

STUDIES ON THE ORGANIC PEROXIDE-DITERTIARY AMINE INITIATION SYSTEMS*

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ABSTRACT

Radical polymerization of methyl methacrylate (MMA) initiated with organic peroxide-ditertiary amine binary systems was studied. Benzoyl peroxide (BPO), lauroyl peroxide (LPO), t-butyl hydroperoxide (TBH), and t-butyl peroxybenzoate (TBPB) were used as organic peroxide components, aromatic ditertiary amine 4,4'-tetramethyldiaminodiphenylmethane (TMDAPM) and aliphatic ditertiary amine tetramethylethylenediamine (TMEDA) were used as amine components. The polymerization rate R_p , the overall activation energy of polymerization E_a , the rate equation of MMA polymerization, and the end group of polymer formed were determined.

INTRODUCTION

Organic peroxide and amine initiation system belongs to organic redox initiator^[1]. The typical examples are BPO-DMA (N, N-dimethyl aniline), BPO-DMT (N, N-dimethyl-p-toluidine)^[2] binary systems. Only some papers were reported on radical polymerization using organic peroxide-polyamine initiation systems, such as cumene hydroperoxide (CHP)-tetraethylenepentamine^[3,4], CHP-diethylenetriamine^[5] binary systems. In this paper, we would like to report some results concerning the radical polymerization of MMA initiated with organic peroxide-ditertiary amine binary systems. It was found that the binary initiation systems consisted of TMDAPM and BPO, LPO, TBH, TBPB respectively could initiate MMA polymerization and enhanced the R_p . While in the organic peroxide-TMEDA binary systems, only TMEDA coupled with LPO or TBH binary systems could initiate MMA polymerization, no polymer was obtained using BPO-TMEDA or TBPB-TMEDA as initiator.

EXPERIMENTAL

Materials

Organic peroxide BPO, LPO, TBH, TBPB, ditertiary amine TMDAPM, TMEDA, and MMA monomer are all chemical reagents and were purified by the common methods. Toluene, methanol, chloroform solvents were used without any purification.

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Polymerization

The polymerization of MMA either in bulk or in solution were carried out in a dilatometer at a constant temperature.

The molecular weights of polymers were determined viscosimetrically and calculated according to the following equation:

$$[\eta] = 0.48 \times 10^{-4} M^{0.80} \quad (25^\circ\text{C}, \text{CHCl}_3, \text{dl/g})^{[6]}$$

RESULTS AND DISCUSSION

1. The effect of organic peroxide and ditertiary amine on MMA polymerization

The effect of initiation system on MMA polymerization was shown in Fig. 1. Which showed the polymerization of MMA at 50°C , using BPO-TMDAPM, LPO-TMDAPM, TBH-TMDAPM, TBPB-TMDAPM, LPO-TMEDA, and TBH-TMEDA binary systems as initiators. The data of MMA polymerization rate R_p were compiled in Table 1. It showed that when

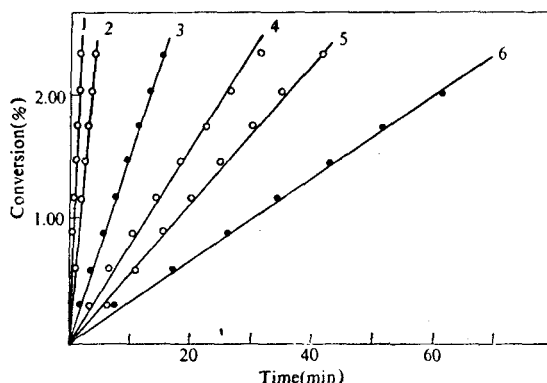


Fig. 1 Correlation between conversion and time (50°C)

[Organic peroxide] = [Amine] = $2 \times 10^{-3} M$

1. BPO-TMDAPM; 2. LPO-TMDAPM;
3. LPO-TMEDA; 4. TBH-TMDAPM;
5. TBPB-TMDAPM; 6. TBH-TMEDA.

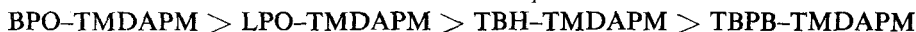
Table 1 MMA polymerization initiated with organic peroxide-ditertiary amine systems

Initiation system	Induction period (min)	$R_p \times 10^4$ (mol/l·s)	MW^* 10^{-4}	Initiation system	Induction period (min)	$R_p \times 10^4$ (mol/l·s)	MW^* 10^{-4}
BPO-TMDAPM	1	18.2	11.4	BPO-TMEDA	no polymerization		
LPO-TMDAPM	1	7.98	39.3	LPO-TMEDA	5	2.24	59.7
TBH-TMDAPM	1	1.14		TBH-TMEDA	40	0.51	101
TBPB-TMDAPM	27	1.00	83.6	TBPB-TMEDA	no polymerization		

[Organic peroxide] = [Ditertiary amine] = 2.0×10^{-3} mol/l, 50°C ;

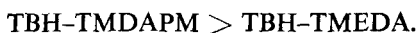
* Molecular weight of PMMA.

TMDAPM was used as amine component the structural effect of organic peroxide on the R_p was pronounced and the descending order of R_p was as follows:



This order is similar to that of the organic peroxide-DMT systems^[7].

In the case of organic peroxide-TMEDA binary systems, MMA would polymerize using LPO-TMEDA, or TBH-TMEDA as initiator, but no polymer was obtained using BPO-TMEDA or TBPB-TMEDA as initiator during 2 h reaction period. The effect of ditertiary aliphatic diamine TMEDA on R_p was smaller than ditertiary aromatic diamine TMDAPM. The descending order of R_p was as follows;



2. Activation energy of MMA polymerization

When the fixed concentration of BPO and TMDAPM was 2.0×10^{-2} mol/l, the polymerization of MMA at temperatures of 25, 35, 40, 45, 50°C gave the polymerization curves as shown in Fig. 2. The values of R_p were obtained from the slopes of these straight lines, and the overall activation energy of polymerization E_a was calculated from the Arrhenius plot. The values of E_a were compiled in Table 2 and were compared with the others. It showed

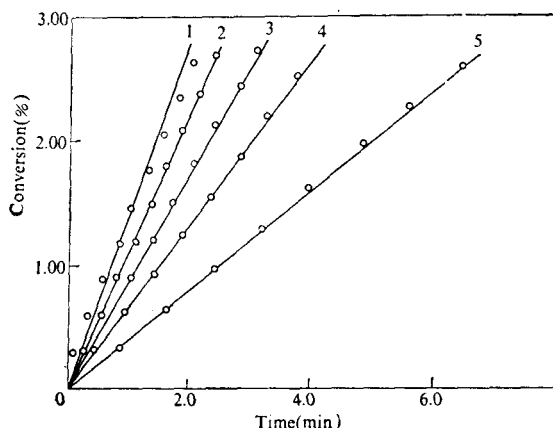


Fig. 2 MMA polymerization at different temperatures
[BPO] = [TMDAPM] = 2.0×10^{-2} M
1. 50°C; 2. 45°C; 3. 40°C; 4. 35°C; 5. 25°C.

Table 2 Overall activation energy E_a of MMA polymerization

Initiation system	E_a (KJ/mol)	(°C)	Initiation system	E_a (KJ/mol)	(°C)
BPO-TMDAPM	38.2	(25-50)	BPO-DMT	35.9	(35-55)
LPO-TMDAPM	47.3	(40-60)	LPO-DMT	56.1	(40-60)
TBH-TMDAPM	55.2	(40-60)	TBH-DMT	54.9	(55-70)
LPO-TMEDA	62.5	(40-60)	BPO	79.9	(50-70)
TBH-TMEDA	65.3	(45-55)	LPO	77.6	(40-60)
			TBH	77.5	(55-70)

that the values of E_a for MMA polymerization initiated with organic peroxide alone were high, around 78 KJ/mol. However, in the presence of TMDAPM or TMEDA ditertiary amine, the values of E_a were always decrease. The E_a of BPO-TMDAPM system is 38.2 KJ/mol, it is very similar to the E_a of BPO-DMT system. Therefore, the TMDAPM is an effective promotor as DMT.

3. The kinetics of MMA polymerization

According to the kinetic studies on MMA polymerization initiated with BPO-TMDAPM, LPO-TMDAPM systems, the double logarithmic plots of R_p versus concentration of initiator and concentration of monomer were shown in Fig. 3 and Fig. 4. Accordingly, the following equations were obtained

$$R_p = K [\text{BPO}]^{0.48} [\text{TMDAPM}]^{0.44} [\text{MMA}]^{1.1}$$

$$R_p = K [\text{LPO}]^{0.47} [\text{TMDAPM}]^{0.43} [\text{MMA}]^{1.01}$$

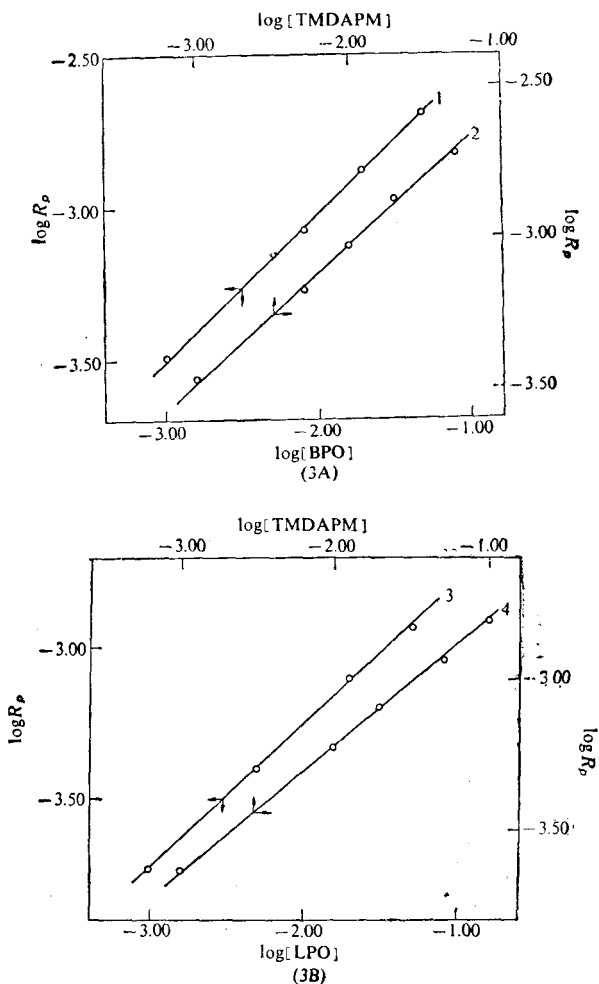


Fig. 3 Double logarithmic plots of the R_p versus the concentration of initiator
 BPO-TMDAPM initiation system: 1 $\log R_p$ vs. $\log [\text{BPO}]$; 2 $\log R_p$ vs. $\log [\text{TMDAPM}]$
 LPO-TMDAPM initiation system: 3 $\log R_p$ vs. $\log [\text{LPO}]$; 4 $\log R_p$ vs. $\log [\text{TMDAPM}]$

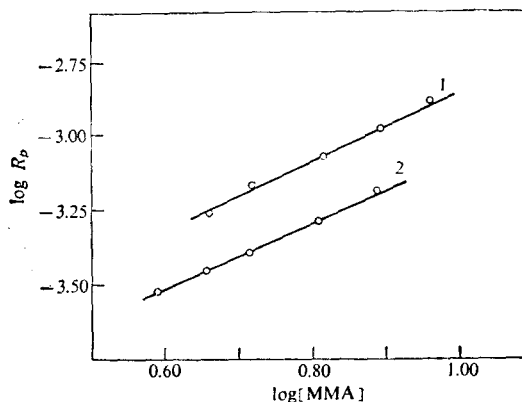


Fig. 4 Double logarithmic plot of R_p versus concentration of monomer
 1 BPO-TMDAPM system, 40°C;
 2 LPO-TMDAPM system, 50°C.

These rate equations from our experimental results are in good agreement with the rate equation of redox initiated polymerization

$$R_p = K [\text{reductant}]^{0.5} [\text{oxidant}]^{0.5} [M]^{1.0}$$

4. The analysis of polymer end group

The polymethyl methacrylate (PMMA) obtained from the organic peroxide-TMDAPM initiated polymerization was dissolved in chloroform, precipitated with methanol, and the precipitate was filtered, washed with methanol, and then reprecipitated for several times

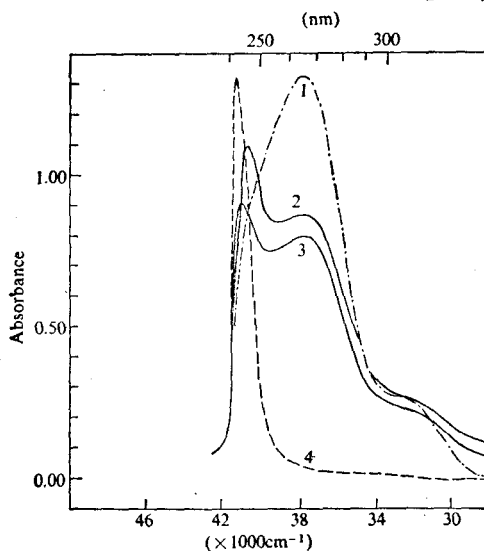


Fig. 5 The UV spectra of PMMA
 1 TMDAPM in CHCl_3 ($4.7 \times 10^{-5} M$),
 2 PMMA in CHCl_3 (10 mg/ml, LPO-TMDAPM),
 3 PMMA in CHCl_3 (5 mg/ml, BPO-TMDAPM),
 4 PMMA in CHCl_3 (13 mg/ml, thermal polymerization).

until its filtrate contained no TMDAPM molecule (i. e. there is not absorption band at 268 nm.) The purified polymer was dissolved in chloroform and the end group of polymer was determined by Specord-UV-VIS spectrometer. The UV spectra of PMMA are shown in Fig. 5. It showed that the TMDAPM moiety in the polymer exhibited its characteristic absorption at 270 nm. This result provides evidence concerning the initiation reaction mechanism of BPO-TMDAPM system is similar to that of BPO-DMA^[8], BPO-DMT^[9] systems, and the aminomethyl radical initiates MMA to polymerize. Furthermore, the PMMA formed by LPO-TEEDA (tetraethylethylenediamine) initiation system contains aliphatic amine end group as determined by HClO_4 -acetic acid titration analysis method^[10].

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