

STUDY OF PHOTSENSITIZED INITIATION SYSTEMS CONTAINING OXYGEN

V. THE EFFECT OF MERCAPTAN ADDITIVES

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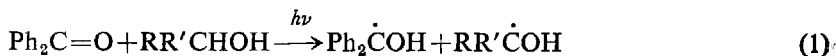
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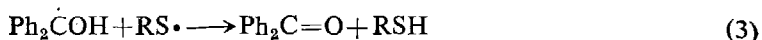
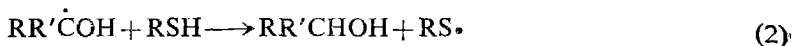
ABSTRACT

A kinetic study on the photopolymerization of methyl methacrylate (MMA) with benzophenone (BP)/triethylamine (TEA)/mercaptan systems as initiator has been carried out in the presence of oxygen. It was found that both aliphatic and aromatic thiols promote the photooxidation process, leading to obvious decrease in induction period of photopolymerization. The rate-acceleration of aromatic thiols is more effective than that of aliphatic ones, such as p-toluene thiol used as additive increases the relative quantum yield ϕ_{O_2}/ϕ_{N_2} to 1.8.

In most photopolymerizations, the retarding effect of oxygen is an important problem, which prevents the application of light-curing technique, especially in the field of UV curing coating and ink etc. In recent years, some initiators, for example benzoin ethers, having a very short triplet-state lifetime and being insensitive to oxygen have been developed, nevertheless the termination of free radical by oxygen remains in effect. Authors have previously shown that benzophenone/triethylamine initiation system was used for transforming oxygen in the system to active hydroperoxides under given condition^[1]. Both the polymerization rate and the quantum yield are increased obviously as a result of forming new radical by subsequent photosensitized decomposition of the peroxides. This paper deals with the transformation of oxygen in the system to another kind of photo-active substance via photochemical way to promote the polymerization.

Mercaptan is a kind of chain transfer reagent usually used in polymerization. The hydrogen transfer reaction between thiol and free radicals and oxidation of thiol itself takes place easily. In the case of photoreduction of benzophenone (BP), through hydrogen transfer reaction and radical disproportionation, such reactions are inhibited by mercaptan which plays a "protecting role" during irradiation^[2].





In the presence of oxygen, mercaptan undergoes sensitized oxidation to yield disulfide^[3]. It has been reported that disulfides were used to initiate photopolymerization of vinyl monomer^[4].

Based on the above results and author's previous work, the present work will also use the BP/TEA/oxygen as initiation system, by addition of different mercaptan to eliminate inhibiting effect of oxygen in photopolymerization and to raise the reaction rate and efficiency through production of disulfides.

EXPERIMENTAL

Reactants

n-Pentyl thiol (PSH), n-dodecyl thiol (LSH) and benzyl thiol (BSH) were purified by distillation under vacuum. p-Toluene thiol (TSH) was recrystallized twice, didodecyl disulfide and p-toluene disulfide were synthesized by oxidation method from LSH and TSH respectively^[6]. The former is a waxy substance, the latter has m.p. 45–45.5°C.

The rate of oxygen uptake was evaluated by measuring the change in volume with micro gas burette. The polymerization rate was determined by dilatometer method at 30°C. The conversions were kept below 10%, the experimental data were treated with the least square method, for details refers to the previous paper^[1].

RESULTS AND DISCUSSION

The effects and reaction mechanism of addition of various mercaptans to methyl methacrylate (MMA) polymerization system initiated by BP/TEA are described as follows:

1. *The effects of adding mercaptans*

The effects of various mercaptans added to the system containing oxygen are shown in Table 1. It is shown that the accelerating effects of aromatic mercaptans on the polymerization are significantly stronger than that of aliphatic ones, however both are able to shorten the induction period of polymerization resulting from the enhancement of photo-oxidation rate in this system.

2. *The effect of concentration of mercaptan*

Influences of the concentration of mercaptans on the reaction are shown in Fig. 1 and Fig. 2. The effect varies obviously with different mercaptans. In the case of aliphatic thiols the rate raises progressively with increasing concentration, while adding aromatic thiol a maximum appeared, after that the rate decreases sharply. In respect of shortening induction periods, aliphatic mercaptans are more efficient.

Table 1 The effect of adding mercaptan on photopolymerization of MMA initiated by BP/TEA

Mercaptan	Polymerization rate ($R_p \times 10^5 \text{M} \cdot \text{S}^{-1}$)		Induction periods τ (min)
	in oxygen	in nitrogen	
non	7.25	5.45	29
PSH	7.65	5.70	21
LSH	7.76	5.57	17
BSH	9.00	5.21	23
TSH	9.87	5.00	22

[BP] $5 \times 10^{-3} \text{M}$; [TEA] $2 \times 10^{-1} \text{M}$; [RSH] $1 \times 10^{-2} \text{M}$; [MMA] 2.8M
Benzene solution 30°C

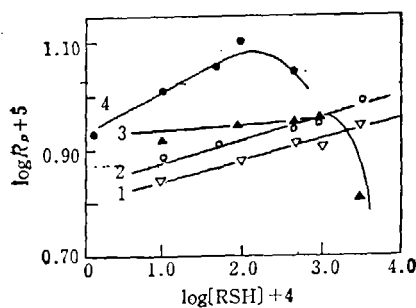


Fig. 1 The relationship between polymerization rates and conc. of mercaptans (condition as Table 1, in oxygen)

1. $\text{C}_5\text{H}_{11}\text{SH}$; 2. $\text{C}_{12}\text{H}_{25}\text{SH}$;
3. $\text{C}_6\text{H}_5\text{SH}$; 4. $\text{CH}_3\text{C}_6\text{H}_4\text{SH}$.

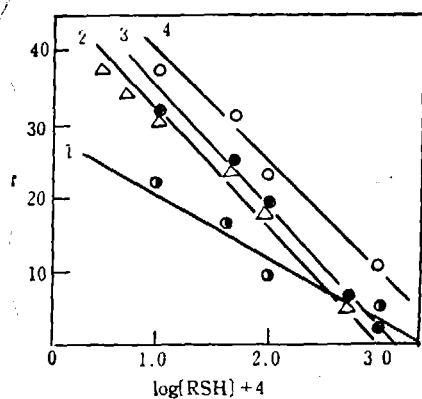


Fig. 2 The effect of conc. of mercaptans on the induction periods (condition as Table 1, in oxygen)

1. $\text{CH}_3\text{C}_6\text{H}_4\text{SH}$; 2. $\text{C}_5\text{H}_{11}\text{SH}$;
3. $\text{C}_{12}\text{H}_{25}\text{SH}$; 4. $\text{C}_6\text{H}_5\text{SH}$.

The influence of different concentration of amine on polymerization is shown in Fig. 3 and Fig. 4. In the presence of mercaptan, the relationship between polymerization rate and concentration of amine is exponential, especially, as the concentration of amine near that of mercaptan, the polymerization rate becomes very slow. The same relationship between the concentration of amine and the induction periods of polymerization has been revealed.

The results mentioned above indicate that mercaptan could not take the place of amine in the reaction system.

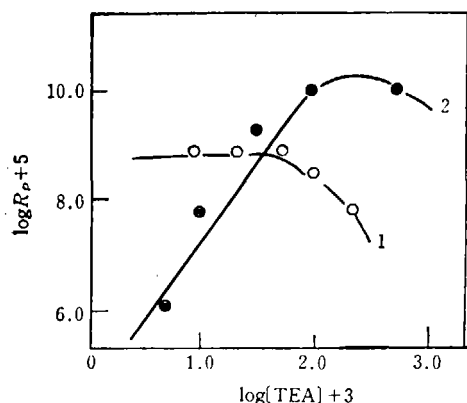


Fig. 3 The relationship between the polymerization rate and conc. of amine
1. $C_6H_{11}SH$; 2. $CH_3C_6H_4SH$.
(the same condition as above)

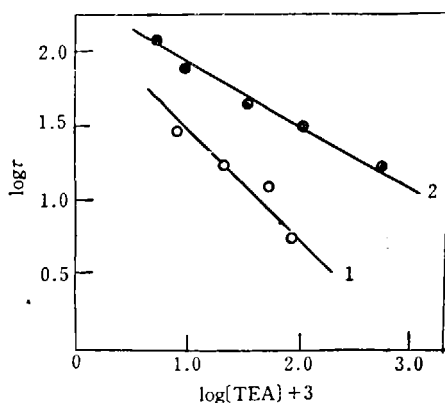


Fig. 4 Effect of conc. of amine on induction period
1. $C_6H_{11}SH$; 2. $CH_3C_6H_4SH$.
(the same condition as above)

3. Reaction mechanism

In the case of presence of oxygen the role of mercaptans in BP/TEA/MMA system is discussed mainly from the following two aspects: shortening induction period and increasing polymerization rate.

(1) Effect of shortening induction period

From the results obtained, it is shown that whether aliphatic or aromatic thiols both diminish induction period of polymerization effectively, as a result of enhancing the rate of oxygen consumption in BP/TEA/MMA system.

The rates of oxygen absorption in various systems are listed in Table 2.

Table 2 The rate of oxygen absorption in different systems (under oxygen)

Reaction system	Rate of oxygen uptake $\times 10^3$ ($M \cdot \min^{-1}$)	
	photoreaction	dark reaction
BP/TEA	0.796×10^{-4}	0
BP/LSH	0	0
BP/TEA/LSH	2.198×10^{-4}	0
BP/TEA/BSH	1.572×10^{-4}	0

[BP] $5 \times 10^{-3}M$; [TEA] $2 \times 10^{-1}M$; [RSH] $1 \times 10^{-3}M$; [MMA] $2.8M$

Either aliphatic or aromatic thiol system are unable to absorb oxygen rapidly in the dark, whereas they possess relative high ability to absorb oxygen under irradiation, except BP/RSH system. The BP/TEA/RSH systems are more effective than BP/TEA system without RSH, in which the dodecyl thiol (LSH) is better than phenyl thiol (BSH). These results may evidence

that oxygen consuming process proceeds mainly via photochemical reaction.

(2) The accelerating effect on polymerization

As mentioned above, various mercaptans display similar efficiencies on shortening induction period, whereas the aliphatic thiols are far less efficient than the aromatic thiols on the accelerating rates of polymerization. These differences in the photopolymerization may be due to the following two reasons. 1) The photoreduction of BP by various mercaptans are different markedly. For example the reaction rate of adding phenyl thiol has an order of magnitude larger than that of aliphatic thiols. 2) The products formed by oxidation of mercaptan, have different reactivity and ability toward initiation under the experimental condition. It is reasonable to consider that after induction period the following polymerization was carried out in the absence of O_2 . Owing to oxygen in the system had been consumed completely within this period, the influence of adding mercaptans on the photopolymerization rate to BP/TEA system should be studied under nitrogen, the results are given in Table 1. The addition of aliphatic thiols are less effective on the polymerization rate, while aromatic thiols has a negative effect.

From the results obtained it may be considered that mercaptans themselves do not obviously affect the photopolymerization of MMA initiated by BP/TEA. So, it is necessary to further clarify the action of oxidation products of mercaptans in polymerization process. Cohen reported^[3] that during photoreduction of BP in the presence of O_2 , the addition of trimethyl benzyl thiol to the system produces the corresponding disulfide, which increases with increasing consumption of mercaptan through the oxidation by peroxide formed in the system. It is reasonable to consider that in the BP/TEA system containing oxygen, mercaptans may be readily oxidized by the peroxide formed to give disulfide, which undergoes photolysis to produce new free radicals. It leads to an increase in the amount of initiating free radical and the polymerization rate.



In order to learn the initiation ability of disulfides. The corresponding RSSR were used for polymerization. The results as shown in Fig. 5 indicate that the effect of aromatic disulfides on the polymerization of MMA is evident, but that of aliphatic ones was ineffective. These are consistent with the results obtained above by addition of mercaptans. These observation may be ascribed to the fact that in comparison with aliphatic, the aromatic disulfides undergoes the radical photogeneration readily due to the dissociation energy of S—S bond for aromatic disulfides are far less than that for aliphatic ones^[7]. So that rate-accelerating effect of aromatic disulfides are more effective.

(3) The quantum yield of the reaction

On the basis of the above, the efficiency of photopolymerization of MMA initiated with BP/TEA system containing different mercaptans are evaluated by relative quantum yield (ϕ_{O_2}/ϕ_{N_2}).

The results are listed in Table 3. The addition of mercaptans could cause further

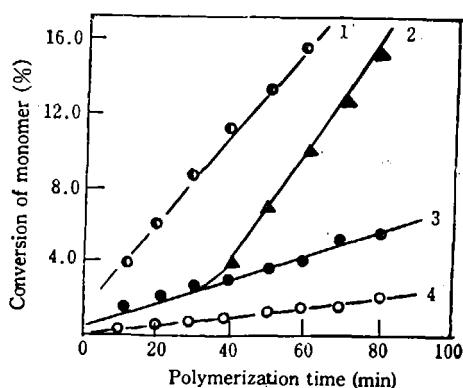


Fig. 5 The initiating effect of disulfides on photopolymerization

1. $(\text{CH}_3\text{C}_6\text{H}_4\text{S})_2$; 2. $(\text{C}_6\text{H}_5\text{S})_2$;
 3. $(\text{C}_4\text{H}_9\text{S})_2$; 4. $(\text{C}_{11}\text{H}_{25}\text{S})_2$.

enhancing the efficiency of the BP/TEA initiation system containing oxygen. The toluene thiol (TSH) is the best one and its relative quantum yield is 1.81.

Table 3 The relative quantum yield of photopolymerization with different initiation systems

Initiating system	Atmosphere	$\phi_{\text{O}_2}/\phi_{\text{N}_2}^*$
BP/TEA	N_2	1
BP/TEA	O_2	1.33
BP/TEA/PSH	O_2	1.40
BP/TEA/LSH	O_2	1.42
BP/TEA/BSH	O_2	1.65
BP/TEA/TSH	O_2	1.81

[BP] $5 \times 10^{-3}M$; [TEA] $2 \times 10^{-1}M$; [RSH] $1 \times 10^{-2}M$; [MMA] $2.8M$; Benzene solution

* ϕ : The number of monomer molecules undergoing polymerization by one photon absorbed (Here the light intensity and concentration of BP are constant). So, $\phi_{\text{O}_2}/\phi_{\text{N}_2} = R_{p_{\text{O}_2}}/R_{p_{\text{N}_2}}$.

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