The Sensitization on Photopolymerization of Some Aromatic Tertiary Amines

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The influence of aromatic tertiary amine (ATA) on the rate of photopolymerization (R_p) was studied in the MMA/BIP (benzoin isopropyl ether) system to improve the photoinitiation activity and anti-oxygen power of the benzoin alkyl ether initiators by using an auto-expander.

Keywords: Sensitization, Aromatic Tertiary Amine, Photopolymerization

1. Introduction

On studying of the photoinitiator system using aromatic tertiary amine (ATA) as hydrogen donor, the researcher [1] found that ATA in the system can act as a co-initiator and/or autoxidant, therefore produces free radical which has initiation activity and consume oxygen in the polymer system to prevent the quenching of excited state, thereby sensitizes on photopolymerization. However, only in the appropriate proportion, ATA can exhibit the sensitization very well. It is believed that [2] only when the Hammett's coefficient of its substituent is between ± 0.9 , ATA can have better sensitization effect. Although there were many reports on photoinitiator system containing tertiary amine compounds [3-6], photoinitiator system containing benzoin ether/ ATA have not been known so far. Benzoin ether is still one of the massively used photoinitiators. The studying of the sensitization of ATA on photopolymerization both in theory and in practice, has specific value.

For this reason, we selected eight substituted ATA whose Hammett's coefficient are between $-0.268 \sim +0.778$, in order to constitute the photoinitiator systems in which benzoin alkyl ether acts as photoinitiator; and to study the kinetic behavior of these systems and fluorescence spectrum in an attempt to seek ways to improve the initiation and antioxidation abilities of the benzoin alkyl ether containing photoinitiators.

2. Experimental

2.1. Synthesis, Purification and Characterization of Aromatic tertiary Amines

We have synthesized a number of ATA by methylation of aromatic primary amine [7]. In this method, to aqueous solution of aromatic primary amine and NaHCO_3 , dimethyl sulfate was added dropwise at a temperature below 15°C . The resulting mixture was heated to 60°C , and the reaction continued at this temperature for 30 minutes to complete the methylation. The reaction mixture was cooled to room temperature, excess solid NaOH was added, the quaternary ammonium salt formed was converted to quaternary ammonium base which was then thermally cracked at a temperature about 110°C to form ATA. The obtained mixture was vacuum distilled, and corresponding fraction was collected. The general formula of the obtained compound is

wherein R represents CH_3 , Cl, Br, I, OCH_3 , (DMMA, DMCA, DMBA, DMIA, DMOMA).

The primary amine, wherein R is isopropyl, is not commercially available. We prepared it [4] by nitration of isopropyl benzene to nitroaniline, which is then reduces to p-isopropyl aniline by Sn/HCl [5].

followed by the methylation to prepare iso-pr- $\text{C}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ (DMIPA).

The crude liquid product obtained was purified by vacuum distillation, collecting the fraction at 100 ~ 105 °C / 20 mmHg and 118 ~ 124 °C / 18 mmHg for $\text{CH}_3\text{C}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ (DMNA) and DMIPA respectively. The crude solid product obtained was purified three times by recrystallization from anhydrous ethanol.

ATA wherein R is iso-amyl (DMBI), is available from Nippon Chemiphar Co., Ltd.

The synthesized ATA was characterized by IR spectrometry, NMR spectrometry, elemental analysis, and melting point test. The results showed that product purity met the requirement of kinetic determination.

2.2. Kinetic Experiment

The kinetic experiment was performed [6,8] using the apparatus shown in Fig. 1.

As the volume contraction of the monomer in M occurs due to photopolymerization, the water level in S decreases, the plunger decreases too, owing to the self-weight of R. An output signal is induced

Fig. 1. Apparatus for Automatic Recording Dilatometer wherein

1,2-metallic cassette	6-light valve
3-quartz glass cooling tube	C-differential transformer
4-constant temperature quartz double pipe armature	K1,K2-rubber cork
5-middle pressure Hg lamp	R-differential transformer armature
	S-syringe
	T-quartz glass tube
	M-PE film bag packed with sample

due to the relative movement of R and C. The signal is amplified through the displacement measuring apparatus and recorded (in millivolt unit) by a recorder. By mv-mm characteristic curve, the mv is converted to the height decrease of plunger. The reaction rate of photopolymerization (R_p) can be calculated from the following equation:

$$R_p = [M_0] \cdot \frac{dc}{dt} = \frac{[M_0]}{H} \cdot \frac{\Delta h}{\Delta t} \left(\frac{\text{mol}}{\text{l} \cdot \text{sec}} \right) \quad (1)$$

wherein

[M_0]—initial concentration of MMA

H—parameter of the app.

$\Delta h / \Delta t$ —height change/second of plunger

C—conversion of monomer

2.3. Fluorescence Spectrum, Ultra-violet Absorption Spectrum

The fluorescence spectrum of the sample was measured with a Nippon Hitachi Fluorescence Spectrometer Model 850, the sample concentration was $8 \times 10^{-4} \text{ mol/l}$.

The ultraviolet spectrum of the sample was measured with a Nippon Shimadzu Spectrometer Model UV — 260, the sample concentration is $6 \times 10^{-4} \sim 1 \times 10^{-4} \text{ mol/l}$.

3. Results and Discussion

3.1. Effect of BIP concentration in MMA — BIP system on photopolymerization rate

Using methyl methacrylate (MMA) as a monomer, benzoin isopropyl ether (BIP) as a photoinitiator, we studied the effect of BIP concentration on MMA photopolymerization rate in MMA—BIP system. The photopolymerization rates at different BIP concentrations were calculated according to equation (1), and $\log R_p$ against $\log C$ was plotted (shown in Fig. 2).

As will be seen from Fig. 2, when the BIP concentration is less than $1.85 \times 10^{-2} \text{ mol/l}$, R_p increases. When the BIP concentration is greater than above-mentioned value, R_p decreases with the increase of concentration. This is in concordance with the general rule of photopolymerization rate-photoinitiator concentration relation.

For this reason, the following kinetic experiments were performed under the conditions that BIP concentration is not greater than 0.50%.

Fig. 2. R_p at different BIP concentration

3.2. Effect of ATA concentration on MMA photopolymerization rate

By fixing the BIP concentration at 0.5%, and varying ATA concentration, we studied the photopolymerization kinetics of MMA/BIP/ATA system. ATA used included DMBI, DMOMA, DMCA. The similar results were obtained (shown in Fig.3).

Fig.3. Rp at different ATA Concentration BIP Concentration:0.5%

As will be seen from Fig.3, photopolymerization rate is influenced without exception by ATA concentration in these systems. The variation tendencies are similar. When a small amount of ATA is added, the photopolymerization rate of the system is even more lower than that where the amine has not added. However, with the continuous increase of ATA concentration, Rp gradually increases again. When a specific concentration has reached, Rp reaches a maximum. With the further increase of ATA concentration, Rp begins to decrease again.

As will be seen from the above results, the photochemical reaction process in these systems studied is relatively complicated. Two factors, inhibiting factor and promoting factor, to photopolymerization may exist. The final outcome is the result of their competition. More specifically, the following several effects may exist:

(i) Photoscreening effect of ATA

The photoinitiator take place most easily α -splitting:

in which two active free radicals (I) and (II) were formed. In MMA system, (I) and (II) initiate MMA polymerization with nearly equal initiation activity [9]. The major requirement of this reaction is that the initiator absorbs photon energy. The UV absorption spectra of BIP and DMBI is shown in Fig.4.

Fig.4. The UV absorption spectra of BIP and DMBI
BIP concentration: 8×10^{-4} mol/l
DMBI concentration: 1×10^{-4} mol/l

As will be seen from Fig.4, even if the DMBI concentration is only about 1/8 of that of BIP, the UV absorption intensity of DMBI is still higher than that of BIP, and both absorption bands are partially overlapped. Therefore, they would absorb competitively the light emitted from the light source. The stronger UV absorption ability of DMBI has weakened the UV absorption of BIP, and inhibited the photospitting reaction to a certain extent.

(ii) Reaction of ATA with monomer

ATA can react with a trace amount of O_2 present in the system to form amine- O_2 compound and then attacks the active hydrogen of MMA's α -methyl group to form a monomer hydroperoxide [10]. The hydroperoxide compound can form redox system with ATA and then decomposes to active free radicals to initiate polymerization. By the reaction of ATA with O_2 present in the system, the primary free radicals will probably be multiplied, therefore the rate of photopolymerization is increased.

(iii) Reaction of ATA with BIP

The α -hydrogen of benzoin alkyl ether's ether group is very active. In the presence of O_2 and H donor (such as ATA) in the system, benzoin alkyl ether can form hydroperoxide compound too and then decomposes to active free radicals [11]. This process is as follows:

RH—hydrogen donor, such as X- $\text{C}_6\text{H}_4\text{-N}(\text{CH}_3)_2$

Now let us turn back to see the curves of Fig.3, the photopolymerization rate of the system increases initially with the increase of amine concentration (some exception at the very onset). When a definite concentration has been reached, R_p appears a maximum. Within the range of said amine concentration, in addition to the occurrence of BIP's partially α -splitting, ATA (as hydrogen donor), after reaction with trace O_2 in the system, can form hydroperoxide compounds with MMA and BIP, and these hydroperoxides can further decompose to active radicals. Therefore the primary free radicals will be multiplied, furthermore the polymerization inhibition of O_2 is restrained. The overall results lead to the increase of R_p .

When ATA concentration exceeds certain critical value, the decrease tendency of R_p occurs. This will probably be the result of strongly competitive UV absorption by ATA and BIP.

Thus it can be seen that if other conditions remain invariant, ATA concentration has very significant influence on the sensitization effect.

3.3. Effect of Different ATA on MMA Photopolymerization Rate

For studying of the effect of different ATA on MMA photopolymerization rate, eight ATA whose Hammett's coefficient of substituting group is

Tab.1 Effect of Different ATA and O_2 on R_p

-R	Hammett constant	$R_p \times 10^4$	$R_p(\text{O}_2) \times 10^4$
CH_3	-0.170	7.587	7.930
iso-pr	-0.150	8.180	7.898
Cl	0.227	7.742	8.400
Br	0.232	7.337	9.135
I	0.180	7.523	7.398
OCH_3	0.268	7.227	7.915
$\text{COOC}_5\text{H}_{11}$	0.45	9.197	8.383
NO_2	0.778	0.422	0.185
control		7.883	

BIP's concentration: 0.5%

between -0.268 ~ +0.778 were selected. Under the condition of the same BIP concentration and compounding ratio, the behavior of ATA during MMA bulk photopolymerization was studied. The results were shown in Tab.1.

It can be seen from Tab.1 that ATA whose substituent's Hammett constant is within above-mentioned range, exhibit no obvious variation rule on MMA photopolymerization rate. Among different kinds of ATA, the sensitization effect of DMBI is the best, that of DMIPA is the second. DMNA not only has no sensitization effect, but has almost completely inhibited the photopolymerization reaction. For this purpose, the sensitization effect of DMBI was further studied as follows:

(i) Fluorescence Spectrum of BIP/DMBI

The mechanism of good sensitization effect of DMBI has not been understood till now. For this reason, the fluorescence spectrum of BIP/DMBI in benzene has been studied (shown in Fig.5).

In BIP/DMBI fluorescence spectrum exhibits a new peak at 393 nm. Under the condition of constant BIP concentration, said peak intensifies with the increase of BIP/DMBI mol ratio, and the relative intensity of 393 nm peak and 366 nm peak (original DMBI peak) becomes stronger (shown in Tab.2)

Fig.5 Fluorescence Spectrum of BIP / DMBI
1- BIP, 2- DMBI, 3- DMBI/BIP

Tab.2 The Effects of Different BIP/DMBI Mol Ratio on Peak Intensity of It's Fluorescence Spectrum

BIP/DMBI	0:1	1:1	2:1	4:1	8:1	16:1
I_{393}/I_{366}	0.857	1.055	1.062	1.070	1.086	1.185

On the fluorescence spectrum of other ATA/BIP systems, this phenomenon was not observed. It is supposed that certain transition state compound between them has been formed.

(ii) Effect of Relative Amount used of DMBI/BIP on R_p

Firstly, by fixing the BIP concentration at 0.25%, and varying the DMBI concentration, MMA's R_p in different mol ratios were determined. The results were shown in Fig.6.

Fig.6. Effect of DMBI/BIP mol ratio on R_p
BIP's concentration:0.25%

It can be seen from Fig.6 that when DMBI / BIP = 0.4~0.5 (mol ratio), the sensitization effect of DMBI is best. Secondly, by fixing the DMBI/BIP mol ratio at 0.409, and varying the BIP concentration, the sensitization effect of DMBI was studied. The results were shown in Tab.3.

Tab.3 Comparison of Sensitization Effect at Different BIP Concentration.

BIP%	3	0.5	0.25	0.125
$R_p \times 10^4$	7.038	9.197	7.633	5.850
$R_p \times 10^4$ (control)	6.898	7.930	7.305	4.787

It can be seen from Tab.3 that BIP exhibits the best sensitization effect only when its concentration is within certain appropriate range, both the above or below the concentration range being unfavorable for giving full play to DMBI's sensitization effect.

As mentioned above, ATA can act as a sensitizer. But why DMBI, as one of ATA, has especially good sensitization effect? The reason has still not been understood. It can only determine that its fluorescence spectrum is completely different from that of other amines studied. From spatial structure analysis, the -C- and γ -H at iso-amyl group of DMBI are within equal distance (shown in Fig.7). The γ -H atom may be active, under the condition of illumination, free radicals from inner molecular H extraction have probably been formed, and lead the number of free radical in the system to

increase. Under this circumstance, DMBI actually functions as photoinitiator.

Fig.7 DMBI's Molecular Structure

When the DMBI concentration in the system is quite low, it is supposed that its sensitization effect can not completely embody due to the prominent polymerization inhibition effect of O_2 on BIP. If excessive DMBI concentration is used, the deactivation between them increases with the steep rise of the number of active free radicals, while the concentration of extinction product in the system increases, thereby the polymerization rate decreases.

The desensitization of ATA with nitro group (DMNA) on MMA/BIP system is very significant. It has nearly (or practically) inhibited the photopolymerization of the system. Owing to the radical containing $-NO_2$ is a retarder, and sometimes even inhibitor of free radical polymerization, it is not hard to understand that said result occurs.

3.4. Sensitivity of MMA / BIP / ATA Systems to Oxygen

For the sake of examining sensitivity of the system to O_2 , kinetic experiment has been performed after aerating with O_2 into each system for 15 minutes. The results are shown in Tab.1.

As will be seen from Tab.1, at the first glance, the sensitivity of each ATA to O_2 is different from each other. Those amines, such as DMBI, DMIPA, which enable R_p of the system to increase fairly before aerating with O_2 , enable R_p of all the system to decrease to some extent after aerating with O_2 . Those amines, such as DMMA and DMOMA in which R_p of the system is a little slow before aerating with O_2 , enable R_p of the system to increase to some extent after aerating with O_2 . When the substituent is halogen (except iodine), ATA system is especially sensitive to O_2 .

As mentioned above, the effect of O_2 on system has duality. On the one hand, it may promote the photopolymerization of the system; on the other hand, owing to its quenching effect on triplet state of BIP, it may retard the photopolymerization.

As will be seen from the data of Tab.1, after aerating with O_2 , the photopolymerization rate of not a few of systems are increased. Even for DMIPA and DMBI, compared with that before aerating with O_2 , R_p are decreased a little at the

first glance, but its absolute value is still much greater compared with the system which contains no ATA. Therefore it shows that they are really not an aerobic. The decrease of R_p of the system after aerating with O_2 is probably the result of overquick multiplication of free radicals in the system, free radical deactivation owing to cage effect and increase of extinction product.

Next, the case of halogen substituted ATA is discussed again. As will be seen from Tab.1, those ATA whose substituent is halogen, are especially sensitive to O_2 , particularly when the substituent is chlorine and bromine atom, both enabling R_p increase greatly. Because halogen atoms are all electrophilic, and oxygen molecule can be regarded as a biradical which has $\cdot O-O \cdot$ structure, it is supposed that halogen atom has attractive force to oxygen atom, ATA containing halogen atom forms amine- O_2 compound even more easily, therefore the formation of system's hydroperoxide compound has been promoted, moreover the photopolymerization rate has been increased. But the case of iodine substituted ATA is somewhat different. It is found by experiment that the solution color of system containing this kind of ATA changes from light violet to deep violet with aerating. This shows that redox reaction has occurred in the system and the free iodine separated. Therefore iodine atom in DMIA do not function as well as other halogen atoms.

4. Conclusion

1). In MMA/BIP photopolymerization system, the sensitization effect of different ATA have been compared. Regardless of oxygen content of the system, DMBI invariably has its optimal

sensitization effect; but DMNA only serves primarily the function of polymerization inhibition. There is no simple linear relationship between the effect of different ATA on MMA photopolymerization rate and Hammett coefficient of their substituents.

2). Only within definite concentration range and under appropriate compounding ratio with photoinitiator can the sensitization effect of ATA on MMA/BIP photopolymerization system be completely embodied. For DMBI, its optimal compounding ratio (mol ratio) with BIP ranges from 0.4 to 0.5.

3). ATA having halogen (except iodine) substituent are very sensitive to the oxygen present in MMA/BIP photopolymerization system. The increase of oxygen content in systems has all increased the MMA photopolymerization rate.

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