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Photopolymerization of methyl methacrylate initiated by benzophenone/aromatic tertiary amines

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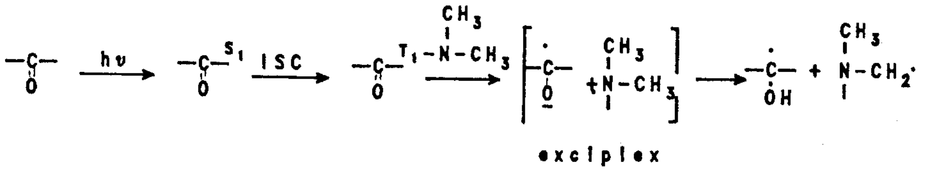
SUMMARY

The photopolymerization of methyl methacrylate initiated by benzophenone-tertiary aromatic amines was studied under irradiation at 365 nm. The initiating amino radicals were investigated with combined ESR and spin-trapping method. The rate of polymerization for different amines was found in the sequence of p-hydroxymethyl-N,N-dimethylaniline > N,N-dimmethyltoluidine > N,N-dimethylaniline > p-methyl-N,N-dihydroxyethylaniline. The influence of diphenylmethanol on the polymerization reveals the incapacity of the benzophenone ketyl radical to initiate, while the amino end-group was detected in the polymers. This end-group can interact with benzophenone again, leading to initiate further polymerization to give a copolymer.

INTRODUCTION

The photoreaction of aromatic ketones especially benzophenone (BP) with tertiary aromatic amines has been known for many years. (1-8) It is proposed that the excited singlet benzophenone undergoes very efficient intersystem crossing(ISC) to become its triplet state, then forms an exciplex with the amine, followed by hydrogen-abstraction to produce radicals:



Ghosh(9) reported the photopolymerization of methyl methacrylate (MMA) initiated by BP/N,N-dimethylaniline(DMA), but no detailed mechinism data were given. Their polymerization was run without filtering the light < 365 nm. Under this condition, as we reported before(10,11), the aromatic tertiary amines alone can photoinitiate. In this paper we want to to reinvestigate this initiation under condititions without much interference of amine-

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*Current address: Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA initiation and intend to present more mechanism results, including utilizing this reaction to prepare block copolymers.

EXPERIMENTAL

Materials

methyl methacrylate (MMA) was dried with CaH_2 and then distilled under nitrogen before use. Aromatic amines were purified by either distillation or recrystallization. Benzophenone (BP) was purified by recrystallization in ethanol/water (1:1), m.p.48-49°C. Diphenyl methanol was recrystallized in petroleum ether (60-90°C), m.p. 66-67°C. p-Hydroxymethyl-N,N-dimethylaniline (HMDMA) was synthesized according to reference (12), b.p. 123°C/1 mm. 2-Methyl-2-nitroso-propane (MNP) was purchased from Aldrich and used without further treatment.

Instrumentation

Fluorescence spectra were recorded with Hitachi-850 Fluorescencephotometer. GPC traces were determined by Shodex A-805 column calibrated with polystyrene standards, with chloroform as eluent.

Procedure

The rate of photopolymerization was measured dilatometrically at 25°C. A 300w high-presure mercury lamp served as the radiation source, and a $CuSO_4$ solution filter ($CuSO_4 \cdot 5H_2O$ 250g/1lH_2O, 1cm) was used to cut off the light above 365 nm wavelengths(13). The reaction solution was bubbled with purified nitrogen before polymerization.

The polymer samples obtained were purified with repeated solution-precipitation method in acetone/methanol until no absorption signal of the initiators was foundin the washing solution and then the end-group was detected by fluorescence spectrophotometry or non-aqueous titration.

Non-aqueous titration was carried out as described in reference (14). The PMMA sample obtained from the photopolymerization was dissolved in benzene/acetic acid mixture solvent and then titrated with perchloric acid with crystal violet as indicator.

ESR signals were measured in freshly distilled benzene solution. The mixture sample composed of BP, amine and MNP in ESR tube was bubbled with purified nitrogen for 5 minutes, then was irradiated with 365 nm light. After a certain period of time the ESR signal was recorded.

The viscosity of PMMA was measured in benzene at 30°C and the molecular weight(MW) was calculated according to the equation(15):

$$[\eta] = 8.69\text{x}10^{-5}MW^{0.75}$$

RESULTS AND DISCUSSION

Exploratory Experiments

Although some authors reported the photopolymerization of MMA initiated by BP alone without H-donor(16), the rate was much slower than in the presence of amines. BP/amine system is very effective for the initiation of MMA polymerization, but not for St and VAc. These donor monomers may physically quench excited BP efficiently(17,18) and, furthermore, react with it to form oxetanes(19). Acrylonitrile(AN) is another active monomer photoinitiated by this system. However, its bulk polymerization produces polymer precipitation which may shield the incident light so complicate the kinetics. N,N-Dimethylformamide(DMF), the most common solvent for PAN, will interact with BP under irradiation to produce initiation radicals. Consequently, AN was also not used in this study.

Table 1 Photopolymerization of MMA with Variuos Initiators

Initiator(mol/l)	Rp(mol/l.s.)
0	2.1×10^{-5}
BP(5×10^{-3})	3.1×10^{-5}
DMA(10^{-2})	3.2×10^{-5}
BP(5×10^{-3})/DMA(10^{-2})	1.9×10^{-4}
BP(5×10^{-3})/DMF(10^{-1})	5.2×10^{-4}

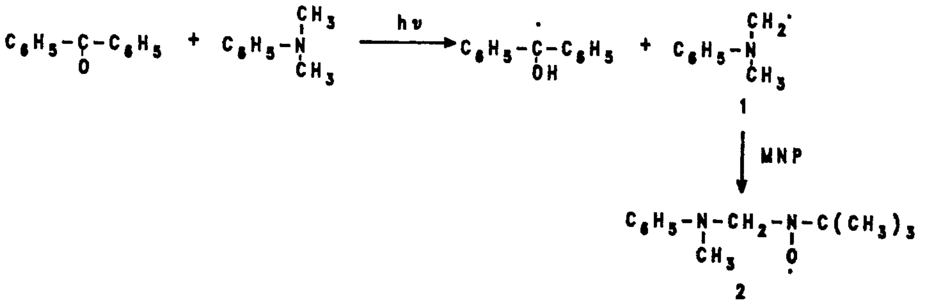
In previous papers, we reported the polymerization of vinyl monomers initiated by aromatic amines alone (10,11). The aromatic tertiary amines have low absorbance at 365 nm.(11) At lower concentration (< 2×10^{-2}mol/l) the amine-initiated polymerization can be neglected compared with the BP/amine-initiated polymerization.

The experimental data is collected in Table 1.

ESR Study on the intermediates

The intermediate radicals produced from BP-aromatic tertiary amine photoreaction system were investigated by combination of spin-trapping reagent (MNP) and ESR.

Fig. 1 shows the ESR signal of BP-DMA-MNP system. The calculated splitting constants ($a_{\alpha N}$ = 13.95G, $a_{\beta H}$ = 7.5G, $a_{\beta N}$ = 3.0G) are identical with the literature data for the combined product of MNP and N,N-dimethylanilino radical(20,21). So we propose the following reactions:



$$C_6H_5\text{-}\underset{O}{C}\text{-}C_6H_5 + C_6H_5\text{-}\overset{CH_3}{\underset{CH_3}{N}} \xrightarrow{h\nu} C_6H_5\text{-}\overset{\cdot}{\underset{OH}{C}}\text{-}C_6H_5 + C_6H_5\text{-}\overset{CH_2^{\cdot}}{\underset{CH_3}{N}}$$

1

$$\downarrow \text{MNP}$$

$$C_6H_5\text{-}\underset{CH_3}{N}\text{-}CH_2\text{-}\underset{\dot{O}}{N}\text{-}C(CH_3)_3$$

2

The ESR signal is assigned to radical 2. BP ketyl radical is not reactive, so no signals from its combined product with MNP is observed.

Fig.2 shows the ESR signal of BP-HDEA-MNP system. DHET possesses α-hydrogen atoms from both amine and hydroxyl groups. However, only the product from combined MNP and amino radical was observed. This implies that excited BP prefers to abstract the α-hydrohen from amine group rather than from hydroxy group:

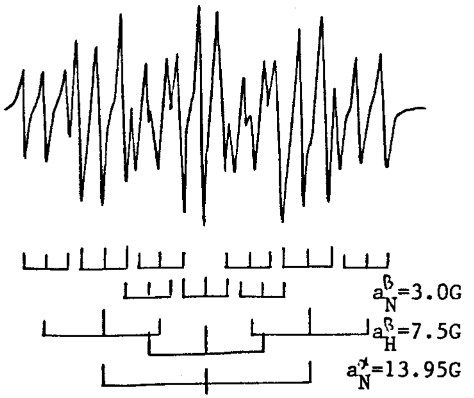


Fig. 1 ESR plot of BP/DMA/MNP after irradiation for 4 minutes

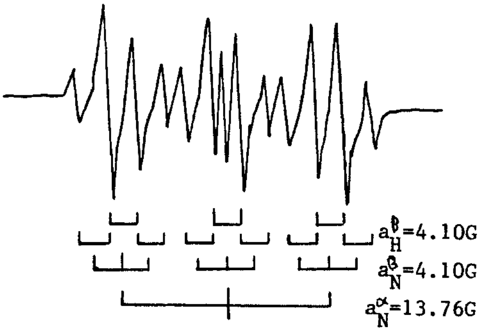
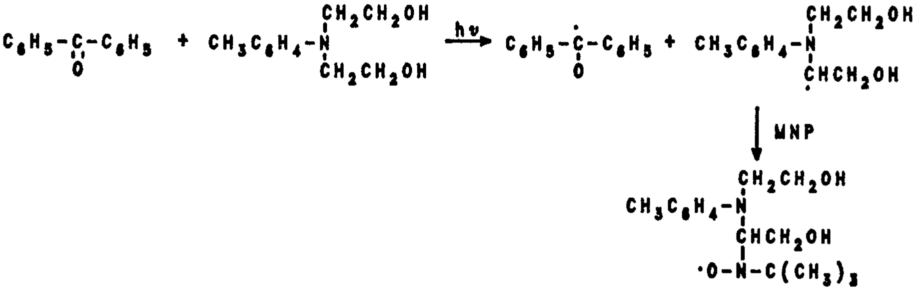


Fig. 2 ESR plot of BP/DHEA/MNP after irradiation for 4 minutes



$$C_6H_5\text{-}\underset{O}{\overset{\|}{C}}\text{-}C_6H_5 + CH_3C_6H_4\text{-}N(CH_2CH_2OH)_2 \xrightarrow{h\nu} C_6H_5\text{-}\underset{O}{\dot{C}}\text{-}C_6H_5 + CH_3C_6H_4\text{-}N(CH_2CH_2OH)(\dot{C}HCH_2OH) \xrightarrow{MNP} CH_3C_6H_4\text{-}N(CH_2CH_2OH)\text{-}CH(CH_2OH)\text{-}N(\cdot O)\text{-}C(CH_3)_3$$

Polymerization Initiated with BP/Different Amines

Table 1 shows that the rate of polymerization for differnt amines decreases in the order of HMDMA > DMT > DMA, which is in agreement with the decreased order of electron-donation abilities of the amines. This reveals the importance of the exciplex as an intermediate in the initiation. Although DHTA is a stronger electron-donor than DMA, the steric effect and electron effect of methyl group may impede the α-H abstraction. So this amine shows a lowest Rp in this sequence.

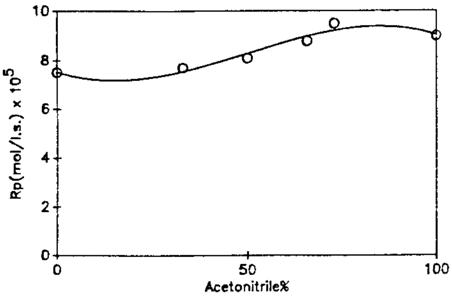
Table 2 Photopolymerization of MMA initiated by BP/different amines

Amine	Rp(mol/l.s.)	
$HOCH_2C_6H_4N(CH_3)_2$ (HMDMA)	2.2×10^{-4}	8.6×10^{4}
$CH_3C_6H_4N(CH_3)_2$ (DMT)	2.0×10^{-4}	9.1×10^{4}
$C_6H_5N(CH_3)_2$ (DMA)	1.9×10^{-4}	9.3×10^{4}
$CH_3C_6H_4N(C_2H_4OH)_2$ (DHEA)	1.7×10^{-4}	9.8×10^{4}

$[BP]=5\times10^{-3}$mol/l, $[amine]=10^{-2}$mol/l

Effect of DPM on the Polymerization

The photoreaction of BP with DPM forms only BP ketyl radicals:



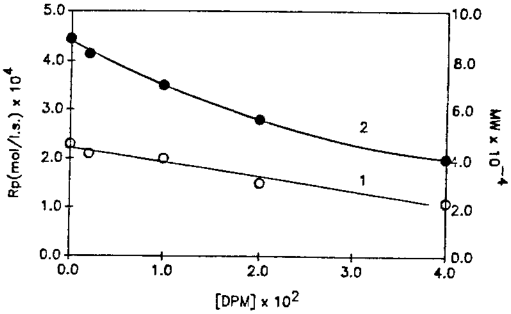
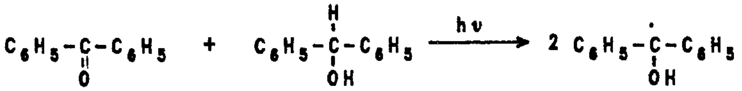


Fig. 3 Effect of DPM on the photopolymerization of MMA initiated by BP/DMA
$[BP]=5x10^{-3}mol/l$, $[DMA]=10^{-2}mol/l$
1. Rp ~[DPM]
2. MW ~[DPM]

Fig. 4 Relationship between Rp and acetonitrile% in the mixture solvent
$[BP]=5x10^{-3}mol/l$
$[DMA]=10^{-2}mol/l$
$[MMA]=3.1mol/l$

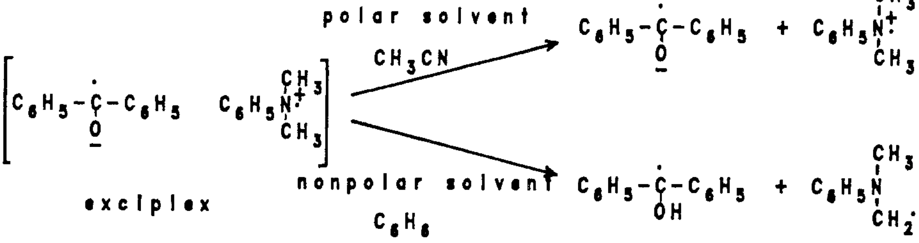


$$C_6H_5-\underset{\underset{O}{\|}}{C}-C_6H_5 + C_6H_5-\overset{H}{\underset{OH}{C}}-C_6H_5 \xrightarrow{h\nu} 2\, C_6H_5-\overset{\cdot}{\underset{OH}{C}}-C_6H_5$$

Adding DPM into this photopolymerization system produces more ketyl radicals, which leads to decrease both of Rp and MW as shown in Fig.3. This confirms that the ketyl radical from BP ia unable to initiate polymerization and responsible for the primary radical termination.

Effect of solvent polarity on the polymerization

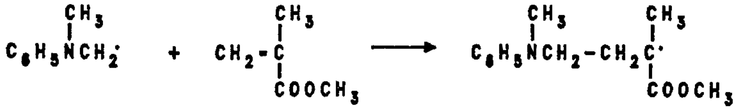
Fig. 4 shows the relationship between Rp and Acetonitrile(%) in the benzene/acetonitrile mixture solvent. With increase of acetonitrile% Rp increases at first because of the favorable exciplex formation, and then it falls down since the exciplex undergoes preferential dissociation to solvated radical-ions at high polar medium rather than proton transfer to produce two radicals(7,8):



$$\left[C_6H_5-\overset{\cdot}{\underset{\underline{O}}{C}}-C_6H_5 \quad C_6H_5\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}\right] \begin{array}{l} \xrightarrow[CH_3CN]{\text{polar solvent}} C_6H_5-\overset{\cdot}{\underset{\underline{O}}{C}}-C_6H_5 + C_6H_5\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}} \\ \xrightarrow[C_6H_6]{\text{nonpolar solvent}} C_6H_5-\overset{\cdot}{\underset{OH}{C}}-C_6H_5 + C_6H_5\overset{CH_3}{\underset{CH_2^{\cdot}}{N}} \end{array}$$

End-Group of the Polymer

Amino radicals are the essential radicals for initiation, which is verified by the end-group analysis of the obtained polymer, as shown in Fig. 5. The PMMA initiated by BP/DMA exhibits the same fluorescence peak (345 nm) as DMA in benzene. This supports the existence of aromatic tertiary group in the polymer and the initiation of amino radicals:



$$C_6H_5N(CH_3)CH_2^{\cdot} + CH_2{-}C(CH_3)COOCH_3 \longrightarrow C_6H_5N(CH_3)CH_2{-}CH_2C^{\cdot}(CH_3)COOCH_3$$

The amino end-group was also quantitively ditermined by non-aqueous titration. Assuming the disproportionation as the major termination model for MMA (22), each polymer chain should have average one amino end-group because only amino radicals are responsible for the initiation. In one of our experiments, the PMMA initiated by BP/DMA was determined to have 5.5×10^{-6} mole of amino end-group. From its MW 1.77×10^{5} we are able to calculate the amino end-group number for each polymer chain is 0.97.

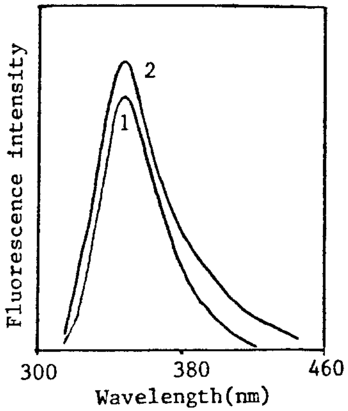


Fig. 5 Fluorescence spectra (in benzene, λ_{ex}=303nm)
1. DMA
2. PMMA initiated by BP/DMA

Photopolymerization Initiated by BP/MMA with Amino End-Group

It is reasonable to propose that the system composed of BP and the polymer with amino end-group can initiate a further polymerization. When PMMA with amino end-group (obtained from the polymerization initiated by BP/DMA) was dissolved in MMA and

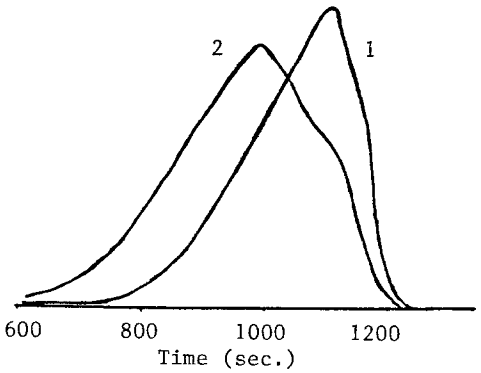


Fig.6 GPC plots
1. PMMA with BP/DMA as photoinitiator
2. PMMA with BP/above PMMA as photoinitiator

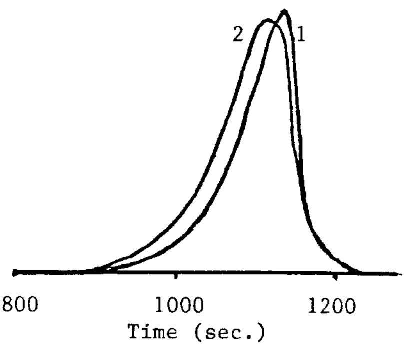
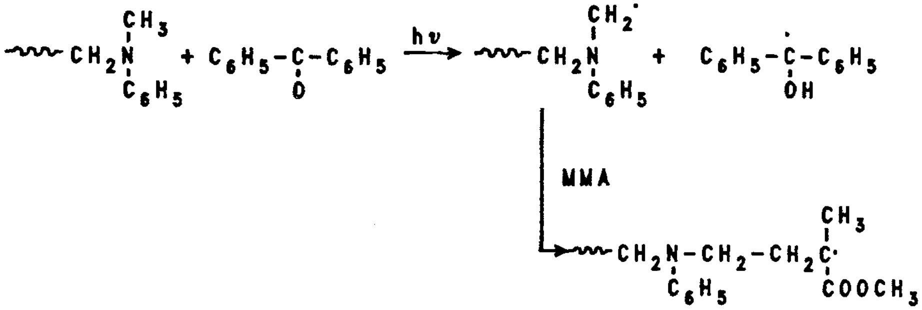


Fig. 7 GPC plots
1. PSt with BP/DMA as photoinitiator
2. PMMA with BP/above PSt as photoinitiator

certain amount of BP was added, the photopolymerization did occur under irradiation. GPC plot (Fig. 6) shows a greater MW after the polymerization. PMMA in benzene solution does not show any MW change after irradiation for 6 hours either in the presence or absence of BP, so the polymerization is unlikely initiated by the chain breaking of PMMA. We propose the mechanism as follows:



$$\sim CH_2N(CH_3)C_6H_5 + C_6H_5-C(=O)-C_6H_5 \xrightarrow{h\nu} \sim CH_2N(CH_2^{\cdot})C_6H_5 + C_6H_5-\dot{C}(OH)-C_6H_5$$

$$\xrightarrow{MMA} \sim CH_2N(C_6H_5)-CH_2-CH_2C^{\cdot}(CH_3)COOCH_3$$

In our another experiment, PSt was prepared by photopolymerization with BP/DMA as initiator. Then it was combined with BP to initiate the photopolymerization of MMA to produce St-MMA block copolymer. Fig. 7 shows the GPC plots with UV detector. In this case only PSt or St-MMA copolymer can be detected. The MW increase for plot 2 is obviously attributed to the block copolymer. Even though there might be some MMA homopolymer by BP-initiated polymerization, it would not show up in this plot.

ACKNOWLEDGEMENT

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