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## Photopolymerization of Methyl Methacrylate and Styrene by Sulfur Ylides

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### ABSTRACT

The photoinitiating ability of some sulfur ylides was studied. Diphenylsulfonium bis(methoxycarbonyl)methylide (DPSY) could photoinitiate methyl methacrylate and styrene. A free radical mechanism was confirmed by a kinetic study, the inhibiting effect of benzoquinone, and the copolymer composition. From an analysis of the photodecomposition products it is suggested that the phenyl radical generated from the bond fission between the sulfur atom and the phenyl group participates in the initiation of this free radical polymerization. Methylphenylsulfonium bis(methoxycarbonyl)methylide, as well as DPSY, served as a photoinitiator, but dimethylsulfonium bis(methoxycarbonyl)methylide did not. The differences are explained based on UV spectra.

### INTRODUCTION

A number of papers on sulfur compounds as photoinitiators for radical polymerization have been published [1-3]. However, there are few reports in which ylide was employed as photoinitiator. Meanwhile, the photolysis of sulfur ylides has been studied by several investigators. For example, Corey et al. [4] found that the photolysis of a ketosulfonium ylide affords a ketocarbene. The evidence of a carbene inter-

mediate in the photolysis of sulfonium ylides was also found by Trost [5].

We previously reported that triphenylphosphonium ylides as well as tetraphenylphosphonium salts serve as photoinitiators for the free radical polymerization of styrene (St) and methyl methacrylate (MMA) [6, 7]. Further, we have recently found that triphenylsulfonium salts also have a photoinitiation ability for free radical polymerization [8]. These initiators undergo bond fission between the phosphorus atom and the phenyl group or the sulfur atom and the phenyl group on irradiation by a high pressure mercury lamp, and the phenyl radical produced participates in the initiation of polymerization. From the structural similarity between sulfonium salts and sulfonium ylides, diphenylsulfonium ylides are expected to work as photoinitiators. This article describes the photoinitiating ability of sulfur ylides; the initiation mechanism is discussed.

## EXPERIMENTAL

### Material

Diphenylsulfonium bis(methoxycarbonyl)methylide (DPSY), methylphenylsulfonium bis(methoxycarbonyl)methylide (MPSY), and dimethylsulfonium bis(methoxycarbonyl)methylide (DMSY) were prepared according to Ando's method: DPSY, mp 120-121°C (Ref. 9, 127-128°C); MPSY, mp 126-127°C (Ref. 9, 126-127°C); DMSY, mp 167-168°C (Ref. 9, 169-170°C). Methyl methacrylate (MMA) and styrene (St) were purified by ordinary methods. Solvents were used after distillation.

### Polymerization Procedure

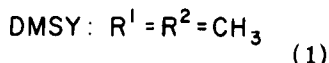
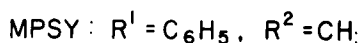
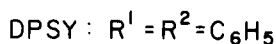
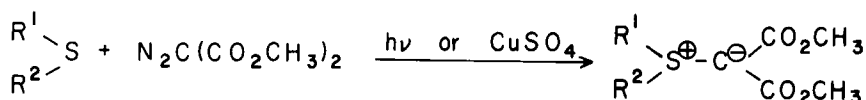
Polymerization was carried out by the method described previously [6]. In the case of copolymerization, the composition of copolymers was determined by elementary analysis of carbon and hydrogen. The monomer reactivity ratio was estimated by the Finemann-Ross method.

### Photolysis of DPSY

A solution of DPSY (1.58 g, 5 mmol) in  $CCl_4$  (200 mL) and ethanol (50 mL) was irradiated by a RIKO 450 W high pressure mercury lamp for 3 d at room temperature under nitrogen atmosphere. From analysis by gas chromatography (Carbowax 20 M, 10%, 2 m), 0.8 mmol of chlorobenzene and 0.03 mmol of hexachloroethane were detected. After evaporation of the solvent, 2.7 mmol of DPSY was recovered by the use of column chromatography (Alumina).

## RESULTS AND DISCUSSION

Though various sulfur ylides have been prepared, we employed DPSY, MPSY, and DMSY. These sulfur ylides were easily obtained by the reaction of sulfides and carbene generated from the decomposition of dimethyl diazomalonate [9]:



Photopolymerization of MMA by these sulfur ylides was attempted by the use of a high pressure mercury lamp as the light source. The results are summarized in Table 1. Although MMA alone is polymerized to a considerable extent by the light employed (> 300 nm), it is evident from Table 1 that DPSY and MPSY serve as photoinitiators. The same tendency was found in the case of the polymerization of St (Table 2). The ylides used here did not initiate polymerization in the dark at room temperature. In addition, these photopolymerizations were inhibited by the addition of benzoquinone as a radical scavenger,

TABLE 1. Photopolymerization of MMA by Several Sulfonium Ylides (11 h)

MMA (mL)	Initiator (10 <sup>2</sup> mol/L)	Benzoquinone (10 <sup>2</sup> mol/L)	Yield (%)
5	-	-	2.1
5	DPSY 1	-	18.5
5	DPSY 1	1	0
5	MPSY 1	-	9.8
5	MPSY 1	1	0
5	DMSY 1	-	2.2
5	DMSY 1	1	0

TABLE 2. Photopolymerization of St by Several Sulfonium Ylides (10 h)

St (mL)	Initiator (10 <sup>2</sup> mol/L)	Benzoquinone (10 <sup>2</sup> mol/L)	Yield (%)
5	-	-	0.5
5	DPSY 1	-	5.3
5	DPSY 1	1	0
5	MPSY 1	-	2.6
5	MPSY 1	1	0
5	DMSY 1	-	0.8
5	DMSY 1	1	0

suggesting that the polymerizations proceed via a free radical mechanism. To understand the order of initiation ability, the ultraviolet spectra of these ylides were measured in ethanol. As can be seen from Fig. 1, there is a relatively large difference in the  $\lambda_{\max}$  of these ylides.

Although the absorption bands of DPPY and MPSY appear at a wavelength longer than 300 nm, DMSY does not have an absorption band in that region. Therefore, DMSY has little initiation ability under the conditions employed here. That is, the order of initiation ability depends on the wavelength of the absorption bands.

The time conversion of the photopolymerization of MMA by DPSY is shown in Fig. 2. From Fig. 2 the overall rate  $R_p$  was calculated as  $4.32 \times 10^{-5}$  mol/L·s and no induction period was observed. This value is about half of that observed with triphenyl-phosphonium ylide [6].

In Fig. 3 the rate of photopolymerization of MMA by DPSY is plotted logarithmically against the initiator concentration, and a straight line having a slope of 0.48 is found. The correlation between  $R_p$  and MMA concentration is shown in Fig. 4;  $R_p$  is directly proportional to the monomer concentration. Accordingly, the equation for  $R_p$  in this polymerization was formulated as

$$R_p = k[\text{MMA}]^{1.0} [\text{DPSY}]^{0.48} \quad (2)$$

This equation also indicates that DPSY initiates the radical polymerization of MMA.

Further, in order to confirm the mechanism of this photopolymerization, copolymerization of St with MMA was carried out. Figure 5

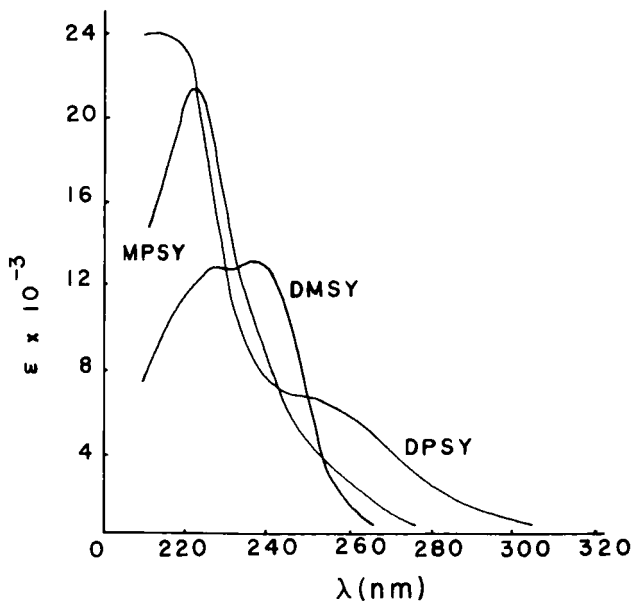


FIG. 1. UV spectra of sulfonium ylides in ethanol.

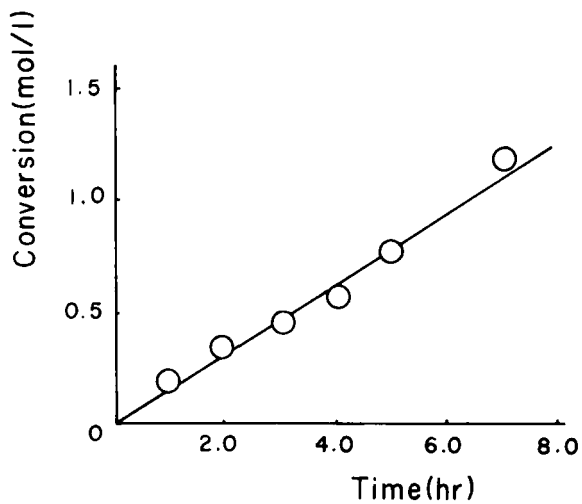


FIG. 2. Time-conversion of photopolymerization of MMA by DPSY.

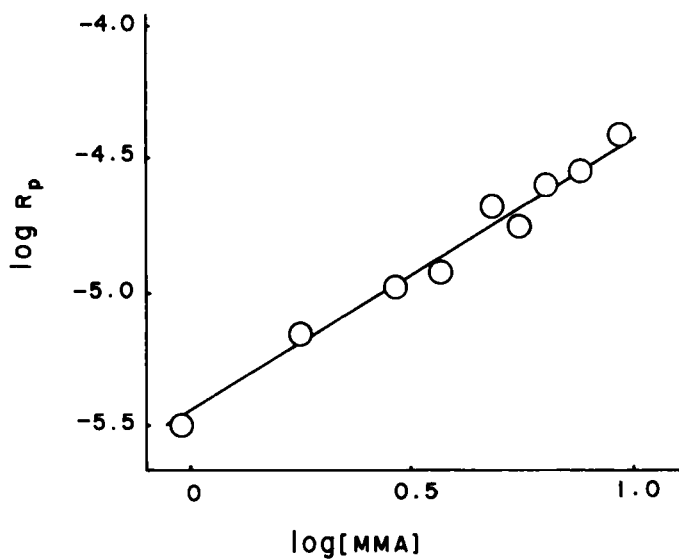


FIG. 3. Relation between  $R_p$  and MMA concentration.

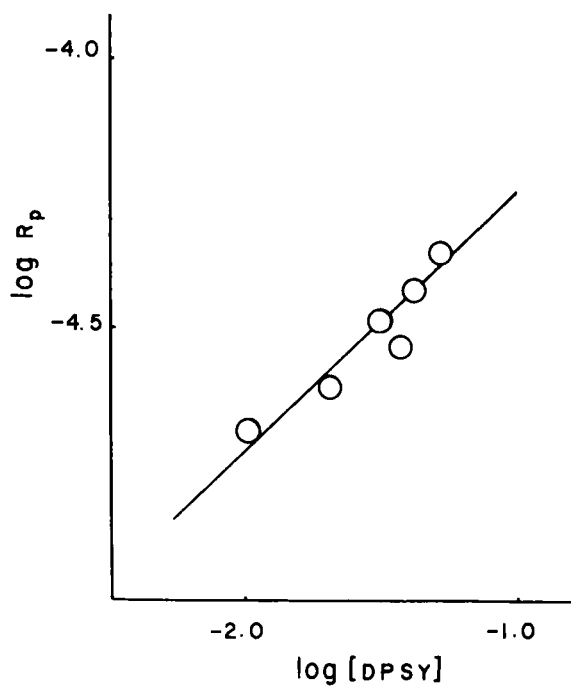


FIG. 4. Relation between  $R_p$  and DPSY concentration.

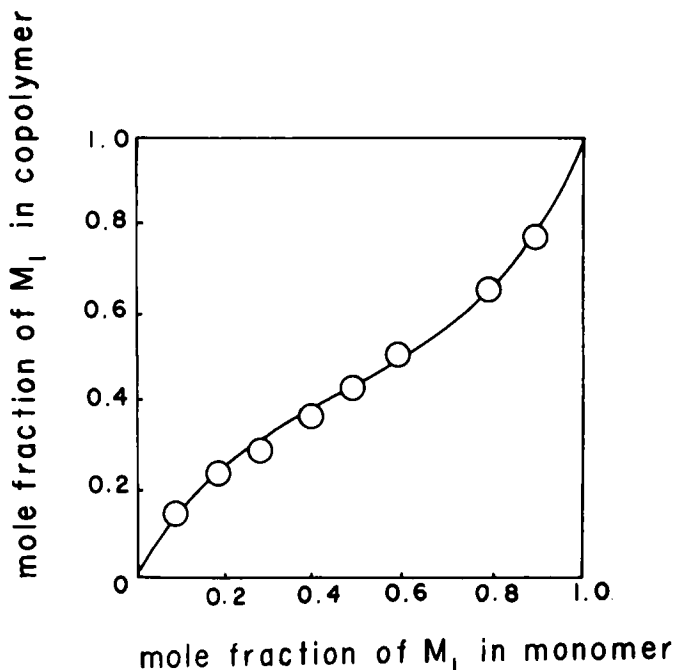
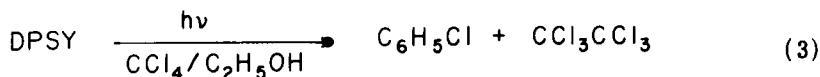


FIG. 5. Monomer-copolymer composition curve of St ( $M_1$ ) and MMA ( $M_2$ ).

shows the monomer-copolymer composition curve. From this figure the monomer reactivity ratio was calculated as  $r_{St} = 0.57$ ,  $r_{MMA} = 0.46$ . This result is in good agreement with the data reported for the radical copolymerization of St with MMA [10].

The effect of a radical scavenger and a kinetic study clarified that photopolymerization of MMA and St by DPSY proceeds by a free radical mechanism.

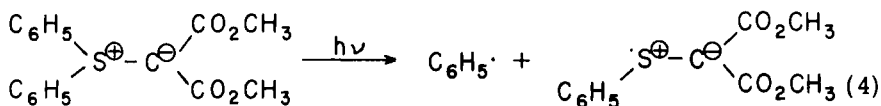
In order to obtain information on the initiation species for this polymerization, the photolysis of DPSY was investigated. Irradiation of a solution of DPSY in carbon tetrachloride and ethanol afforded chlorobenzene, hexachloroethane, and unknown compounds:



These products indicate the existence of phenyl radicals as intermediates in this reaction. The phenyl radical may be generated by bond



fission between the phenyl group and the sulfur atom as observed with triphenylsulfonium salts [8]:



From this consideration it is concluded that the phenyl radical is an initiation species in the photopolymerization by DPSY. However, the fate of the cation radical produced together with the phenyl radical is not clear at present.

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