Photopolymerization of Methyl Methacrylate Initiated by Iodine—Triethylamine System

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ABSTRACT: The photopolymerization of methyl methacrylate in the presence of iodine and triethylamine was investigated to clarify the initiation mechanism in this system. The polymerization proceeded according to a radical mechanism. It was confirmed that triethylamine hydroiodide formed during the polymerization process did not act as a photosensitizer by itself. On the other hand the red-brown oily material, which was obtained from the mother liquor of the crystalline triethylamine hydroiodide, initiated the photopolymerization of methyl methacrylate in the presence of triethylamine or sodium thiosulfate without an induction period. The results of elementary analysis, measurements of infrared spectra, and thin-layer chromatography, suggest that the oily material contained, *inter alia*, *N,N*-diethyl- α -iodoethylamine.

A graft polymer was obtained in the photopolymerization of methyl methacrylate in the presence of iodine and poly(*N,N*-diethylallylamine). This fact also would suggest that with irradiation by ultraviolet light the iodine—triethylamine charge-transfer complex was converted into *N,N*-diethyl- α -iodoethylamine, the photolysis of which provided the primary radicals to initiate the polymerization of methyl methacrylate.

KEY WORDS Photopolymerization / Methyl Methacrylate / Iodine / Triethylamine / Radical / Triethylamine Hydroiodide / Charge-Transfer Complex / Sodium Thiosulfate / Graft Polymer / Poly(*N,N*-diethylallylamine) /

It is well known that iodine can act as an electron acceptor to form charge-transfer complexes with electron donors such as amines,¹⁻³ amides,⁴ ethers,⁵ alcohols,⁵ aromatic hydrocarbons,⁶ and some of the olefins.⁷ On the iodine—triethylamine charge-transfer complex in particular, a number of studies have been reported.⁸⁻¹² The cationic polymerization of alkyl vinyl ethers,¹³ styrene,¹⁴ substituted styrenes,¹⁵ and *N*-vinylcarbazole¹⁶ with iodine have already been investigated, and in these cases it was proposed that charge-transfer complexes of iodine and vinyl monomers participated directly in the initiation of the polymerization. Tsuji, *et al.*,¹⁷ however, have detected free radicals in the polymerization system of iodine and alkyl vinyl ether by ESR, and have suggested the possibility

of a radical polymerization by iodine in the presence of an appropriate vinyl monomer. Although Pramanick and his coworker¹⁸ described how the radical polymerization of methyl methacrylate could be thermally initiated in the presence of iodine and some types of amines, no detailed initiation mechanism has yet been put forward. In this study the initiation mechanism in the photopolymerization of methyl methacrylate in the presence of iodine and triethylamine is discussed.

EXPERIMENTAL

Materials

Methyl methacrylate(MMA) was washed with a saturated aqueous solution of sodium bisulfite,

an aqueous solution containing 20-% sodium chloride and 5-% sodium hydroxide, and a 20-% aqueous solution of sodium chloride, successively. It was dried over anhydrous sodium sulfate and then distilled in a nitrogen stream under reduced pressure. Iodine was purified by sublimation several times in the presence of potassium iodide and calcium oxide. Triethylamine (TEA) was dried over potassium hydroxide and calcium hydride, and then distilled. The fraction distilled at 89.2–90.0°C was used for the experiments. The other amines were also purified by drying over potassium hydroxide and by fractional distillation. Poly(*N,N*-diethylallylamine) (PDEAA) was prepared by reduction of poly(*N,N*-diethylacrylamide) according to the method of Cohen, *et al.*¹⁹ It showed no absorption band of the carbonyl group in the infrared spectrum, and its intrinsic viscosity was 0.336 in tetrahydrofuran solution at 30°C.

Procedure

Defined amounts of MMA, I₂, and amine for polymerization were placed in a glass tube which was then degassed by the freeze-thaw method. The photopolymerization was carried out by irradiating the sealed tubes with ultraviolet light from a 300 W high-pressure mercury lamp (PIH 300 made by Eiko). The sealed tubes were placed on a rotating drum around the lamp in an air bath at 35°C. A low-pressure luminescent discharge tube (FL-20 BL made by Toshiba) was also used for the preliminary experiments detailed in Table I. The reaction mixture obtained by photopolymerization was poured into an excess of methanol. The polymer was filtered off and dried *in vacuo* at 60°C for 24 hr. The polymerization rates were determined from the amounts of polymer at each reaction time. The separation of graft polymer from the reaction product in the I₂–PDEAA system was achieved by extraction with acetonitrile in a Soxhlet extractor for 20 hr.

The electronic spectrum of the I₂–TEA complex was determined with a 2-mm cell in MMA solution using a Jasco Model ORD/UV 5 Spectropolarimeter.

RESULTS AND DISCUSSION

The results of the photosensitized polymeri-

Table I. Polymerization of MMA by various donors (D) and I₂ systems

Donor	conversion, % ^c		
	Photopolymerization I ₂ + D	D	Thermal polymerization I ₂ + D
Ammonia ^a	0	—	—
Ethylamine ^b	0	2.6	0
Diethylamine	5.6	4.3	0
Triethylamine	13.4	3.8	0
Cyclohexylamine	9.9	2.7	0.1
Piperidine	10.3	3.6	0.3
Ethylenediamine	18.4	1.2	2.3
Hexamethylenediamine	19.6	3.1	0
Diethylenetriamine	15.8	3.5	6.4
Triethylenetetramine	14.1	3.7	14.3
Pyridine	0	1.9	0
Aniline	0	—	—
Dimethylaniline	0	—	—
Ethanolamine	21.0	1.5	0.5
Triethanolamine	33.4	3.3	1.7
Dimethylacetamide	0	—	—
Ethyl Alcohol	0	—	—
Ethyl Ether	0	—	—

^a 25-% Aqueous solution.

^b 60-% Aqueous solution.

^c MMA, 5 ml; [I₂], 8 × 10⁻³ mol/l; [D], 2 × 10⁻¹ mol/l. Photopolymerizations were carried out for 5 hr at 30°C, and thermal polymerizations for 5 hr at 33°C.

zation of MMA in the presence of I₂ and various amines are shown in Table I. I₂ seems to act as a photosensitizer in the presence of aliphatic di- and tri-alkyl amines, and the accelerating effect of tertiary amines are distinguishable from those of primary and secondary amines for the polymerization of MMA. In other experiments the photosensitizing effect of the iodine–triethylamine system has also been confirmed for the polymerization of acrylonitrile, styrene, and ethyl acrylate.

Although I₂, known as a powerful radical scavenger, inhibited the photopolymerization of MMA by itself, it was able to initiate the photopolymerization of MMA in the presence of TEA with an induction period (Figure 1). In the presence of only TEA, however, a rate of polymerization slightly higher than that of MMA alone was obtained. This

Figure 1. Photopolymerization of MMA by I_2 -TEA system at 35°C: —●—, MMA, 5 ml; —○—, MMA, 5 ml, $[TEA]$, 4×10^{-1} mol/l, —○—, MMA, 5 ml; $[TEA]$, 4×10^{-1} mol/l, $[I_2]$, 8×10^{-3} mol/l.

Figure 2. Copolymerization of MMA with styrene at 35°C: MMA+St, 6 ml; $[TEA]$, 2×10^{-1} mol/l; $[I_2]$, 4×10^{-3} mol/l.

fact would be explained by the relatively large photolysability of the $H-C_\alpha$ linkage of TEA, and by the participation of the TEA radicals in the photopolymerization of MMA. Moreover, polymerization by this system was inhibited with oxygen and was also retarded by hydroquinone, but was accelerated with water. As shown in Figure 2, the photosensitized copolymerization of MMA and styrene by the I_2 -TEA system indicates a characteristic composition curve of radical polymerization. The overall rate of photopolymerization of MMA (R_p), when the molar ratio of I_2 to TEA was kept constant at 1/50 and the concentration of I_2 was varied

Figure 3. Effect of iodine concentration on the rate of photopolymerization of MMA at 35°C: MMA, 5 ml; $[I_2]/[TEA]$, 1/50.

from 0.001 to 0.008 mol/l, was measured and plotted against the square root of the I_2 concentration in Figure 3. As already mentioned, MMA can photopolymerize in the presence of TEA a little faster than without TEA and, therefore, the R_p s should not be strictly zero without I_2 . However, in relatively higher concentrations of I_2 , the photopolymerization by TEA could be ignored. Hence, the result in Figure 3 indicates that at higher I_2 concentrations the polymerization rate is proportional to the square root of the concentration of the I_2 -TEA charge-transfer complex. The molecular weights²⁷ (in benzene at 30°C) of poly-MMA obtained at $[I_2] = 8 \times 10^{-3}$, 4×10^{-3} , and 2×10^{-3} ($[I_2]/[TEA] = 1/50$) were 160000, 185000, and 228000, respectively. These facts indicate that the photo-

Table II. Effect of solvent on the photopolymerization of MMA at 30°C^a

Solvent	Induction period, min	R_p , %/hr	ϵ^b
Acetone	0	8.7	20.7
1,2-Dichloroethane	0	7.3	
Acetonitrile	0	6.5	37.5
Methyl Alcohol	0	6.3	32.6
Benzene	36	4.3	2.3
Ethyl Acetate	37	3.5	
None	28	5.6	

^a MMA, 4 ml; Solvent, 3 ml; $[I_2]$, 4×10^{-3} mol/l; $[TEA]$, 2×10^{-1} mol/l.

^b Dielectric constant.

polymerization of MMA in this system proceeds according to a radical mechanism accompanied by bimolecular termination.

The solvent effect on the photopolymerization of MMA by the I_2 —TEA system is shown in Table II, which indicates that no induction period is observed in the use of solvents with high dielectric constant.

The conversion vs. time curves of the polymerization are shown in Figure 4, in which the concentrations of TEA are varied within the range of 0.04 and 0.8 mol/l at a constant concentration of I_2 (8×10^{-3} mol/l). It is obvious that the R_p increases and the induction period becomes shorter with the increase of TEA concentration. Nagakura⁸ has reported that the equilibrium constants of the I_2 —TEA charge-transfer complex in *n*-heptane were 3310 at 30°C and 1740 at 40°C. In Figure 5, the equilibrium constants of the I_2 —TEA complex in MMA were assumed to be 1000, 2500, and 4000 at 35°C, and the concentration of free iodine estimated from this assumption were plotted against induction periods obtained from Figure 4. It was found that even in the absence of the free iodine molecule the induction period still remained. This suggests that primary radicals for the initiation could not be produced directly by the

Figure 4. Effect of TEA concentration on the rate of photopolymerization of MMA at 35°C: $[I_2]$, 8×10^{-3} mol/l; —○—, $[TEA]$, 8×10^{-1} mol/l; —●—, $[TEA]$, 4×10^{-1} mol/l; —×—, $[TEA]$, 2×10^{-1} mol/l; —◐—, $[TEA]$, 8×10^{-2} mol/l; —●—, $[TEA]$, 4×10^{-2} mol/l.

Figure 5. Dependence of induction period on free iodine concentration.

photolysis of the I_2 —TEA charge-transfer complex but from the intermediate compounds derived from the complex by irradiation.

In the course of the photopolymerization with the I_2 —TEA system a crystalline material appeared at higher concentrations of I_2 and was identified as triethylamine hydroiodide by elementary analysis; measurement of melting point and by infrared spectrum. Boule,⁹ and Bist and Person¹⁰ pointed out that triethylamine hydroiodide (TEA-HI) was formed by thermal decomposition of the I_2 —TEA charge-transfer complex in dioxane. Schmulbach, *et al.*,¹¹ have also suggested that the formation of triethylamine hydroiodide could take place by hydrolysis of the I_2 —TEA complex in *n*-heptane. In our investigation, however, we confirmed that triethylamine hydroiodide was formed even in the completely moisture-free MMA solution, by adding I_2 with an excess amount of TEA and allowing it overnight in the dark at room temperature. Polymerization was found not to have occurred by that time when crystalline TEA-HI precipitated out. Therefore, it is reasonable to believe that triethylamine hydroiodide was produced not by hydrolysis with moisture but

Figure 6. Effect of TEA-HI and oily product on photopolymerization of MMA at 35°C: —○—, MMA, 5 ml, TEA-HI, 10 mg; —●—, MMA, 5 ml, TEA, 0.3 ml; —○—, MMA, 5 ml, TEA, 0.3 ml, TEA-HI, 10 mg; —×—, MMA, 5 ml, TEA, 0.3 ml, I₂, 10 mg; —○—, MMA, 5 ml, TEA, 0.3 ml, oily product, 10 mg.

by the abstraction of an hydrogen atom from the TEA molecule. Since the photopolymerization rate of MMA by the I₂—TEA system is larger than that of the TEA-HI system in Figure 6, triethylamine hydroiodide seems not to play a direct role in the initiation reaction.

On the other hand, the red-brown oily product which was obtained by vacuum concentration of the mother liquid of crystalline TEA-HI was able to initiate the photopolymerization of MMA in the presence of TEA without any induction period, as shown in Figure 6. The infrared spectrum of the oily product showed no absorption band for the carbonyl group and differed from that of ethyl α -iodomethyl acrylate. The elementary analysis of the oily product, which was purified by means of extraction with chloroform and then washed with aqueous solution of sodium thiosulfate, gave results of C, 52.87%; H, 6.95%; N, 7.68%. The oily material was

also found to contain 34.23% of total iodine and 25.63% of ionic iodine. The results of thin-layer chromatography suggested that more than three compounds were contained in the oily product. These facts suggest that the oily product might be a mixture of *N,N*-diethyl- α -iodoethylamine, α -*N,N*-diethylaminoethyltriethyl ammonium iodide, *N,N*-diethylvinylamine and so on which could be derived from the abstraction of hydrogen atoms from TEA. According to Lahan, *et al.*,²⁰ however, *N,N*-diethylvinylamine was unstable and gave a polymer very easily—hence the presence of the compound in the oily product is doubtful.

In this work, triethylamine hydroiodide was also obtained from the tetrahydrofuran solution of iodine and an excess of triethylamine, as well as MMA solution. After filtration of the crystalline TEA-HI, the tetrahydrofuran solution was subjected to vacuum concentration. The residual material gave an infrared absorption spectrum similar to that of the oily material obtained from the MMA solution, and also indicated it had a photosensitizing effect on the polymerization of MMA. The rate of polymerization by this material was equal to that of the oily material obtained from I₂—TEA in MMA.

The photopolymerization of MMA was carried out in the presence of I₂ and poly(*N,N*-diethylallylamine) (PDEAA) which has a similar chemical structure to that of TEA. Table III shows that the I₂—PDEAA system has the same sensitizing action as I₂—TEA. The high graft ratio in this system showed larger graft efficiency than that of PDEAA—2,2-azobisisobutyronitrile (AIBN). These facts suggest that the photopolymerization of MMA with I₂—PDEAA is initiated by the same mechanism as with I₂—TEA, and that the graft polymer does not appear to have resulted from the chain transfer reaction

Table III. Photopolymerization of MMA by PDEAA—I₂ system

System	Conversion, %	Graft polymer, g	Graft ratio, %	Graft efficiency, %
PDEAA—I ₂ ^a	11.6	0.3074	514.8	47.2
PDEAA ^b	3.4	0.1168	133.6	41.7
PDEAA—AIBN ^c	10.5	0.0580	16.0	1.6

^a MMA, 5 ml; PDEAA, 50 mg; I₂, 10 mg; 3 hr at 35°C.

^b MMA, 5 ml; PDEAA, 50 mg; 3 hr at 35°C.

^c MMA, 5 ml; PDEAA, 50 mg; AIBN, 8 mg; 40 min at 35°C.

Figure 7. Electronic spectra of I_2 -TEA system in MMA: 1, $[I_2]$, 2×10^{-4} mol/l; 2, $[I_2]$, 2×10^{-4} mol/l, $[TEA]$, 4×10^{-5} mol/l; 3, $[I_2]$, 2×10^{-4} mol/l, $[TEA]$, 8×10^{-5} mol/l; 4, $[I_2]$, 2×10^{-4} mol/l, $[TEA]$, 1.2×10^{-4} mol/l; 5, $[I_2]$, 2×10^{-4} mol/l, $[TEA]$, 2×10^{-4} mol/l; 6, $[I_2]$, 2×10^{-4} mol/l, $[TEA]$, 8×10^{-4} mol/l.

of PDEAA with growing poly-MMA radicals.

In this study, iodine in MMA was found to have an absorption maximum at 475 $m\mu$. In the presence of air, the absorbance at 475 $m\mu$ decreased with the irradiation time of UV light, and *in vacuo*, the decrease in irradiation was accompanied by the appearance of a new band at 360 $m\mu$. Adding TEA to the solution of I_2 in MMA, the absorbance of the 475- $m\mu$ band decreased with increasing concentrations of TEA, and then a new band appeared at 360 $m\mu$. The electronic spectra of I_2 and TEA in MMA are shown in Figure 7. The molar extinction coefficient of the 360 $m\mu$ absorption band of I_2 -TEA in MMA ($\epsilon_{360} = 1.13 \times 10^4$) is about three times as large as that observed in *n*-heptane.⁸ Thus, the 360- $m\mu$ absorption band of I_2 -TEA in MMA, which appeared on irradiation, apparently cannot be ascribed only to the complexed iodine molecule. According to the results obtained by Buckles, *et al.*, the I_3^- ion has two absorption maxima in ethylene chloride ($\epsilon_{295} = 4.51 \times 10^4$ and $\epsilon_{365} = 2.53 \times 10^4$).²¹ Toyoda and Person¹² have also reported that the absorption bands of the I_3^- ion appeared at 363 $m\mu$ and 295 $m\mu$ in a dioxane solution of I_2 -TEA. Consequently, the 360- $m\mu$ charge-transfer band of I_2 -TEA in MMA (Figure 7) might be considered to involve the absorption band of the I_3^- ion.

From these results, the following reaction

schemes are suggested for the photolysis of the I_2 -TEA complex in MMA.

The iodine radicals produced by eq 3 would recombine with each other to form an iodine molecule, and otherwise abstract a hydrogen atom from TEA or MMA to produce HI.

Bhorne and Krause²² reported that from the reaction of trimethylamine with chlorine, chlorotrimethyl ammonium chloride was produced. It is also known that in the case of the ring-formation reaction of *N*-haloamine with sulfuric acid, the first step is the salt formation between *N*-haloamine and sulfuric acid, and then the cation is converted into a free radical by either heat or irradiation of ultraviolet light.²³

Recently, Romans, *et al.*,²⁴ suggested that iodine and the tetramethylhydrazine(TMh) complex decomposed in various polar solvents as follows

These reaction mechanisms may be applicable to the I_2 -TEA system, and at any rate it is reasonable to assume that the radical cation (I) must be formed by eq 1 and 2. γ -Iodomethyl

pyridine is believed to have been formed as the intermediate of the reaction of iodine and γ -pycoline.²⁵ The authors ascertained that alkyl iodides were able to initiate the photopolymerization of MMA in the presence of TEA or sodium thiosulfate, though the system of alkyl iodide and the ammonium salt of TEA could not initiate the polymerization of MMA by UV irradiation.²⁶ The details will be described in a later report.

These considerations, therefore, suggest that the intermediate radical (I) may produce *N,N*-diethyl- α -iodoethylamine (III), the photolysis of which presumably forms the radical (IV) initiating the polymerization of MMA, and that the other reactions of (III) may produce *N,N*-diethylvinylamine, α -*N,N*-diethylaminoethyltriethyl ammonium iodide and so on.

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