerization. That is, it is clear that the concentration of radical in the system formed due to irradiation shows a maximum at an optimum concentration of alcohol.

As the result of above experiments, it is supposed that the phenomenon yielding maximum conversion at a certain alcohol concentration in the photopolymerization system using a sensitizer in a

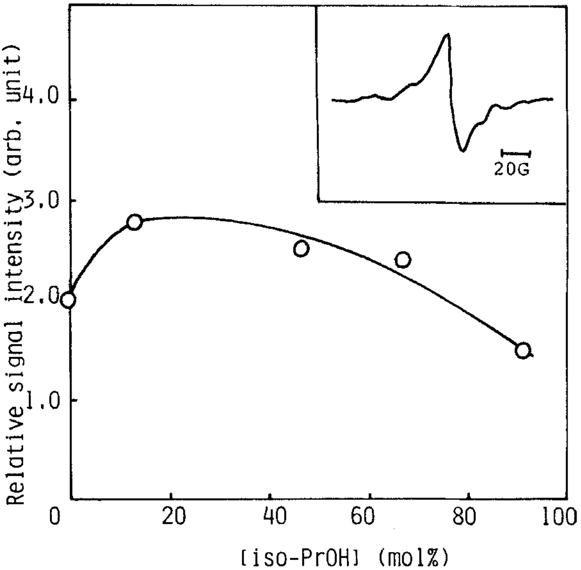
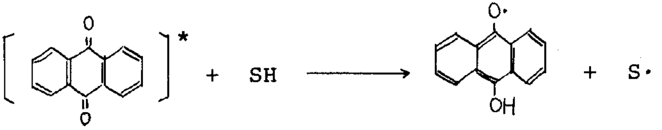
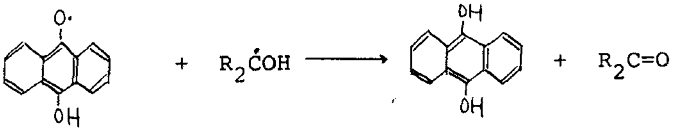


FIG. 7. Relationship between ESR signal intensity and iso-PrOH content in cyclohexane-iso-PrOH system. Irradiation was carried out at 77 K for 60 min. [TBAQ] = 3 × 10^{-3} mol/L.

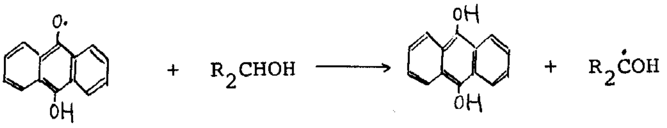
hydrocarbon-alcohol mixture is peculiar to quinones. Quinones have two conjugated carbonyl groups which are capable of abstracting a hydrogen atom at the excited state from a solvent to yield semihydroquinone radicals [2, 4, 5]. The radicals are supposed to abstract hydrogen atom further according to Eqs. (2) and (3) to produce AQH_2 in the presence of alcohol solvents. On the other hand, Eqs. (2) and (3) may not be worth consideration in the system of cyclohexane alone since no formation of AQH_2 is observed for irradiated AQ in cyclohexane as shown in Figs. 5 and 6.



(1)



(2)



(3)

where SH and R_2CHOH denote solvent and iso-PrOH, respectively.

The alcohol radical formed by Eq. (1) is consumed by Eq. (2), while the special formation of alcohol radicals can be performed by Eq. (3). These two reactions, in which one works to increase and the other to decrease the yield of conversion, may be closely related to the concentration of alcohol, which is the major cause for maximum conversion at a certain concentration of alcohol.

On the other hand, the excited BP [6, 7] may abstract a hydrogen atom from alcohol as well as the excited AQ, resulting in the formation of the ketyl radical of BP. However, the radical is unable to abstract a hydrogen atom according to Eq. (3). This may be the essential reason for the maximum peak not appearing in the conversion curve due to BP sensitizer.

Reactivities of alcohols in Eqs. (2) and (3) are sure to differ according to the kind of alcohol. Therefore, each concentration of alcohol yielding maximum conversion may differ due to the different reactivities of alcohols. If the reaction temperature is increased, the formation of alcohol radicals may be increased by Eq. (1), which corresponds to the use of a higher concentration of alcohol. This may result in a lowering of the alcohol concentration to yield the maximum conversion to some extent.

Thus the reason for maximum conversion at an optimum concentration of alcohol can be explained by the reactions of Eqs. (1) to (3).

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