

# Photopolymerization of Methyl Methacrylate Using Benzoin Isopropyl Ether as Photoinitiator: Effect of Thiophenol Compounds

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## SYNOPSIS

Effects of a series of thiophenols  $R\text{—ArSH}$  with substituting groups  $R$  in the *para*-position and 2-mercaptobenzoic acid on the kinetics of polymerization of methyl methacrylate (MMA) photoinitiated by benzoin isopropyl ether (BIPE) were investigated using an autotrecording dilatometer. Thiophenols were found to have a dual effect on polymerization: reducing induction time and accelerating rate of polymerization. A mechanism was proposed suggesting that this increased rate of polymerization and reduced induction time with addition of a thiophenol is due to the fact that, instead of consuming radicals, the dissolved oxygen in the MMA/BIPE system can be converted into active radicals through effective photooxidation of the thiophenol. Although the maximum increase in rate of polymerization is of a minor difference between various thiophenol compounds, reduction in induction time is strongly dependent on the nature of substituting groups in the following order:  $\text{—CH}_3 > \text{—CH}(\text{CH}_3)_2 > \text{—OCH}_3$  or  $\text{—Cl} > \text{—H}$ . 2-Mercaptobenzoic acid, on the other hand, increases induction time and decreases rate of polymerization. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Recent years have witnessed a steady growth in the use of photocurable polymer materials in the areas of coatings, inks, adhesives, photoresists, etc.<sup>1–3</sup> These industrial interests have stimulated research on fundamental aspects of photopolymerization, including reaction kinetics<sup>4–7</sup> and new types of photoinitiators.<sup>7–10</sup> One disadvantage of the use of photopolymerization, however, is the susceptibility of many materials to polymerization inhibition due to oxygen, which may not only affect properties of the cured polymers, but also make some applications impossible when fast reactions are required. A survey of the literature has revealed that there has been a lack of research on this important problem. It is the aim of this paper to present attempts at reducing induction time and accelerating the rate of photo-

polymerization of the methyl methacrylate/benzoin isopropyl ether (MMA/BIPE) system using some thiophenol compounds as sensitizers.

## EXPERIMENTAL

### Materials

The removal of inhibitors from MMA was carried out by passing the inhibited MMA (from Aldrich) over a column packed with alternative layers of basic and acidic aluminum oxide powder. BIPE (from Pfaltz & Bauer) was crystallized twice from petroleum ether before use. Table I gathers properties of interest of thiophenol compounds and 2-mercaptobenzoic acid, which were used as sensitizers.

### Methods

Conversion of MMA into poly(methyl methacrylate) (PMMA) was determined using an autotrecording dilatometer, which is similar to that reported

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**Table I** Properties of Sensitizers<sup>a</sup>

Sensitizer (abbreviation)	mp (°C)	bp (°C)
Thiophenol (ArSH)	-15	169
4-Methylthiophenol (MeArSH)	43	195
4-Chlorothiophenol (ClArSH)	50	206
4-Methoxythiophenol (MeOArSH)	—	102/13 mmHg
4-Isopropylthiophenol <sup>b</sup> (iPArSH)	—	210
2-Mercaptobenzoic acid (MBA)	167	—

<sup>a</sup> These sensitizers were purchased from the Aldrich Co., and data herein are quoted from its catalog.

<sup>b</sup> This product was synthesized and its boiling point measured in our laboratory.

in Ref. 5. Figure 1 is a schematic presentation of our apparatus. A 2.0 cm<sup>3</sup> polyethylene bag containing the monomer (MMA) is immersed in a 20 cm<sup>3</sup> quartz tube filled with water. The bottom part of this quartz tube is flat, and its upper part, circular. Placed on the top of the quartz tube is a cork, which is connected to a 5 cm<sup>3</sup> syringe through a needle. The quartz tube and part of the syringe are immersed in a larger quartz tube filled with circulated water of a constant temperature (20.0 ± 0.1°C). A high-pressure 125 W quartz mercury-vapor lamp is installed 36.5 cm away from the polyethylene sample bag, generating a maximum wavelength of 300 nm. A metal plate is inserted between the light source and the sample bag as a light switch. A volume contraction of the sample bag due to polymerization of MMA results in a drop of water level inside the syringe, causing a fall of the magnetic rod downward. The relative movement between the magnetic rod and a low-voltage detecting coil (LVDC) produces a signal, which is amplified through an amplifier and then displayed continuously on a digital autorecorder in terms of voltage. A calibration curve is established between the voltage and the drop distance ( $h$ ) for determination of conversion. Let us denote  $\Delta V_\infty$  and  $H$  as the volume contraction of the polymerizing system and drop distance of the syringe when all monomer is converted into polymer, respectively, and  $\Delta V$  and  $h$  are volume contraction and drop distance at time  $t$ , respectively. Then, at low conversions (0–10%), conversion  $p\%$  at time  $t$  can be expressed by the equation

$$p\% = \frac{\Delta V}{\Delta V_\infty} \% = \frac{h}{H} \% \quad (1)$$

The total drop distance ( $H$ ) in eq. (1) can be determined by the following equation:

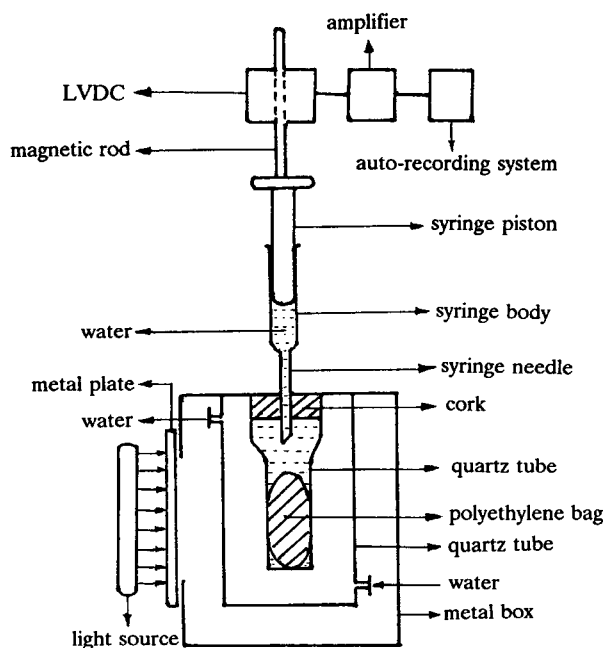
$$H = \frac{\Delta V_\infty}{\pi r^2} = \frac{V_m - V_p}{\pi r^2} \quad (2)$$

where  $r$  is the inner radius of the syringe,  $V_m$  denotes the total volume of the added monomer, and  $V_p$  represents the volume when all monomer is converted into polymer.  $V_m$  and  $V_p$  can be calculated from the density of the monomer  $d_m$  and that of the polymer  $d_p$  using eqs. (3) and (4), respectively:

$$V_m = \frac{W}{d_m} \quad (3)$$

$$V_p = \frac{W}{d_p} \quad (4)$$

where  $W$  is the total weight of the monomer before polymerization.



**Figure 1** Scheme of the autorecording dilatometer.

## RESULTS AND DISCUSSION

### Polymerization of the MMA/BIPE System

Polymerization of the MMA/BIPE system at low conversion displays a double feature of interest as indicated in Figure 2: First, the conversion of MMA into PMMA is a linear function of reaction time; and second, there exists an inhibition of polymerization at the initial stage of the reaction. The latter is a strong function of the concentration of BIPE, i.e., the higher the concentration of BIPE, the shorter the inhibition time. We characterize this induction period by introducing an induction time ( $t_{id}$ ).<sup>†</sup> Induction times and rates of polymerization ( $R_p$ ) were determined for a range of BIPE concentrations.  $R_p$  is defined as

$$R_p = - \frac{d[M]}{dt} = [M]_0 \frac{dp}{dt}$$

$$= [M]_0 \times \text{slope of the conversion curve} \quad (5)$$

Figure 3 shows rate of polymerization against the square root of BIPE concentration. At the low BIPE concentration region,  $R_p$  increases linearly with the square root of BIPE concentration, conforming to classic radical polymerization theory<sup>11</sup> and findings in the literature.<sup>6</sup> It is noted, however, that beyond a certain BIPE concentration (0.0185 M in our case)  $R_p$  starts decreasing. Explanations for this phenomenon can be found in the literature.<sup>‡</sup>

Figure 4 indicates that induction time decreases sharply with increasing concentration of BIPE and then levels off to a plateau at about 3.6 min. If we believe that induction time is caused by the presence of oxygen that deactivates free radicals,<sup>13,14</sup> then we may say that induction time is actually the time necessary for the generated free radicals to consume

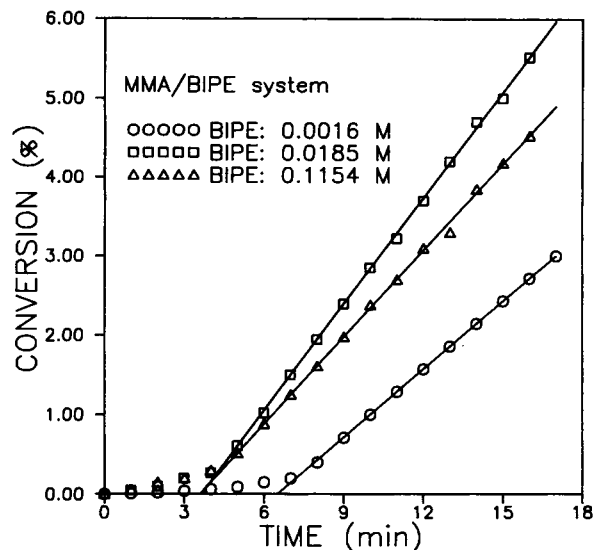


Figure 2 Conversion vs. time at different concentrations of BIPE.

oxygen present in the system. Three elementary reaction steps should be taken into account in order to interpret the observed behavior of  $t_{id}$  as a function of the concentration of BIPE: photoinitiation, deactivation of free radicals by oxygen, and primary propagation. It should be noted that rate of photoinitiation depends primarily upon the number of photons generated from the light source. Existence of induction time indicates that the second step is much faster than the other two steps; consequently, it is the first step that actually determines  $t_{id}$ . As the concentration of BIPE starts increasing from zero, the concentration of the generated radicals from BIPE increases as long as photons emitted from the light source are in excess, therefore decreasing  $t_{id}$ . When it reaches a certain value at which all emitted photons are absorbed by BIPE, the induction time is the shortest. Further increase in BIPE will not accelerate rate of initiation because of insufficiency of photons. As a result,  $t_{id}$  can no longer be reduced. We can conclude then that a minimum induction time is characteristic of a particular photoinitiating system under a given light intensity. Changing the nature of monomer and photoinitiator or varying light intensity should affect induction time. The maximum rate of  $R_p$  for the MMA/BIPE system corresponds to an induction time of 3.65 min under our reaction conditions. With the belief that the presence of oxygen is responsible for inhibited polymerization, we may then expect that polymerization under an inert gas such as nitrogen will reduce induction time. Indeed, Figure 5

<sup>†</sup> The induction time ( $t_{id}$ ) is defined as the intersection between the straight line of the conversion curve and the X-axis. This implies that the X-axis is chosen as the tangential line of the initial part of the conversion curve, which seems more reasonable in our particular case.

<sup>‡</sup> Hutchison and Ledwith<sup>6</sup> made the same observation for the MMA/benzoin methyl ether (BME) system: that  $R_p$  starts decreasing for BME concentrations above 0.020 M, a value very close to ours (0.0185 M). They attributed this decreased  $R_p$  at high BME concentrations to a nonuniformity of the distribution of initiating radicals, since more radicals are formed in a relatively narrow region nearest to the light source. Because free-radical polymerization rate depends upon the rate of initiation, this non-uniformity tends to decrease the overall rate of polymerization. In fact, we can say that this nonuniform distribution of free radicals is a result of the gradient of light intensity across the polymerizing system, because rate of initiation is directly related to light intensity.<sup>11,12</sup>

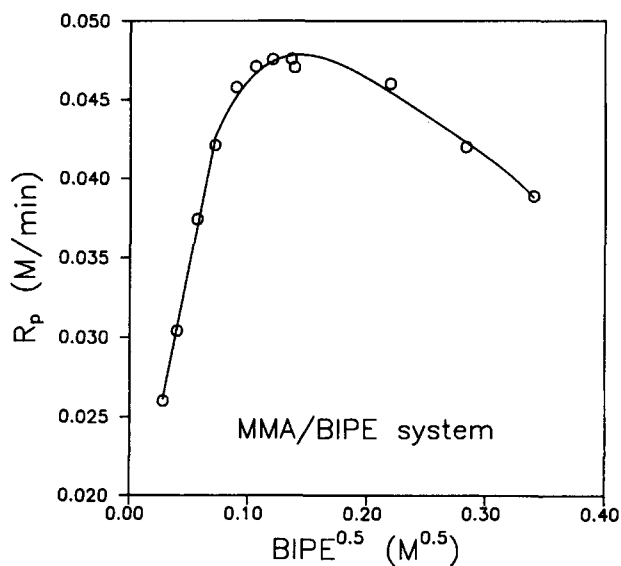


Figure 3  $R_p$  vs. square root of the concentration of BIPE.

shows that induction time drops from 3.65 min under air to 1.8 min under nitrogen. However, there are cases where the polymerization process has to be exposed to air or oxygen and much shorter induction times than what we observed are required. Under these conditions, this MMA/BIPE system will no longer be applicable.

**Effects of MeArSH on Polymerization**

We first used MeArSH as a sensitizer in an attempt to examine its effects on rate of polymerization and induction time. To do so, we fixed the BIPE con-

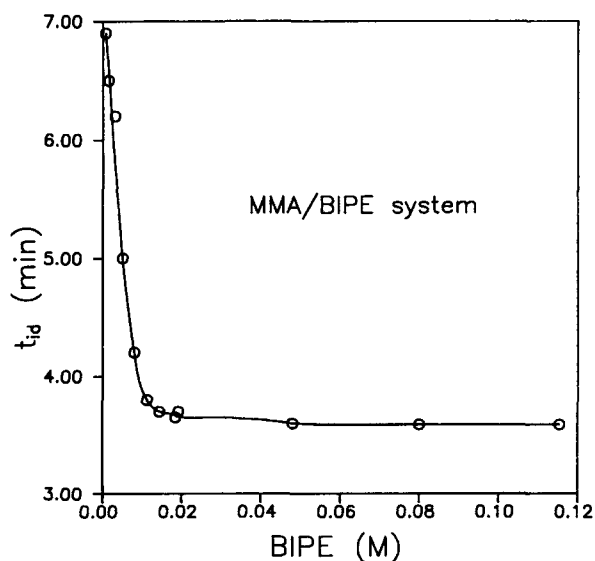


Figure 4  $t_{id}$  vs. concentration of BIPE.

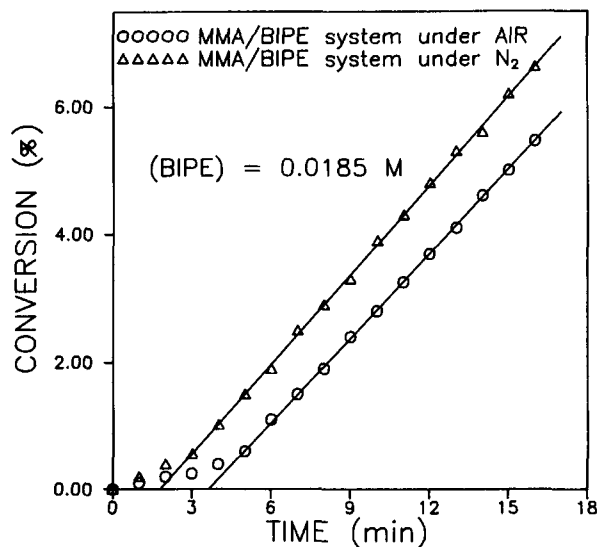


Figure 5 Conversion vs. time under air and nitrogen.

centration at the value that corresponds to the maximum rate of polymerization (0.0185 M) and varied the concentration of the thiophenol. It should be noted first that in comparison to BIPE this thiophenol compound itself is not an efficient photoinitiator, as we can see from Figure 6, but the corresponding induction time is much shorter (6.4 min for BIPE and 3.2 min for MeArSH). Addition of MeArSH (0.00242 M) into the MMA/BIPE (0.0185 M) system reduces induction time substantially under an air environment from 3.65 to 1.3 min (cf. Fig. 7). Furthermore, it increases the rate of polymerization from 0.0476 to 0.0541 M/min.

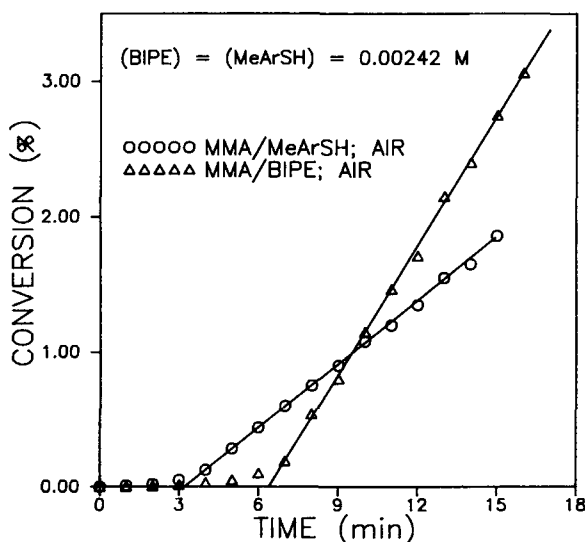
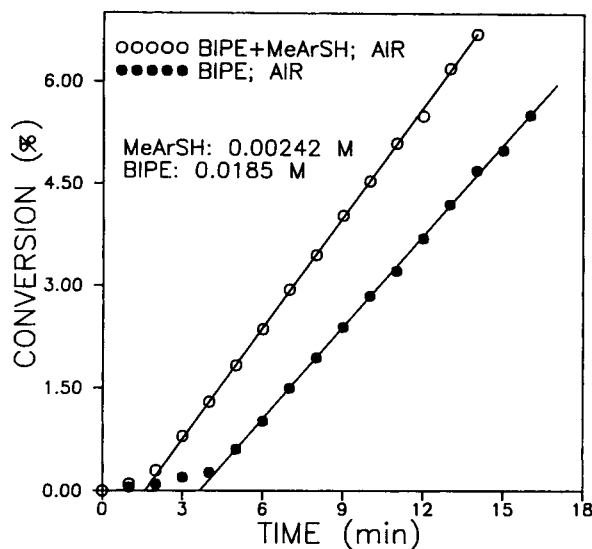


Figure 6 Activity comparison between BIPE and MeArSH.

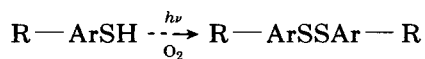


**Figure 7** Effect of MeArSH on polymerization of MMA/BIPE system.

Figure 8 shows the MeArSH concentration dependence of rate of polymerization and induction time of the MMA/BIPE system. It is noteworthy that the rate of polymerization decreases with increasing MeArSH concentration in its low concentration region. At high concentrations, however,  $R_p$  decreases. The decreased  $R_p$  in this high concentration region greatly resembles the behavior we have already seen in Figure 2 for the MMA/BIPE system and may be explained by the same arguments mentioned there. On the other hand, induction time decreases with increasing concentration of thiophenol, reaching a plateau at about 0.9 min. This plateau is much lower than that for the MMA/BIPE system, suggesting that MeArSH is a very good "anti-oxygen agent."

#### Mechanism of Reduction of $t_{id}$ and Acceleration of $R_p$ by MeArSH

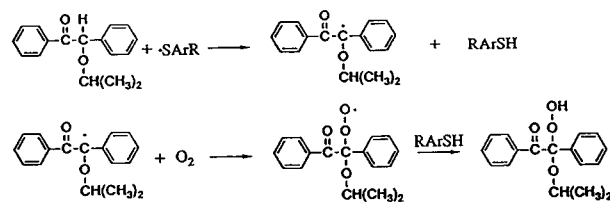
A thiophenol is susceptible to photooxidation<sup>15</sup> in the presence of oxygen:



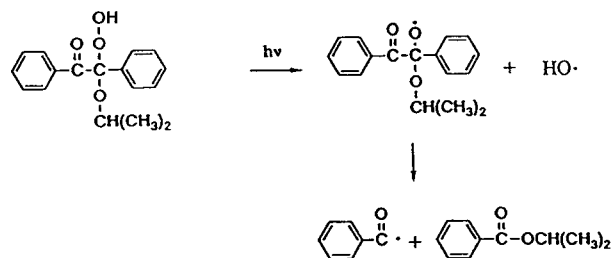
The generated disulfide under irradiation subsequently decomposes into sulfur radicals  $\text{R}-\text{ArS}^{\bullet}$ , which are capable of initiating polymerization. In addition to  $\text{RArS}^{\bullet}$ ,  $\text{R}-\text{ArSH}$  under irradiation can directly produce radicals  $\text{RS}^{\bullet}$  and  $\text{H}^{\bullet}$ , because the bond-association energy of S—H in a thiophenol is very low due to  $p$ - $\pi$  resonance between the sulfur

atom and the benzene ring.<sup>16</sup> These two radicals are also capable of initiating polymerization of MMA.<sup>17</sup> In short, not only does a thiophenol undergo photoinitiation generating free radicals, but it also consumes oxygen during photooxidation. This double effect is responsible for the increased rate of polymerization and reduced induction time.

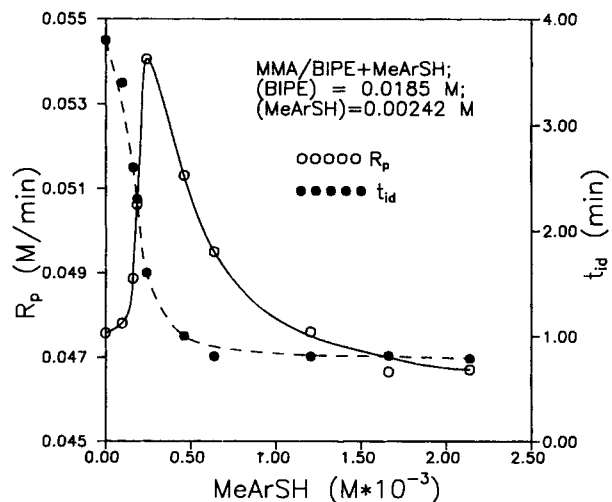
The generated radical  $\text{R}-\text{ArS}^{\bullet}$  is also known as a good hydrogen atom transfer agent.<sup>16</sup> It is conceivable that this radical can interact with BIPE by extracting its very labile  $\alpha$ -hydrogen atom, undergoing the following reactions:



The peroxide product can decompose easily under irradiation, forming active benzoyl and hydroxyl radicals:



By virtue of these reactions, MeArSH not only enhances the antioxidant capability of BIPE, but also



**Figure 8** Effect of MeArSH on rate of polymerization.

increases its reactivity. To support the idea of the hydrogen atom transfer character of R—ArS<sup>•</sup>, polymerization of the MMA/BIPE + MeArSH system was carried out both under air and nitrogen atmospheres. Figure 9 clearly shows that although induction times are equivalent in both cases, the rate of polymerization under oxygen is faster. Although this may be very surprising at first glance, it implies that some oxygen must have been converted into active free radicals, thus increasing the overall rate of polymerization in accordance with our proposed mechanism. Interestingly, Kobayashi et al.<sup>18</sup> studied the addition reaction of thiophenols to styrene initiated by a peroxide, and they also found that a trace of air present in the system increases the reaction rate, whereas a large amount of air decreases the reaction rate.

There has been a considerable amount of work done on the use of phenols as antioxidants.<sup>19-21</sup> Although the reaction between a phenol compound and oxygen is very complicated, it is generally believed that this reaction probably involves phenoxy radicals that react sufficiently easily with oxygen.<sup>22</sup> It is expected that a thiophenol should also play a role similar to a phenol, as discussed above.

To sum up, the capability of converting oxygen into active free radicals by MeArSH, in addition to its susceptibility to irradiation generating free radicals and its hydrogen atom transfer character, is responsible for the reduced induction time and enhanced rate of polymerization. Since MeArSH can

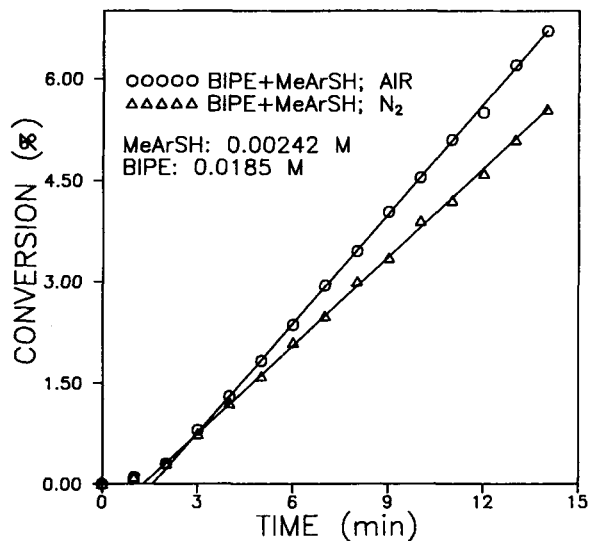


Figure 9 Conversion vs. time for MMA/BIPE + MeArSH system under air and N<sub>2</sub>.

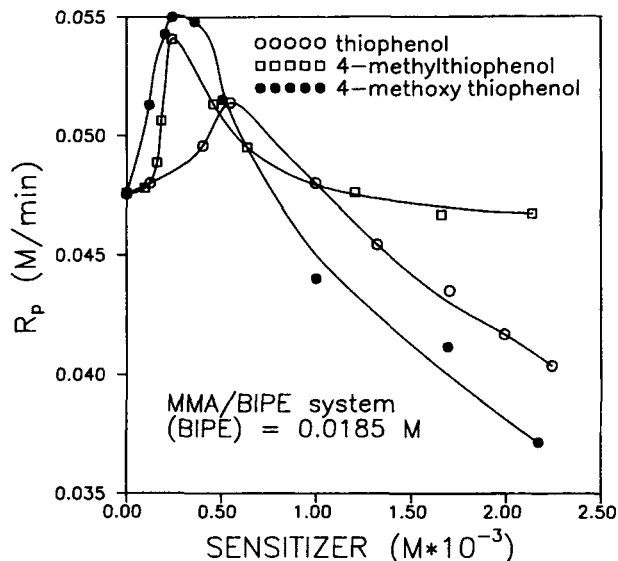
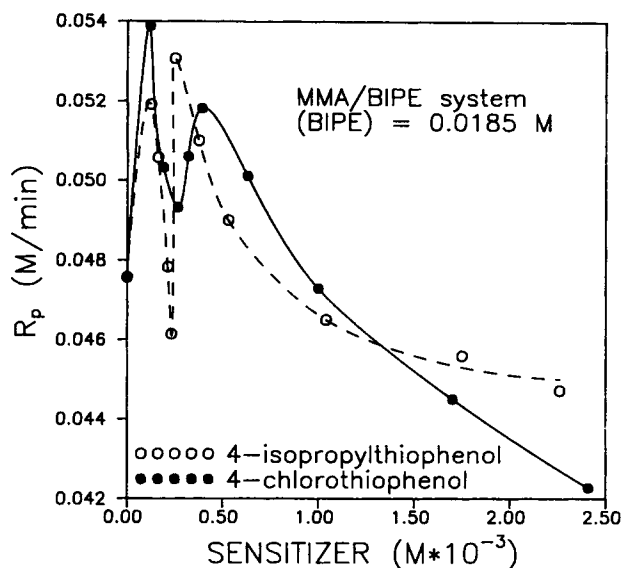


Figure 10 Effect of ArSH, MeArSH, or MeOArSH on rate of polymerization.

produce free radicals, it should no longer be surprising that the dependence of R<sub>p</sub> on the concentration of BIPE or MeArSH is similar (cf. Figs. 3 and 8).

### Effects of Several Thiophenol Compounds on Polymerization

We determined rates of polymerization and induction times in the presence of BIPE combined with one of the thiophenol compounds presented in Table I, in addition to 4-methylthiophenol (MeArSH). For the sake of clarity, two plots are used to show R<sub>p</sub> (cf. Figs. 10 and 11), and one, for induction times (cf. Fig. 12). Here, again, for all these thiophenols including MeArSH, R<sub>p</sub> increases with increasing concentrations of sensitizers at low concentrations and decreases at high concentrations. It is also noteworthy that in the cases of 4-isopropylthiophenol and 4-chlorothiophenol there exists a sharp drop in R<sub>p</sub> in the middle concentration region. This phenomenon is unexpected and needs further investigation. In any event, one point is conclusive: that addition of a thiophenol significantly decreases induction time, as we can see from Figure 12. Moreover, the extent of decrease in t<sub>id</sub> depends, to a great degree, upon the nature of the substituting group of thiophenol. Figure 13 shows the effect of 2-mercaptobenzoic acid on polymerization of the MMA/BIPE system. We note that instead of increasing

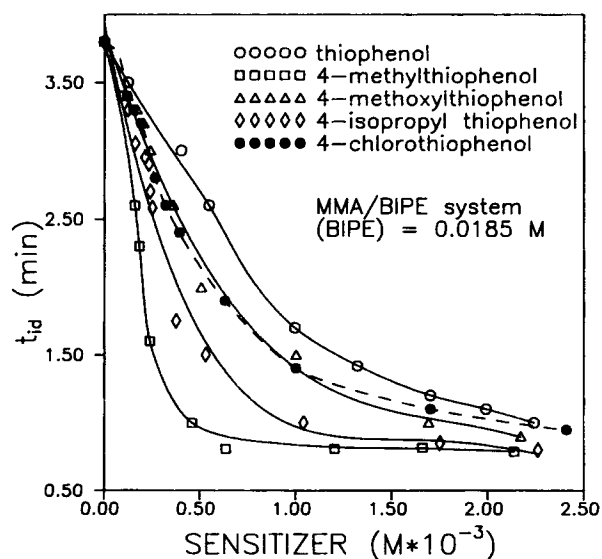


**Figure 11** Effect of iParSH or ClArSH on rate of polymerization.

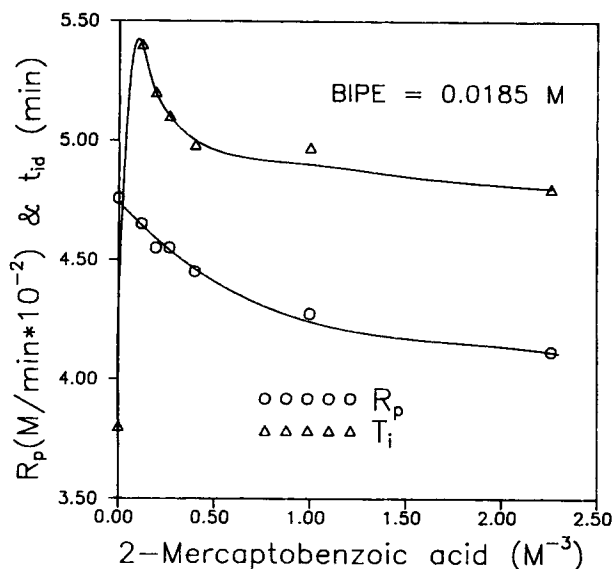
$R_p$  and reducing  $t_{id}$ , this thiophenol compound has the opposite effect. Obviously, the carboxylic acid group of this compound, capable of trapping free radicals, is responsible for these effects.

## CONCLUSION

In this paper, we have shown that thiophenol compounds  $R$ -ArSH with  $R$  in the *para*-position have



**Figure 12** Effect of sensitizers on induction time.



**Figure 13** Effect of 2-mercaptobenzoic acid on  $R_p$  and  $t_{id}$ .

a dual effect on polymerization of methyl methacrylate and benzoin isopropyl ether systems: reducing induction time and accelerating rate of polymerization. In addition to susceptibility of these thiophenol compounds to irradiation producing active free radicals and their hydrogen atom transfer character, their capability of converting oxygen into initiating radicals is responsible for these effects. Maximum increases in rate of polymerization are practically the same for various thiophenols. Extent of reduction in induction time, on the other hand, is strongly dependent on the nature of substituting groups following the order:  $-\text{CH}_3 > -\text{CH}(\text{CH}_3)_2 > -\text{OCH}_3$  or  $-\text{Cl} > -\text{H}$ . 2-Mercaptobenzoic acid displays negative effects on polymerization: increasing induction time and reducing the rate of polymerization.

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