Polymer Journal, Vol. 3, No. 1, pp 44—51 (1972)

Photopolymerization of Methyl Methacrylate Initiated by Iodobenzene—Triethylamine and Iodobenzene—Sodium Thiosulfate Systems

Sumihiro SAKAI

Kanae Paint Co. Ltd., Joto-ku, Osaka, Japan.

Toyohiko NAGASAKI, and Naokazu SAKOTA

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama, Japan.

(Received June 14, 1971)

ABSTRACT: The photopolymerization of methyl methacrylate was investigated in both iodobenzene—triethylamine and iodobenzene—sodium thiosulfate systems. The polymerization reactions proceeded according to a radical mechanism, and were initiated by the phenyl radical which was generated by photolysis of iodobenzene. Iodine radicals are expected to recombine with each other to form an iodine molecule, which would be immediately consumed by the reaction with triethylamine or sodium thiosulfate. In an iodobenzene—triethylamine system, therefore, the polymerization of methyl methacrylate would be partly initiated by the same mechanism as in the case of the photopolymerization with the iodine—triethylamine system which was discussed in our previous paper.

The photopolymerization of methyl methacrylate with polyiodostyrene—triethylamine and polyiodostyrene—sodium thiosulfate systems yielded a graft polymer, and the graft efficiency was lower in the former system than in the latter one. These facts would also suggest that the iodine—triethylamine complex was partly involved in the initiation of the photopolymerization with the polyiodostyrene—triethylamine system.

KEY WORDS Photopolymerization / Methyl Methacrylate / Iodine—Triethylamine Complex / Iodobenzene / Triethylamine / Sodium Thiosulfate / Graft Polymer / Poly(iodostyrene) / Photolysis / Phenyl Radical /

In the previous paper,[1] the photopolymerization of methyl methacrylate(MMA) was carried out in the presence of iodine and triethylamine. In this system, iodine forms a charge-transfer complex with triethylamine, which in the presence of excess triethylamine decomposes to triethylamine hydroiodide and *N*, *N*-diethyl-α-iodoethylamine. Triethylamine hydroiodide, however, showed no sensitizing effect for the polymerization of MMA. The photograftpolymerization of MMA to poly(*N*, *N*-diethylallylamine) by iodine, therefore, suggests that the triethylamine radical derived from the photolysis of *N*, *N*-diethyl-α-iodoethylamine can initiate the polymerization of MMA.

In this paper, the photopolymerization of MMA was examined in the presence of various kinds of alkyl iodides, allyl iodide, and iodobenzene with many kinds of amines and sodium thiosulfate. In the presence of amines or sodium thiosulfate, allyl iodide and iodobenzene were more effective for the photopolymerization of MMA than alkyl iodides.

Although many photochemical reactions of aryl iodides have already been reported,[2] none of them is concerned with the photosensitizing polymerization of vinyl monomer. To clarify the initiation mechanism, therefore, the photopolymerization of MMA in the presence of iodobenzene with triethylamine and with sodium thiosulfate were studied in detail. In further experiments poly(iodostyrene)s with varying content of iodine were used instead of iodobenzene, when high graft efficiencies were obtained. The results show that the phenyl radical which resulted from the photolysis of iodobenzene can

initiate the polymerization of MMA.

EXPERIMENTAL

Materials

MMA was purified according to the usual method and was distilled under reduced pressure in a nitrogen stream before use.[1] Iodobenzene (IBz) was synthesized from aniline through the diazonium compound[3] and the fraction distilling at 186°C was used. The alkyl iodides such as methyl, ethyl, *n*-butyl, *sec*-butyl, and *tert*-butyl, and allyl iodide were prepared from the corresponding alcohols and potassium iodide, and were used after distillation. Triethylamine(TEA) was dried over potassium hydroxide and then over calcium hydride. The fraction of TEA which was distilled at 89.2—90.0°C in a nitrogen stream was used for the experiments. The extra grade reagent of sodium thiosulfate($Na_2S_2O_3$) was used. The various alkyl ammonium iodides of TEA were prepared by the reaction of the corresponding alkyl iodide with TEA in methanol at room temperature for a few days. The methanol solution was concentrated under reduced pressure, and the precipitated alkyl ammonium iodide of TEA was recrystallized from ethyl acetate—ethanol several times. Polyiodostyrenes(PISt) with varying contents of iodine were synthesized from polystyrene (molecular weight 145000) according to the method of Okawara and Mizuta.[4]

Procedure

MMA solution of alkyl iodide, and methanolic solution of amine (or aqueous solution of sodium thiosulfate) were placed in a glass ampoule for polymerization. The glass ampoule was degassed by the freeze-thaw method, and then was sealed. The photopolymerization was carried out in a sealed tube rotating around a 300-W high-pressure mercury lamp (PIH 300 made by Eiko Co.) at 35°C. The polymerization rates were determined from the amount of polymer obtained by pouring the reaction mixture into an excess of methanol.

The separation of the graft polymer from the reaction product in MMA—PISt—$Na_2S_2O_3$ systems was achieved by fractional precipitation with acetonitrile—methanol as follows. The product obtained by the photopolymerization (0.5 g) was dissolved in 25 m*l* of acetonitrile, and the solution was added to methanol little by little. Each precipitated fraction was separated off and the presence of the graft polymer in the precipitate was examined by the infrared absorption band at 695 cm^{-1} assigned to the phenyl group. In another experiment, 0.35 g of PISt with 39.5-% iodine content and 0.35 g of poly-MMA obtained by normal radical polymerization were added to 25 m*l* of acetonitrile, but all of the PISt added remained as insoluble. On the other hand, the polymers obtained in the MMA—PISt—TEA system were completely soluble in acetonitrile. In the case of the polymers obtained with the MMA—PISt—$Na_2S_2O_3$ system, they left an insoluble part in acetonitrile, which, however, showed the IR absorption band based on the carbonyl group and decreased with the lowering of the I_2 content in PISt. Such an insoluble fraction, therefore, would not be merely unreacted PISt, but grafted PISt with a small amount of MMA.

Fractional precipitation curves of the polymers obtained in the presence of MMA—TEA (or MMA—$Na_2S_2O_3$) and PISt (containing 21.5-%

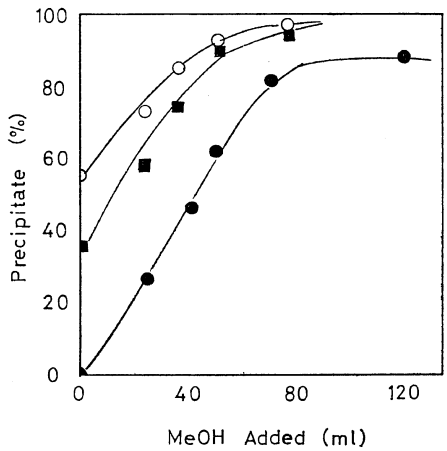


Figure 1. Fractional precipitation of the polymers obtained from MMA—PISt—TEA and MMA—PISt—$Na_2S_2O_3$ systems: polymer, 0.5 g; acetonitrile, 25 m*l*; —●—, MMA—PISt—TEA system (iodine content of PISt, 21.5%); —○—, MMA—PISt—$Na_2S_2O_3$ system (iodine content of PISt, 21.5%); —■—, MMA—PISt—$Na_2S_2O_3$ system (iodine content of PISt, 3.5%).

iodine) are shown in Figure 1. Each fraction showed the IR absorption band based on phenyl group except for the last fraction in the PISt—$Na_2S_2O_3$ system. All the polymers obtained with PISt of varied I_2 content showed fractional precipitation curves similar to that shown in Figure 1.

The electronic spectra of iodobenzene were determined in *n*-heptane and MMA using a 2-mm cell with a Jasco Model ORD/UV 5 Spectropolarimeter.

RESULTS AND DISCUSSION

The photosensitized polymerization of MMA was carried out in the presence of alkyl iodides and amines (or $Na_2S_2O_3$), and the results are shown in Table I. The conversions of the monomer initiated with amine-alkyl ammonium iodide of TEA systems are also shown in Table I. To get a homogeneous system in the polymerization reaction with the latter systems, methanol was added. In the other polymerization systems, therefore, methanol was also added to get the same condition as mentioned above. The results show that in the presence of amine alkyl iodides act as the photosensitizer for the polymerization of MMA, and also that allyl iodide and iodobenzene can act as a more effective photosensitizer. Relatively high conversions are obtained in TEA—alkyl iodides systems. Pyridine and dimethylaniline, however, provide no significant effect in comparison with aliphatic amines. Among the amines having the same alkyl group, tertiary amine is the most effective photosensitizer as compared with secondary and primary amines, and the result corresponds with that of the photopolymerization of MMA in the presence of iodine and amines.[1] Because every alkyl ammonium iodide of TEA seems to be a less effective photosensitizer for the polymerization of MMA than the corresponding alkyl iodide—TEA system, it is not reasonable to consider that the polymerization of MMA in the presence of alkyl iodides and amines would be initiated by the photolysis of the corresponding ammonium salts formed as intermediates.

From Table I, alkyl iodides are also shown to act as photosensitizer in the presence of $Na_2S_2O_3$. In iodine—$Na_2S_2O_3$ system, however, the polymerization of MMA is completely inhibited. Therefore, alkyl iodide is photodecomposed to

Table I. Photopolymerization of MMA in the presence of alkyl iodide—amine and alkyl iodide—$Na_2S_2O_3$ systems[a]

	Conversion, %[b]									
	CH_3I	C_2H_5I	*n*-C_4H_9I	*sec*-C_4H_9I	*tert*-C_4H_9I	Allyl iodide	C_6H_5I	I_2	——	HI
Diethylamine	3.8	13.6	10.1	11.2	14.4	13.8	16.9	16.1	5.7	—
Triethylamine	6.3	16.0	10.3	12.1	15.9	27.1	21.8	23.3	5.2	7.2
Alkyl Ammonium Iodide of TEA	7.4	7.4	7.3	8.0	8.0	7.6	—	—	—	—
Monoethanolamine	4.6	13.2	9.3	11.5	11.2	15.5	17.3	8.5[c]	2.8	—
Diethanolamine	6.9	14.0	11.6	11.8	14.2	16.7	18.3	13.6	3.9	—
Triethanolamine	11.3	13.7	10.4	12.1	16.3	40.8	18.4	19.5	5.1	—
Ethylenediamine	4.0	12.4	9.5	11.9	14.0	12.5	18.9	11.7	2.8	—
Diethylenetriamine	4.2	11.7	10.1	12.3	15.7	8.9	19.4	16.2	5.9	—
Pyridine	3.4	5.5	4.2	4.0	4.1	6.6	6.9	0	3.0	—
Dimethylaniline	6.7	7.7	6.7	6.2	9.4	15.6	8.2	0	9.1	—
——	4.9	5.1	3.7	3.9	2.2	8.0	6.3	0	3.0	—
$Na_2S_2O_3$[d]	13.8	14.0	14.8	12.6	3.0	31.3	23.4	0	—	—

[a] MMA, 4 m*l*; MeOH, 1 m*l*: [Amine], 2×10^{-1} mol/*l*; [Iodide], 8×10^{-3} mol/*l*; [$Na_2S_2O_3$], 8×10^{-3} mol/*l*; [Ammonium iodide], 8×10^{-3} mol/*l*.
[b] After photopolymerization for 3 hr at 35°C.
[c] [I_2], 4×10^{-1} mol/*l*.
[d] Added as 0.25 m*l* of $Na_2S_2O_3$ aqueous solution.

both alkyl and iodine radicals, the former of which would initiate polymerization of MMA losing an iodine radical by the reaction with $Na_2S_2O_3$.

As indicated in Table I, IBz showed an excellent photosensitizing effect with amines or with $Na_2S_2O_3$, and so the initiation mechanism of the photopolymerization of MMA in the presence of IBz—TEA and of IBz—$Na_2S_2O_3$ were studied in detail. The photosensitized polymerizations of MMA in these systems were inhibited by oxygen and by 2, 2-diphenyl-1-picrylhydrazyl and also were retarded with hydroquinone. Thus the polymerization seems to proceed by a radical mechanism.

At a constant concentration of IBz (8×10^{-3} mol/l), the relationship between the concentration of TEA and the polymerization rate (R_p) is shown in Figure 2. At concentrations of

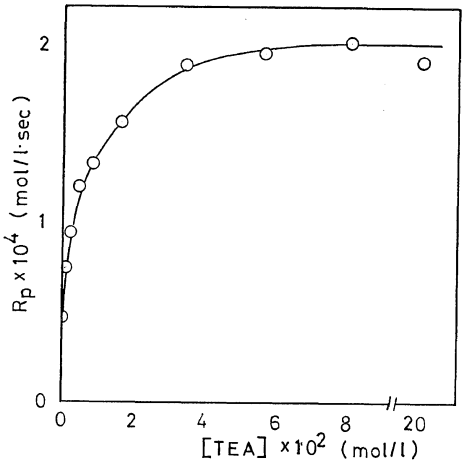


Figure 2. Relationship between the photopolymerization rate of MMA (R_p) and the concentration of TEA in MMA—IBz—TEA system at 35°C: MMA, 4 ml; MeOH, 1 ml; [IBz], 8×10^{-3} mol/l.

IBz higher than 4×10^{-3} mol/l, the concentration of TEA bring about no significant effect on R_p. At varying concentrations of $Na_2S_2O_3$ (2×10^{-3} to 8×10^{-3} mol/l) with a constant IBz concentration (4×10^{-3} mol/l), the conversion *vs.* time curves were obtained as shown in Figure 3.

The rate of polymerization of MMA was not affected by the concentration of $Na_2S_2O_3$ in this range. In the presence of 2×10^{-1} mol/l of TEA and 4×10^{-3} mol/l of $Na_2S_2O_3$, the rate of photo-

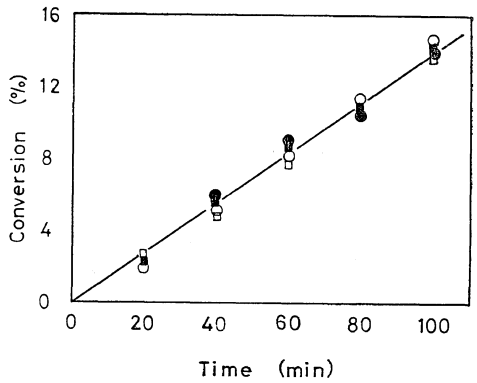


Figure 3. Conversion *vs.* time curves of photopolymerization of MMA in the presence of IBz—$Na_2S_2O_3$ at 35°C: MMA, 4 ml; MeOH, 0.75 ml; H_2O, 0.25 ml; [IBz], 4×10^{-3} mol/l; —○—, [$Na_2S_2O_3$], 2×10^{-3} mol/l; —□—, [$Na_2S_2O_3$], 4×10^{-3} mol/l; —●—, [$Na_2S_2O_3$], 6×10^{-3} mol/l; —■—, [$Na_2S_2O_3$], 8×10^{-3} mol/l.

sensitized polymerization of MMA by IBz was proportional to the square root of the IBz concentration as shown in Figure 4. In the conversion *vs.* time curves below 4×10^{-5} mol/l of $Na_2S_2O_3$ with a constant concentration of IBz, a yielding point was observed. Beyond the yielding point R_p becomes equal to that in the system without $Na_2S_2O_3$ (Figure 5).

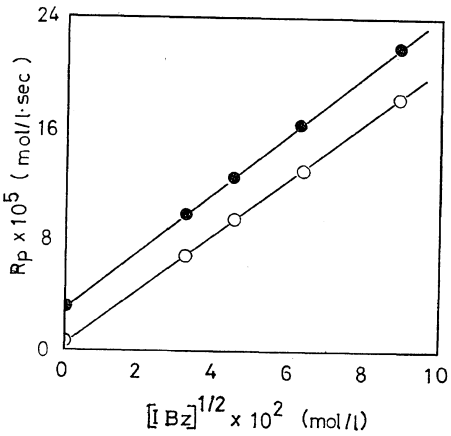


Figure 4. Relationships between the photopolymerization rate of MMA and the square root of IBz concentration in MMA—IBz—TEA system and MMA—IBz—$Na_2S_2O_3$ system at 35°C: MMA, 4 ml, MeOH, 1 ml; —○—, [TEA], 2×10^{-1} mol/l; —●—, [$Na_2S_2O_3$], 4×10^{-3} mol/l.

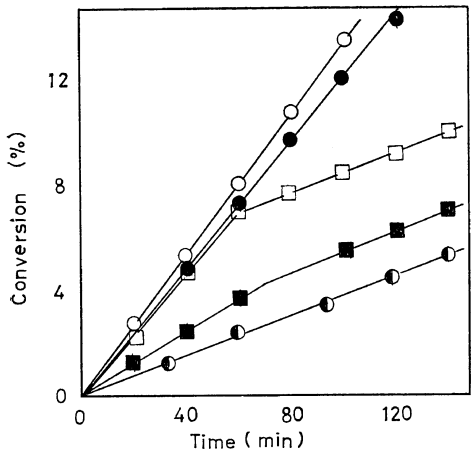


Figure 5. Conversion *vs.* time curves of the photopolymerization of MMA at varying concentrations of $Na_2S_2O_3$ in MMA—IBz—$Na_2S_2O_3$ system: MMA, 4 m*l*; MeOH, 0.75 m*l*; H_2O, 0.25 m*l*; [IBz], 4×10^{-3} mol/*l*; —◐—, [$Na_2S_2O_3$], 0; —■—, [$Na_2S_2O_3$] 4×10^{-6} mol/*l*; —□—, [$Na_2S_2O_3$], 4×10^{-5} mol/*l*, —●—, [$Na_2S_2O_3$], 1.3×10^{-4} mol/*l*; —○—, [$Na_2S_2O_3$], 4×10^{-4} mol/*l*.

In the presence of IBz—TEA, the polymerization rate in dichloroethane was proportional to the MMA concentration as shown in Figure 6. In the case of IBz—$Na_2S_2O_3$ in dichloroethane or in acetonitrile R_ps were proportional to the concentration of MMA as shown in

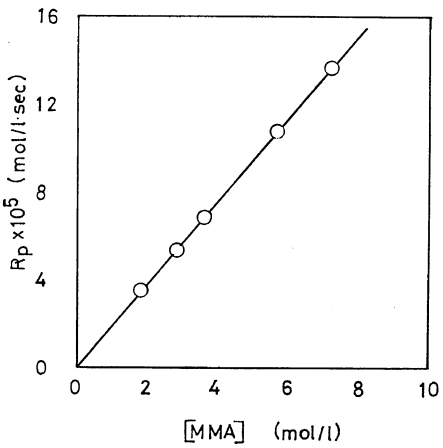


Figure 6. Relationship between the photopolymerization rate of MMA and the concentration of MMA in MMA—IBz—TEA system at 35°C: MMA+$C_2H_4Cl_2$, 4 m*l*; MeOH, 1 m*l*; [IBz], 4×10^{-3} mol/*l*; [TEA], 2×10^{-1} mol/*l*.

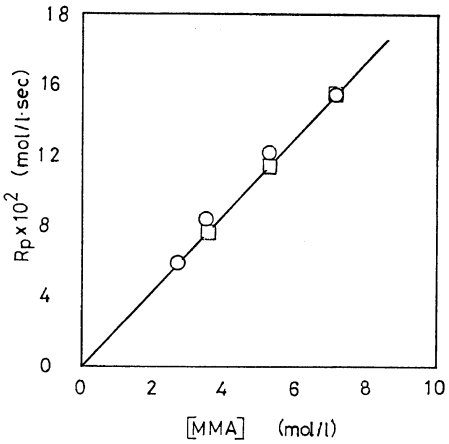


Figure 7. Relationship between the photopolymerization rate of MMA and the concentration of MMA in MMA—IBz—$Na_2S_2O_3$ system at 35°C: MMA+Solvent, 4 m*l*; MeOH, 1 m*l*; H_2O, 0.25 m*l*; [IBz], 4×10^{-3} mol/*l*; [$Na_2S_2O_3$], 4×10^{-3} mol/*l*; —○—, $C_2H_4Cl_2$; —□—, CH_3CN.

Figure 7. On the basis of these facts, the photopolymerization rates of MMA with IBz—TEA and with IBz—$Na_2S_2O_3$ systems would be expressed by the following eq 1 and 2, respectively.

$$R_{p1}=k_1[\mathrm{IBz}]^{1/2}[\mathrm{TEA}]^0[\mathrm{MMA}] \quad ([\mathrm{TEA}]/[\mathrm{IBz}]>5) \tag{1}$$

$$R_{p2}=k_2[\mathrm{IBz}]^{1/2}[\mathrm{Na_2S_2O_3}]^0[\mathrm{MMA}] \quad ([\mathrm{Na_2S_2O_3}]/[\mathrm{IBz}]>0.1) \tag{2}$$

The molecular weights of poly-MMA were determined by viscometry in benzene at 30°C.[5] In IBz—TEA system ([IBz]/[TEA]=1/50), the molecular weights of poly-MMA obtained at [IBz]=8×10^{-3}, 4×10^{-3}, and 1×10^{-3} mol/*l* were 124000, 215000, and 586000, respectively. Poly-MMA obtained in the presence of IBz—$Na_2S_2O_3$ ([IBz]/[$Na_2S_2O_3$]=1/2) showed the molecular weights of 466000, 650000, and 1950000 when the IBz concentration were 8×10^{-3}, 4×10^{-3} and 1×10^{-3} mol/*l*, respectively.

The electronic spectra of IBz in *n*-heptane and in MMA solutions after irradiation by UV light *in vacuo* are shown in Figures 8 and 9, respectively. In *n*-heptane, the absorption maximum of the iodine molecule appeared at 520 mμ[6] and increased with the UV-irradiation time. On the other hand, the typical absorption of iodine

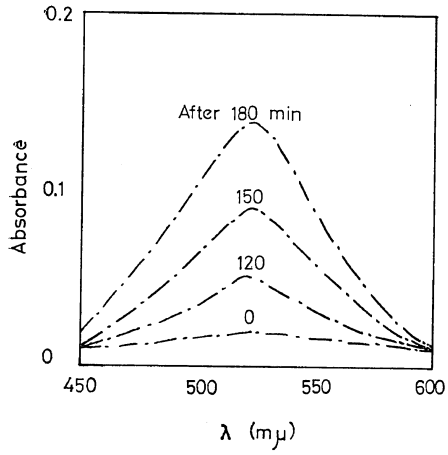


Figure 8. Photolysis of IBz in *n*-heptane at 35°C: [IBz], 1×10^{-2} mol/*l*.

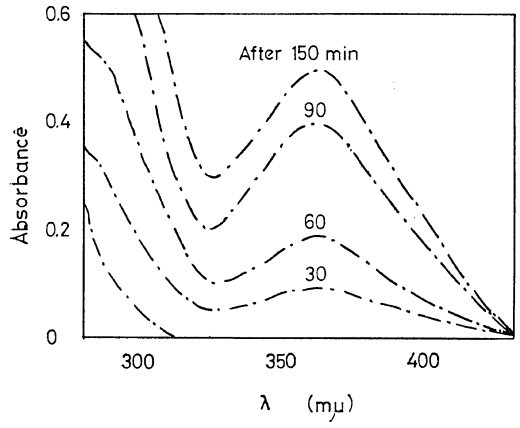
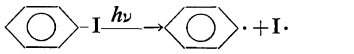


Figure 9. Photolysis of IBz in MMA at 35°C: [IBz], 8×10^{-3} mol/*l*.

was not observed in MMA, but two absorption maxima which would be ascribed to the I_3^- ion appeared at 360 mμ and 295 mμ, and their absorbances also increased with the irradiation time of UV light. In another experiment, the absorption maximum of the iodine molecule in MMA was recognized at 475 mμ ($\varepsilon_{475}=470$). When the MMA solution of I_2 was irradiated with UV light *in vacuo*, the absorption maximum at 475 mμ disappeared gradually and an absorption maximum of I_3^- ion at 360 mμ appeared and was intensified with the irradiation time. Since the photopolymerization of MMA does not take place in the presence of iodine, it is obvious that the photopolymerization of MMA is not initiated by any product of the reaction of MMA with iodine.

The results show that by UV light irradiation, IBz in MMA splits into iodine and phenyl radicals, and the former radical recombines into an iodine molecule, or abstracts a hydrogen atom from MMA as indicated in eq 3 and 4. As the photopolymerization of MMA is completely inhibited by iodine, the MMA radical formed by the abstraction of hydrogen atom with iodine radical should not initiate the polymerization. The phenyl radical produced by photolysis of IBz, therefore, should be responsible for the initiation.

Fueno, *et al.*,[7] reported that dimethylphenylbenzyl ammonium chloride was the initiating species for the thermal polymerization of MMA in the presence of dimethylaniline and benzyl chloride. In the present study, however, the ammonium salts of alkyl iodides and TEA showed no photosensitizing activity for the polymerization of MMA (Table I). We suggest the following reaction scheme for the photopolymerization of MMA initiated by IBz—TEA and by IBz—$Na_2S_2O_3$ systems.



(3)

$$I\cdot + I\cdot \longrightarrow I_2$$

and/or $$I\cdot + H\text{-}R \longrightarrow HI + R\cdot \quad (4)$$

$$I_2 + HI \longrightarrow {}^{+}HI_3^{-} \quad (5)$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6 \quad (6)$$

The pyrex glass ampoule used for the photopolymerization had a relatively large transmittance in the region over 310-mμ wave length, and iodobenzene in MMA showed a low value of absorbance in the same wavelength region. It was also shown in Figure 9 that the absorption maximum of I_3^- generated by the UV light irradiation to MMA solution of iodobenzene had a relatively small absorbance in this wave length region. Therefore, assuming the bimolecular termination for the photoplymerization in IBz—TEA—MMA and IBz—$Na_2S_2O_3$—MMA systems, the rates of polymerizations would be explained by eq 1 and 2, respectively.

Wolf and Kharasch[8] reported that iodine and biphenyl were produced by the photolysis of IBz in benzene. In the IBz—TEA system,

iodine and phenyl radicals are produced by the photolysis of IBz in MMA as shown in eq 3, and then the phenyl radical would initiate the polymerization of MMA. Iodine has been reported to be a powerful radical scavenger and to inhibit the photosensitized polymerization of vinyl monomer.[9,10] Iodine, however, forms a charge-transfer complex with TEA in the presence of an excess of TEA, and by UV light irradiation, the CT complex was photolyzed to TEA radical which initiate the polymerization of MMA according to the mechanism discussed in the previous paper.[1] Consequently, the photopolymerization of MMA by IBz—TEA system must be initiated by the phenyl radical and partly by the TEA radical derived from the I_2—TEA complex.

In IBz—$Na_2S_2O_3$ system, iodine produced by photolysis of IBz is reduced with sodium thiosulfate (eq 6) and only phenyl radicals play a role as initiator in the polymerization of MMA. It is reasonable to consider that the yielding points in Figure 5 correspond to the point at which $Na_2S_2O_3$ has been completely consumed by iodine. However the question still remains as to why the different $Na_2S_2O_3$ concentrations showed yielding points at almost equal reaction time.

If the photopolymerizations of MMA in the presence of IBz—TEA and of IBz—$Na_2S_2O_3$ were initiated according to the above-mentioned mechanisms, it could be expected that a graft polymer was to be produced in the photopolymerization of MMA with TEA—PISt system instead of TEA—IBz system. Experimental results showed that the graft polymer was obtained with extremely high graft efficiency in the photopolymerization of MMA with PISt—TEA and PISt—$Na_2S_2O_3$ systems as shown in Table II, in which PISt—$Na_2S_2O_3$ system showed the higher graft efficiency than that of the PISt—TEA system. These results are consistent with the assumption that the initiation by the I_2—TEA complex is involved in the initiation with the PISt—TEA system. The polymerization rate of MMA showed a linear relation with the square root of iodine content in PISt as shown in Figure 10, and the results also support the

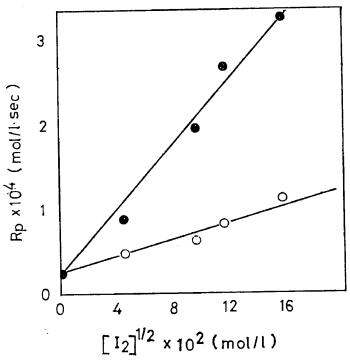


Figure 10. Relationships between the photopolymerization rate of MMA and $[I_2]$ in MMA—PISt—TEA and MMA—PISt—$Na_2S_2O_3$ systems at 35°C: MMA, 5 m*l*; PISt, 80 mg; H_2O, 0.25 m*l*; —●—, TEA, 0.15 m*l*; —○—, $[Na_2S_2O_3]$, 4×10^{-3} mol/*l*. $[I_2]$ were calculated from the amounts of I_2 in the used PISt.

Table II. Photopolymerization of MMA with PISt—TEA system and with PISt—$Na_2S_2O_3$ system[a]

I_2 content in PISt, %	System	Conversion, %	Graft ratio, %	Graft efficiency, %
3.5	TEA	5.1	219.1	57.7
3.5	$Na_2S_2O_3$	3.5	273.8	95.0
14.4	TEA	13.6	547.9	69.0
14.4	$Na_2S_2O_3$	5.1	328.8	95.5
21.5	TEA	22.2	544.0	80.9
21.5	$Na_2S_2O_3$	7.1	621.2	96.1
39.5	TEA	27.0	438.0	63.2
39.5	$Na_2S_2O_3$	10.3	574.0	95.0
39.5	AIBN[b]	5.2	63.6	20.9

[a] MMA, 5 m*l*; PISt, 80 mg; TEA, 0.15 m*l*; $[Na_2S_2O_3]$, $4\times10^{-}$ mol/*l* in 0.25 m*l* of H_2O, at 35°C for 2 hr.
[b] [AIBN], 4×10^{-3} mol/*l*.

above-mentioned mechanism.

REFERENCES

1. N. Sakota, T. Nagasaki, and S. Sakai, This Journal, **2**, 192 (1971).
2. R. K. Sharma and N. Kharasch, *Angew. Chem.* International ed, **7**, 36 (1968).
3. H. S. Kennedy, "Organic Syntheses," Col. Vol. II, John Wiley & Sons, Inc., New York, N.Y., 1943, p 351.
4. S. Okawara and K. Mizuta, *Kogyo Kagaku Zasshi* (*J. Chem. Soc., Japan, Ind. Chem. Sect.*), **64**, 232 (1961) (in Japanese).
5. E.S.C. Ginsberg, T.G. Fox, and H.F. Marson, *Polymer*, **3**, 97 (1962).
6. S. Nagakura, *J. Amer. Chem, Soc.*, **80**, 520 (1958).
7. T. Fueno, H. Okamoto, T. Tsuruta, and J. Furukawa, *J. Polym. Sci., Part A-1*, **36**, 407 (1959).
8. W. Wolf and N. Kharasch, *J. Org. Chem.* **30**, 2493 (1965).
9. P. D. Bartlett and H. Kwart, *J. Amer. Chem. Soc.*, **72**, 1051 (1950).
10. G. Fraenkel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **81**, 5582 (1959).