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PHOTOPOLYMERIZATION OF METHYL METHACRYLATE AND OTHER ACRYLATES WITH THE USE OF [HYDROXY(TOSYLOXY)IODO]BENZENE AS PHOTOINITIATOR

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ABSTRACT

[Hydroxy(tosyloxy)iodo]benzene (HTIB) was found to be an effective photoinitiator for the solution polymerization of methyl methacrylate. The polymerization is strongly inhibited in the presence of hydroquinone, it is not affected by air, and it is favored in the presence of nucleophilic solvents. A kinetic study of solution polymerization in *N,N*-dimethylformamide indicated a free radical polymerization mechanism involving complexation of initiator molecules with the solvent prior to radical generation, and bimolecular termination of chain radicals. Methyl acrylate and 2-hydroxyethyl methacrylate were also polymerized with HTIB as photoinitiator, but styrene could not be polymerized under similar conditions.

INTRODUCTION

The photoinitiated polymerization of monomers and photocrosslinking of polymers are well-established fields of industrial and academic research and development. An essential ingredient of all these systems is the photoinitiator [1, 2].

Organic polyvalent iodine compounds containing iodine in the +3 valence state have been demonstrated to be useful initiators for a number of polymerizations. Diaryl iodonium salts, $Ar_2I^+ X^-$, have been established as valuable initiators for the photo- and thermally-initiated cationic and radical polymerization of several monomer systems [3]. Irradiation of these salts results in homolytic cleavage of the Ar—I bond to yield reactive radical and radical cation:

$$Ar_2I^+X^- \rightarrow ArI^{\cdot +} X^- + Ar^{\cdot}$$

(Diacyloxyiodo)arenes, $(RCOO)_2IPh$, were also found to be efficient photoinitiators for both radical and cationic polymerizations [4].

In a recent paper we described the use of [hydroxy(tosyloxy)iodo]benzene, PhI(OH)OTs, (HTIB) as a thermal initiator for the radical polymerization of acrylic monomers [5]. HTIB is a readily stable crystalline organoiodine(III) compound which may be viewed as the tosylate salt of phenylhydroxyiodonium ion [6]. It is prepared in a one-pot synthesis by the peracetic acid oxidation of iodobenzene followed by the in-situ addition of *p*-toluenesulfonic acid [7]. It is used as a precursor for the synthesis of alkoxy-substituted diaryliodonium salts, which are excellent photo- and thermal initiators [8]. HTIB was found to be an effective thermal initiator for the radical polymerization of acrylates, so it was thought interesting to study also its use as photoinitiator for the photopolymerization of methyl methacrylate (MMA), methyl acrylate (MA), and 2-hydroxyethyl methacrylate (HEMA). The results obtained are presented in this paper.

EXPERIMENTAL

Reagents

Methyl methacrylate (MMA), methyl acrylate (MA), 2-hydroxyethylmethacrylate (2-HEMA) and styrene (St; from Merck) were vacuum distilled before use. [Hydroxy(tosyloxy)iodo]benzene (HTIB; Aldrich, 96%, mp 134-136°C) was used without further purification. α,α'-Azobisisobutyronitrile (AIBN; from Fluka) was recrystallized from methanol. All solvents were of analytical grade and used after degassing by bubbling nitrogen for 30 minutes.

Photopolymerizations

Polymerizations were conducted in Pyrex tubes. The required amounts of monomer, initiator, and solvent were charged into tubes which were stoppered and placed in a bath thermostated at 20°C. The tubes were illuminated by a Hanovia 450-W high pressure arc lamp. Surrounding the lamp were a glass filter and a quartz well through which pumped cooling water. Tubes were placed at a distance of 10 cm from the lamp. Polymers formed at low concentrations after a given time were removed from the tube and isolated by precipitation in acidified cold methanol (poly-MMA, poly-MA, poly-St) or an excess of water (poly-2-HEMA).

Measurements

The intrinsic viscosities $[\eta]$ of the poly-MMA were determined by measurements in benzene solution at 30°C by use of an Ubbelohde viscometer. The number-average molecular weights $(\overline{M}_n)$ of poly-MMA was then calculated from the viscosity data by using the equation [9]:

$$[\eta] = 8.69 \times 10^{-5} \overline{M}_n^{0.76}$$

The number-average degree of polymerization ($\overline{P}_n$) was also calculated from the equation [10]:

$$\log(\overline{P}_n) = 3.342 + 1.13 \log [\eta]$$

RESULTS AND DISCUSSION

Photopolymerization of MMA

The polymerization of MMA photoinduced by HTIB was carried out in the presence of a solvent because HTIB is not soluble in MMA. In order to ensure homogeneous polymerization, a polar solvent was used such as dimethylsulfoxide (DMSO), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), methanol, acetonitrile (ACN), or tetrahydrofuran (THF). The results obtained are presented in Table 1. Polymerizations were associated with practically no induction time. When irradiation was performed in the absence of HTIB, no polymerization took place.

The rate of polymerization (R_p) was different in the various solvents, indicating that the solvents do not act just as inert diluents but are involved in the polymeri-

TABLE 1. Experimental Data of Solution Polymerization of MMA Induced by HTIB in Various Solvents

Solvent	ϵ[a]	δ,[b] (cal/cm^3)$^{1/2}$	$\Delta\nu_D$,[c] cm^{-1}	$R_p \times 10^4$ mol·L^{-1}·s^{-1} [d]	$R_p \times 10^4$ mol·L^{-1}·s^{-1} [e]
DMSO	45.0	12.0 (m)	141	1.51	0.002
MeOH	32.6	14.5 (s)	–	1.22	0.14
DMF	36.1	12.1 (m)	107	0.91	2.9
DMF[f]				0.76	
DMF[g]				0.75	
DMA	38.9	10.8 (m)	113	0.64	2.8
THF	7.6	9.1 (m)	90	0.56	0.004
ACN	37.5	11.9 (p)	49	0.42	0.6
MMA			37		

[a] Dielectic constant of solvent.

[b] Solubility parameter of solvent, expressed as poor (p), medium (m), or strong (s) hydrogen bonding, taken from Ref. 11.

[c] Electron donating power of solvent [12].

[d] Rate of photopolymerization: [MMA] = 4.71 mol·L^{-1}, [HTIB] = 4.71 × 10^{-3} mol·L^{-1}.

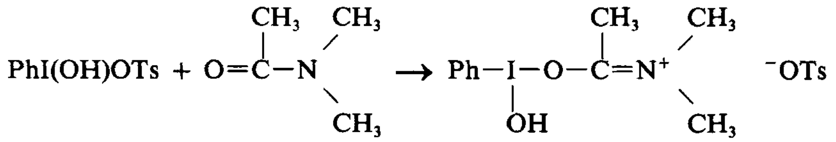
[e] Rate of thermal polymerization at 70°C: [MMA] = 4.71 mol·L^{-1}, [HTIB] = 1.4 × 10^{-3} mol·L^{-1}. Data taken from Ref. 5.

[f] [HTIB] = 2.35 × 10^{-3} mol·L^{-1}.

[g] α,α'-Azobisisobutyronitrile (AIBN) was used instead of HTIB; [AIBN] = 2.35 × 10^{-3} mol·L^{-1}.

zation process. Obviously, there is no linear relationship between R_p and the dielectric constant of the solvent. However, it seems that as the ability of the solvent to form intermolecular hydrogen bonds increases, R_p also increases. The same effect was also observed for the electron-donor properties of the solvent. DMSO, with the highest nucleophilic character, gave the highest R_p value.

HTIB exhibits a strong electrophilic behavior [13, 14], so that complexation between HTIB and solvent is likely to occur, e.g., the following equilibrium in DMF:



$$\mathrm{PhI(OH)OTs} + \mathrm{O{=}C(CH_3){-}N(CH_3)_2} \longrightarrow \mathrm{Ph{-}I(OH){-}O{-}C(CH_3){=}N^{+}(CH_3)_2}\ \ {}^{-}\mathrm{OTs}$$

Additionally, MMA is known to form hydrogen bonds with proton donor solvents through its carbonyl group [15]. As a result of this complexation, the electron acceptor properties of the carbonyl group increase, leading to a reduction in the electron density of the vinyl β-carbon atom, a fact that increases R_p.

In order to gain insight into the photopolymerization mechanism, the polymerization of MMA in DMF solution was further investigated. By using various concentrations of HTIB, R_p was determined (Table 2). From the plot of log R_p vs log [HTIB] (Fig. 1), the initiator exponent was calculated to be 0.5. The plot of the reciprocal degree of polymerization ($1/\bar{P}_n$) vs $[\mathrm{HTIB}]^{0.5}$ gives a straight line which does not pass through the origin (Fig. 2).

R_p values were also measured at several monomer concentrations while using a fixed initiator concentration value. A linear plot of log R_p vs log [MMA] is shown in Fig. 3. From the slope of this plot, the monomer exponent is calculated to be 1.0.

The photopolymerization remained practically uninhibited in the presence of air, but was strongly inhibited by hydroquinone. This observation and the kinetic features clearly support a free radical mechanism. The mode of termination is indicated to be bimolecular in nature. The presence of an intercept on the $1/\bar{P}_n$ axis in the plot of $1/\bar{P}_n$ vs R_p (Fig. 2) indicates that chain-transfer reactions also occur in this polymerization, mainly due to the solvent. The radical generation step may be considered to follow an initial complexation reaction between solvent and initiator

TABLE 2. Photopolymerization of MMA in DMF Solution[a] Induced by Various Amounts of HTIB

[HTIB] × 10^3 mol·L^{-1}	$R_p \times 10^4$ mol·L^{-1}·s^{-1}	$[\eta]$,[b] dL/g	$\bar{M}_n$	$1/\bar{P}_n \times 10^3$
1.41	0.55	0.58	106,650	0.849
2.36	0.74	0.52	94,100	0.945
4.71	0.94	0.43	71,900	1.191
23.57	1.90	0.32	49,200	1.660

[a] [MMA] = 4.71 mol·L^{-1}.

[b] Determined in benzene at 30°C.

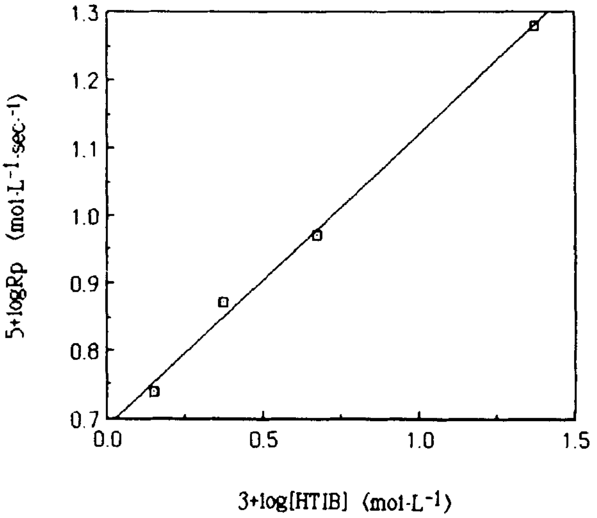


FIG. 1. Rate of photopolymerization (R_p) versus initial concentration of HTIB; [MMA] = 4.71 mol·L^{-1} in DMF.

molecules to form a complex, which is then decomposed upon irradiation, as in the case of diaryl iodonium salts [3]:

$$\text{PhI(OH)OTs} + \text{Solvent}{-}\text{H} \overset{K}{\rightleftharpoons} [\text{PhI(OH)OTs} \cdots \text{SH}] \xrightarrow[k_d]{h\nu}$$

$$\text{PhI} + {}^{\cdot}\text{OH} + \text{TsOH} + \text{S}^{\cdot}$$

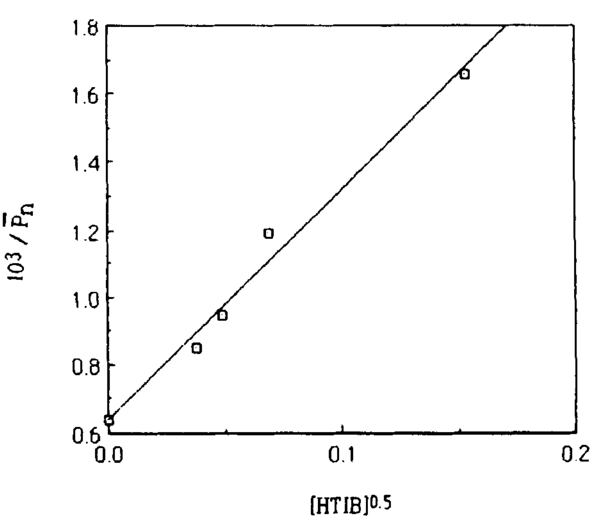


FIG. 2. Plot of $1/\overline{P}_n$ versus [HTIB]$^{0.5}$; [MMA] = 4.71 mol·L^{-1} in DMF.

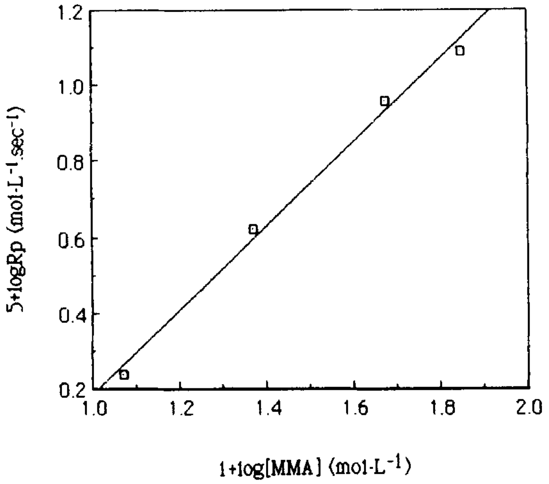


FIG. 3. Rate of photopolymerization versus initial concentration of MMA; [HTIB] = 4.71 × 10^{-3} mol·L^{-1} in DMF.

Taking into account that termination is bimolecular, R_p may be expressed as

$$R_p = k_p(k_dK/2k_t)^{0.5}[\mathrm{HTIB}]^{0.5}[\mathrm{MMA}]^{1.0}$$

where K is the equilibrium constant of the complexation reaction between solvent and initiator molecules, and k_p, k_d, and k_t have their usual significance.

The photopolymerization of MMA was also carried out with the use of α,α'-azobisisobutyronitrile (AIBN) as photoinitiator. The R_p observed was about equal with that obtained with HTIB under similar polymerization conditions (Table 1). This indicates an identical fk_i value for the two initiators.

In Table 1 the R_p values determined in previous work [5] for the thermal polymerization of MMA with HTIB are also presented. Comparison of these data with those obtained in this work shows that the effect of the solvent on R_p is quite different in thermally and photoinduced polymerization. In thermal polymerization, practically no polymerization occurred in DMSO and THF, and R_p in methanol was lower than that in ACN. Also, a unity dependence of R_p (in DMF) on initiator concentration was found, indicating that a complicated nucleophilic reaction of solvent occurred with HTIB at the high temperature of thermal polymerization (70°C). However, R_p in ACN was similar for both thermal and photoinitiation. This may be due to the low electron donor ability of ACN; in ACN the thermal decomposition of HTIB probably follows the homolytic path already proposed for photodecomposition.

It is known [14] that treatment of HTIB with various alkenes gives the corresponding 1,2-bis(tosyloxy)alkanes via electrophilic addition of the phenyl(hydroxy)-iodonium ion to the double bond of the alkene. Isolation of the ditosylate derivatives requires careful control of the reaction temperature, because in some cases they are decomposed even on standing at room temperature. Although MMA is an electron-poor olefinic compound (it is polymerized only by radical or anionic polymerization), it may react under polymerization conditions with HTIB to form

TABLE 3. Photopolymerization of Vinyl Monomers with HTIB

Monomer (M)	[M], $\mathrm{mol \cdot L^{-1}}$	[HTIB] × 10^3 $\mathrm{mol \cdot L^{-1}}$	Solvent	$R_p \times 10^4$ $\mathrm{mol \cdot L^{-1} \cdot s^{-1}}$
MMA	4.7	2.36	DMF	0.74
MA	5.5	2.78	DMF	6.78
HEMA	4.1	1.64	DMF	0.86
HEMA	4.1	2.47	DMF	1.69
HEMA	8.2	4.11	–	2.45
HEMA	8.2	4.93	–	2.72
HEMA	8.2	6.58	–	3.12
HEMA	8.2	8.22	–	3.37
St	4.4	21.80	–	0.11

the corresponding ditosylate. This should be subject to facile thermal decomposition, producing radicals capable of initiating the polymerization of MMA. Such a reaction scheme as the initiation mechanism of thermal polymerization could explain the strong influence of the solvent on R_p. However, a reaction between HTIB and the polymerization solvent also occurs, as shown in a polarographic study [16]; actually, HTIB oxidized all common organic solvents at room temperature, so aqueous solutions had to be used.

Photopolymerization of Other Vinyl Monomers

Besides MMA, three other vinyl monomers (MA, HEMA, and St) were photopolymerized by HTIB (Table 3). MA showed the highest polymerizability while St polymerized poorly with HTIB. HTIB is soluble in HEMA, so the bulk polymerization of this monomer was also studied at various concentrations of HTIB. All polymerizations showed an induction period of about 10–20 minutes. A plot of log R_p against log [HTIB] gave a straight line having a slope of 0.5. This is further proof for the free radical mechanism of the HTIB-photoinduced polymerization of acrylates.

When HTIB was added to HEMA, a yellow color appeared, then gradually disappeared on irradiation; the solution finally became colorless. A complex between the hydroxyl group of HEMA and the phenyl(hydroxy)iodonium ion of HTIB may occur in this case, which is then decomposed upon irradiation. However, no UV absorption spectra showed the formation of such a complex. St, which is an electron-rich monomer and can be polymerized by both radical and cationic polymerization, is not polymerized by HTIB because it reacts with HTIB at room temperature to give an addition product, bis(tosyloxy)phenyl ethane [14].

CONCLUSION

[Hydroxy(tosyloxy)iodo]benzene is another organoiodine(III) compound which is an effective photoinitiator for the free radical solution polymerization of acrylates. The initiation is believed to involve complexation of initiator molecules with the solvent and homolytic decomposition of the complex upon irradiation.

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