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[Hydroxy(tosyloxy)iodo]benzene as Thermal initiator for the Radical Polymerization of Methyl Methacrylate

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[HYDROXY(TOSYLOXY)IODO]BENZENE AS THERMAL INITIATOR FOR THE RADICAL POLYMERIZATION OF METHYL METHACRYLATE

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ABSTRACT

The thermal polymerization of methyl methacrylate in a solution of *N,N*-dimethylacetamide has been studied using [hydroxy(tosyloxy)-iodo]benzene (HTIB) as the initiator. The rate of polymerization was a direct function of the monomer and initiator concentrations. The initiator and monomer exponent values expressing this dependence were found to be 1.0 and 0.8, respectively. The overall activation energy of polymerization was estimated to be 45 $\mathrm{kJ \cdot mol^{-1}}$. The polymerization was inhibited in the presence of hydroquinone. The effect of various solvents on the polymerization rate was studied. The polymer prepared with HTIB (0.47×10^{-3} $\mathrm{mol \cdot L^{-1}}$) had a number-average molecular weight of 138,000 and a glass transition temperature of 106°C. The polymer showed good thermal stability as determined by thermogravimetric analysis.

INTRODUCTION

Organic compounds of polycoordinated iodine are increasingly finding use as initiators in a number of polymerizations. Thus, diaryliodonium salts (DAS) have been established as a class of efficient photoinitiators for cationic [1, 2] as well as radical [3, 4] polymerizations. Several detailed mechanistic studies [5] have been

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performed on their photolysis, whose gross decomposition mode may be represented by the following equations:

$$\mathrm{Ar_2I^+X^-} \xrightarrow{h\nu} \mathrm{ArI^{+\cdot}} + \mathrm{Ar^{\cdot}} + \mathrm{X^-}$$

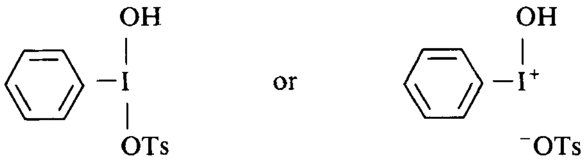
$$\mathrm{Ar_2I^+X^-} + \mathrm{Solvent{-}H} \rightarrow \mathrm{Ar^{\cdot}} + \mathrm{ArI} + \mathrm{S^{\cdot}} + \mathrm{HX}$$

(DAS)

where X = $\mathrm{ClO_4^-}$, $\mathrm{BF_4^-}$, $\mathrm{PF_6^-}$, $\mathrm{AsF_6^-}$, etc.

These salts can also be used as thermal initiators in the presence of catalytic amounts of copper compounds [6, 7]. Recently, it was found that (diacyloxyiodo)-benzenes, $\mathrm{(RCOO)_2IPh}$, are also efficient photoinitiators for both radical and cationic polymerization [8].

[Hydroxy(tosyloxy)iodo]benzene (HTIB) is a stable crystalline organoiodine-(III) compound which may be viewed as the tosylate salt of phenylhydroxyiodonium ion [9]. In the present work, its use as a thermal initiator for the polymerization of methyl methacrylate (MMA) is studied. It is found that HTIB initiates the radical solution polymerization of MMA in various polar solvents. 2-Hydroxyethyl methacrylate (HEMA) and styrene (St) were also polymerized by HTIB both in bulk and in DMA solution.



(HTIB)

EXPERIMENTAL

Reagents

Methyl methacrylate (Merck) was distilled before use. Polymerization solvents were of analytical grade and used without further purification but after degassing by bubbling nitrogen for 30 minutes. [Hydroxy(tosyloxy)iodo]benzene (HTIB) (Aldrich, 96%, mp 134–136°C) was used without further purification.

Polymerizations

Polymerizations were conducted in Pyrex tubes. The required amounts of monomer, initiator, and solvent were charged into a tube which was flushed with nitrogen, stoppered, and placed in a thermostated bath. After a given time the content of the tube was poured into a large amount of acidified cold methanol to precipitate the polymer. This was isolated by decanting and drying in a vacuum oven at 70°C to constant weight.

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Measurements

The intrinsic viscosity $[\eta]$ of the polymers was measured in benzene at 30°C by an Ubbelohde viscometer. Number-average molecular weights ($\overline{M}_n$) of poly(methyl methacrylate) (PMMA) were calculated from the viscosity data by using the equation [10]:

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

From the viscosity data in benzene, the number-average degree of polymerization ($\overline{P}_n$) was calculated from the equation [11]:

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

The IR spectrum of PMMA was obtained on a Perkin-Elmer 1310 spectrophotometer. The glass transition temperature (T_g) of PMMA was determined by a Differential Scanning Calorimeter (DSC-2, Perkin-Elmer) at a heating rate of 20°C/min. The thermal stabilities of HTIB and PMMA were studied by thermogravimetric analysis (TGA), accompanied by derivative thermogravimetric analysis (DTGA). The apparatus used for these measurements was a Perkin-Elmer Thermobalance (TG-2).

RESULTS AND DISCUSSION

[Hydroxy(tosyloxy)iodo]benzene (HTIB) is not soluble in MMA, even after heating at 70°C. The homogeneous polymerization of MMA by HTIB was carried out in DMA at 70°C. The effect of HTIB concentration on the polymerization rate (R_p) was studied by varying its concentration from 0.47 to 2.36×10^{-3} mol·L^{-1} and keeping that of MMA constant. From the slopes of the conversion-time plots (Fig. 1), the initial rates of polymerization were calculated. These values are presented in the second column of Table 1. Polymerizations were associated with practically no induction period.

A study of Table 1 shows that R_p increases with increasing HTIB concentration whereas the molecular weight ($\overline{M}_n$) decreases.

The plot of log R_p versus log [HTIB] (Fig. 2) is linear, and its slope gives the initiator exponent as 1.0. This value is fairly higher than 0.50, i.e., the value expected for a simple radical polymerization of a mutual bimolecular termination.

The reaction order of MMA was estimated by changing the concentration of MMA as shown in Fig. 3. The monomer exponent obtained from the slope of the linear plot of log R_p against log M is found to be 0.8, close to the 1.0 expected for a simple free radical polymerization. From the results obtained, R_p can be expressed by

$$R_p = [\mathrm{HTIB}]^{1.0}[\mathrm{MMA}]^{0.8}$$

The thermal polymerization of MMA by HTIB was also carried out in the presence of oxygen and hydroquinone. Oxygen had little inhibition effect, but hydroquinone produced a profound inhibitory effect, corroborating the radical character of the polymerization.

The plot of the reciprocal degree of polymerization ($1/\overline{P}_n$) against R_p is linear

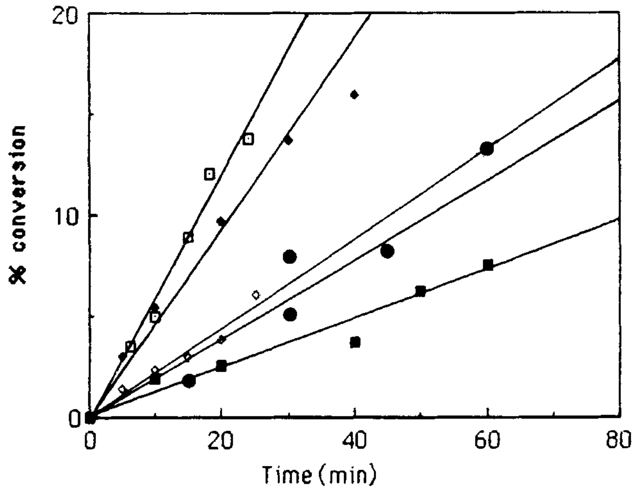

FIG. 1. Plots of percent conversion of MMA in DMA at 70°C with HTIB as initiator at various HTIB concentrations: (□) [HTIB] = 2.36 × 10^{-3} mol·L^{-1}; (◆) 1.40 × 10^{-3} mol·L^{-1}; (●) 0.94 × 10^{-3} mol·L^{-1}; (◇) 0.78 × 10^{-3} mol·L^{-1}; (■) 0.47 × 10^{-3} mol·L^{-1}; [MMA] = 4.71 mol·L^{-1}.

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(Fig. 4), revealing a bimolecular termination mode of polymerization. The presence of an intercept on the $1/\overline{P}_n$ axis indicates that chain transfer reactions also take place in the polymerization.

On the basis of the above observations, it is concluded that the polymerization proceeds via a radical mechanism with bimolecular termination but with a complicated initiation mechanism as indicated by the first-order dependence of R_p on the initiator concentration.

The apparent activation energy (E_a) of MMA polymerization by HTIB in DMA was calculated from the observed rates of polymerization at four different

TABLE 1. Polymerization of MMA[a] Initiated by [Hydroxy(tosyloxy)iodo]benzene in DMA at 70°C

[Initiator] × 10^3 mol·L^{-1}	R_p × 10^4 mol·L^{-1}·s^{-1}	[η],[b] dL·g^{-1}	$\overline{M}_n$	$1/\overline{P}_n$ × 10^3
0.47	0.92	0.70	138,000	0.681
0.78	1.47	0.68	132,300	0.703
0.94	1.71	0.64	122,500	0.750
0.94	1.78			
1.40	3.15	0.61	115,000	0.795
2.36	4.73	0.57	106,500	0.859

[a] [MMA] = 4.71 mol·L^{-1}.

[b] Determined in benzene at 30°C.

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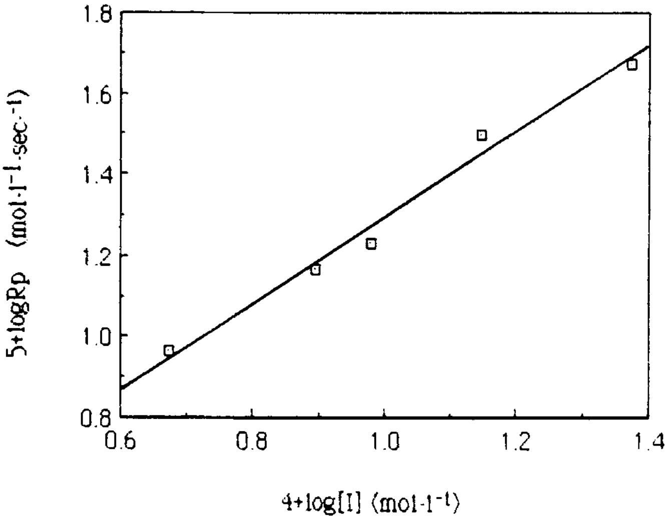


FIG. 2. Rate of polymerization versus initial concentration of HTIB; [MMA] = 4.71 mol·L^{-1} in DMA at 70°C.

temperatures (40, 50, 60, and 70°C). From the Arrhenius plot of log R_p vs $1/T$ (Fig. 5), E_a was found to be 45 kJ·mol^{-1} (10.6 kcal·mol^{-1}). This value is smaller than that of the ordinary radical polymerization of MMA (~ 16 kcal·mol^{-1}).

The polymerization of MMA by HTIB was also carried out in some other solvents (Fig. 6). The polymerization rate in DMF is almost the same as that in DMA, but it is smaller in the less polar CH_3CN or CH_3OH. The presence of water

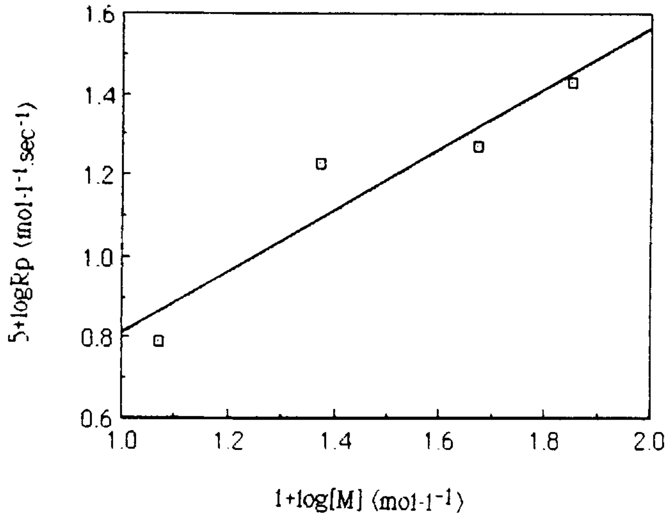


FIG. 3. Rate of polymerization versus initial concentration of MMA; [HTIB] = 1.4 × 10^{-3} mol·L^{-1} in DMA at 70°C.

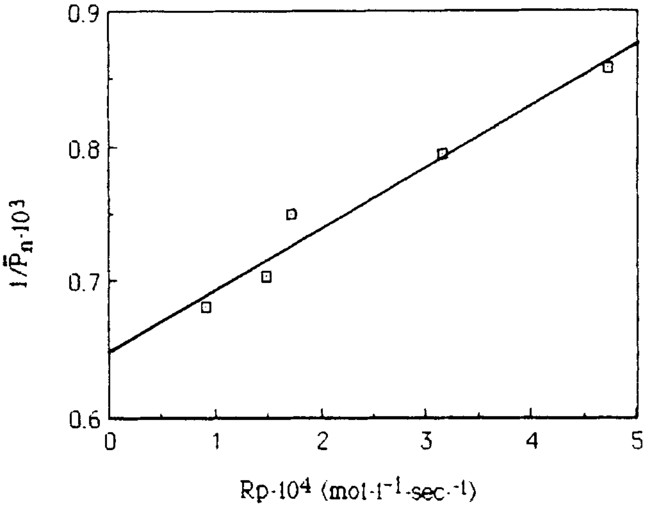
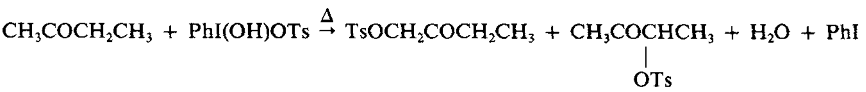


FIG. 4. Plots of $1/\overline{P}_n$ versus R_p in DMA at 70°C. [MMA] = 4.71 mol·L^{-1}.

in the reaction mixture caused a decrease of R_p. When DMSO, THF, or methyl ethyl ketone (MEK) was used, no practical polymerization was observed. It has been reported that HTIB reacts thermally with MEK according to the following, apparently ionic [12], scheme:



$$CH_3COCH_2CH_3 + PhI(OH)OTs \xrightarrow{\Delta} TsOCH_2COCH_2CH_3 + CH_3CO\underset{\substack{|\\ OTs}}{C}HCH_3 + H_2O + PhI$$

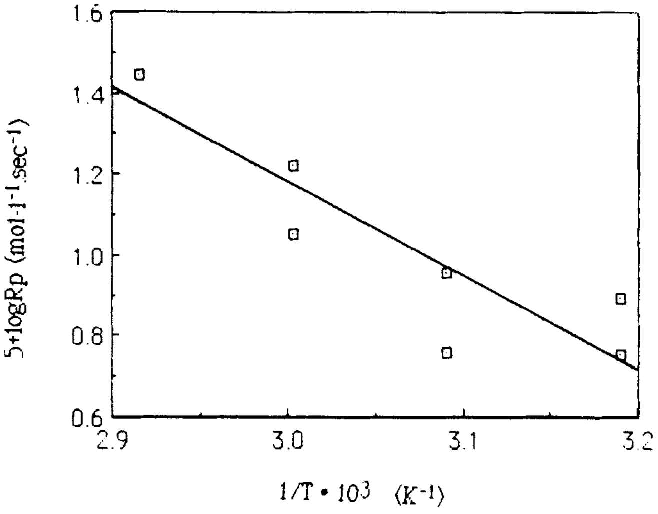


FIG. 5. Arrhenius plot of log R_p versus $1/T$; [MMA] = 4.71 mol·L^{-1}, [HTIB] = 1.4×10^{-3} mol·L^{-1}.

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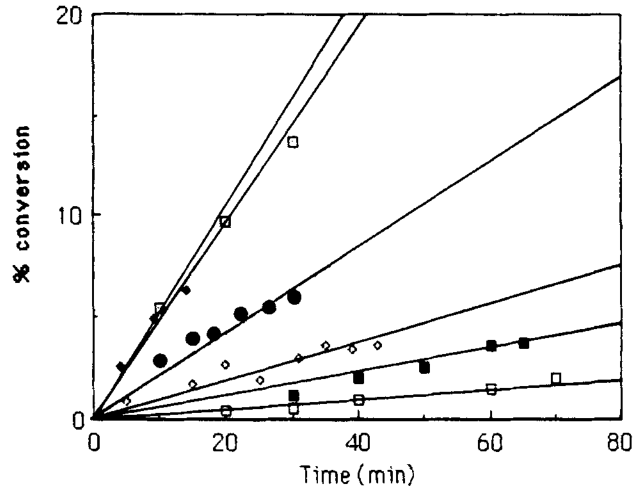

FIG. 6. Effect of solvent on the polymerization rate of MMA with HTIB at 70°C. [MMA] = 4.71 mol·L^{-1}, [HTIB] = 1.4 × 10^{-3} mol·L^{-1}; (⊡) DMF, (◆) DMA, (●) DMA: H_2O (3:1), (◇) DMA:H_2O (1:1), (■) CH_3CN, (□) CH_3OH.

Two more vinyl monomers, i.e., 2-hydroxyethyl methacrylate (HEMA) and styrene (St), were also polymerized by HTIB at 70°C, both in bulk and in DMA solution. The use of DMA caused an increase of the R_p in the case of HEMA but a decrease in St (Table 2). Comparison of the R_p of the solution polymerization of MMA, HEMA, and St with HTIB in DMA under the same conditions (Table 2) showed that their polymerizability is in the order MMA > HEMA $\gg$ St. It is known [13] 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 decompose even on standing at room temperature. Although MMA and HEMA are electron-poor olefinic compounds, they may react with HTIB under the polymerization conditions to form the corresponding ditosylates; these should be subject to facile

TABLE 2. Polymerization of Vinyl Monomer Initiated by [Hydroxy(tosyloxy)iodo]benzene at 70°C

Monomer	[Monomer], mol·L^{-1}	Solvent	[Initiator] × 10^3 mol·L^{-1}	R_p × 10^3 mol·L^{-1}·s^{-1}
MMA	4.7	DMA	2.4	0.395
HEMA	4.1	DMA	8.2	0.102
HEMA	8.2	–	16.4	0.009
St	4.4	DMA	8.7	0.003
St	8.7	–	17.5	0.013

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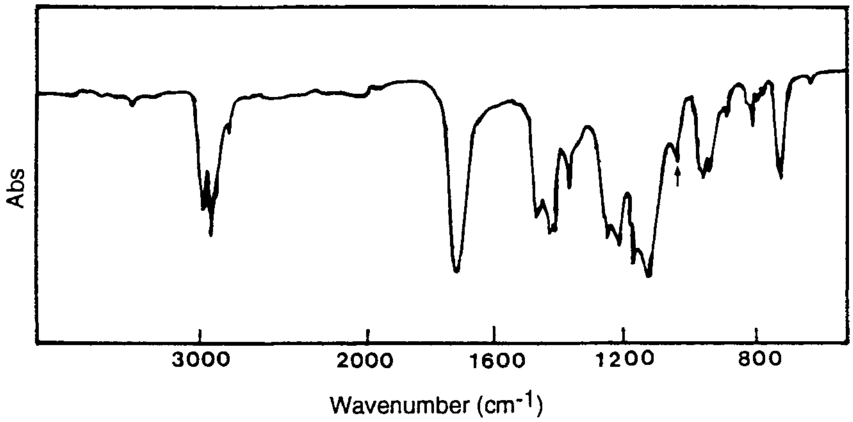

FIG. 7. IR spectrum of PMMA prepared by solution polymerization in DMA at 70°C with HTIB.

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thermal decomposition, producing radicals capable of initiating the polymerization of MMA and HEMA. Such a reaction scheme for the initiation mechanism of polymerization could explain the strong influence of solvent on the R_p values.

However, a reaction between HTIB and the polymerization solvent also occurs, as shown in a polarographic study [14]; actually, HTIB oxidized all common organic solvents at room temperature, so that aqueous solutions had to be used.

HTIB is relatively stable in the solid state. DSC showed that it decomposes upon melting. This decomposition was also observed by TGA and DTGA. The maximum rate of this decomposition occurs at 145°C; its weight loss (5%) indicates that it is probably due to the elimination of water by scission of the I—OH bond. We have not conducted any experiment on the thermal stability of HTIB in solution. However, in our polymerizations we observed that when solutions of HTIB in DMA were allowed to stand for several hours at room temperature, they became ineffective. This behavior is believed to be the result of decomposition of the initiator.

As far as the polymerization of St by HTIB is concerned, it must be mentioned that St, an electron-rich olefinic compound, is known [13] to react neat with HTIB, affording 1,1-bis(tosyloxy)-2-phenylethane (mp 92.5-95°C); in CH_2Cl_2 solution, however, the more thermally stable 1,2-bis(tosyloxy)-1-phenylethane (mp 116-118°C) is formed. This behavior could explain the lower polymerization rate of St observed in the presence of DMA than that in bulk, and also the diminished polymerizability of St in comparison with that of MMA and HEMA.

Poly(methyl methacrylate) (PMMA), obtained by HTIB ($c = 0.47 \times 10^{-3}$ mol·L^{-1}), was characterized by IR spectroscopy, DSC, TG, and DTG analysis. The IR spectrum of a film of PMMA in $CHCl_3$ showed a band at 1060 cm^{-1} (Fig. 7), characteristic of its syndiotactic structure [15]. This polymer had a T_g at 106°C, as determined by DSC, which was accompanied by a small endothermic peak due to the relaxation phenomena. A second endothermic peak was also observed in the

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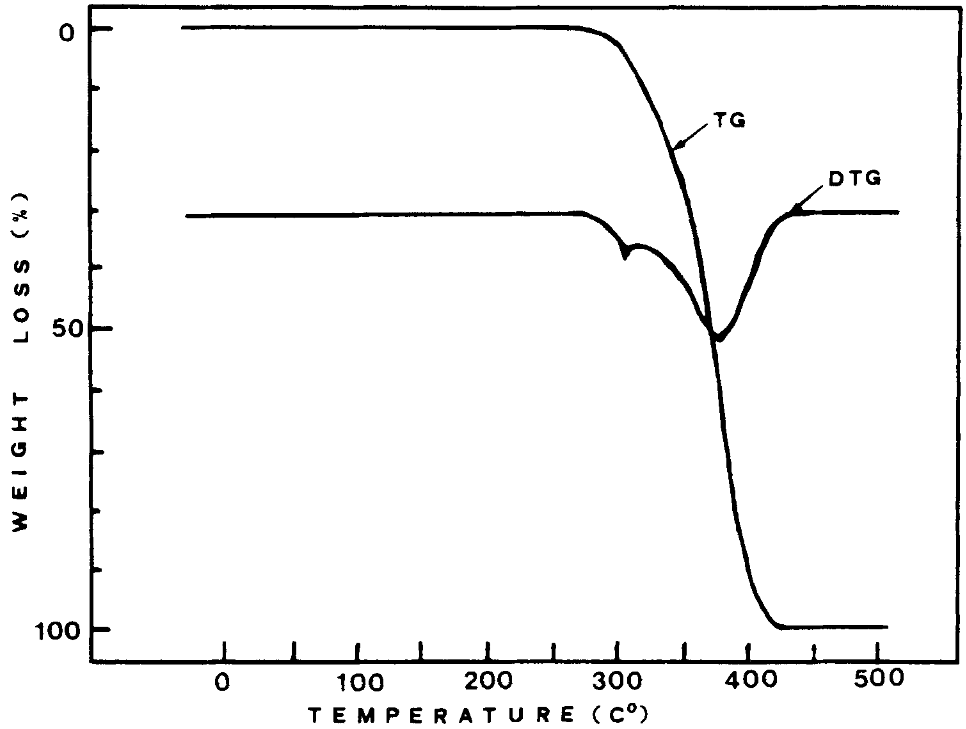

FIG. 8. TGA and DTGA curves of PMMA prepared by HTIB.

DSC curve at 185°C, which is characteristic of high molecular weight PMMA and is believed to be due to disentanglements of the high molecular weight chains [16]. PMMA showed good thermal stability (Fig. 8). In radically prepared PMMA, two main degradation reactions generally occur [17]. The first, at lower temperatures, is monomer evolution initiated at the unstable terminal double bonds present in some of the macromolecules as a consequence of the disproportionation termination reaction, while the second follows the random bond scission of the polymer chains. These reactions have different energies of activation depending on the chain length, the mechanism of degradation process, the range of conversion, and percentage of double-bonded chain ends in the polymer [17]. The thermal stability of PMMA also depends on the type of initiator used in the polymerization and the structure of initiator residue incorporated at the chain end [18].

The PMMA prepared by HTIB showed a small weight loss (11%) during the first stage of decomposition between 270-320°C with a maximum rate at 300°C, and a high weight loss (89%) during the second stage between 320-420°C with a maximum rate at 380°C. The relatively low weight loss observed at the first stage of decomposition suggests that the initiator residual bound to the chain ends is thermally stable and that this weight loss is rather due to the unstable double terminal bonds. No residue has been found at the end of degradation. The thermal stability of PMMA was similar in both nitrogen and air atmospheres.

CONCLUSIONS

HTIB was found to be an efficient initiator for the thermal polymerization of several vinylic monomers. The polymerization seems to proceed via a radical mechanism with bimolecular termination but with a complicated initiation mechanism presumably involving monomer–HTIB and solvent–HTIB interactions as well. The polymerization rate showed a strong solvent effect. The polymerizability of the monomers studied followed the order MMA $>$ HEMA $\gg$ St.

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