

STUDIES ON RADICAL POLYMERIZATION OF METHYL METHACRYLATE INITIATED WITH ORGANIC PEROXIDE-AMINE SYSTEMS*

QIU Kunyuan (丘坤元), SHUI Li (水 力) and FENG Xinde (冯新德)

(Department of Chemistry, Peking University, Beijing)

ABSTRACT

Radical polymerization of methyl methacrylate (MMA) initiated with various diacyl peroxide-amine systems was studied. Benzoyl peroxide (BPO) and lauroyl peroxide (LPO) were used as diacyl peroxide component, N,N-dimethyl aniline (DMA) and its para substituted derivatives, i.e., N,N-dimethyl-*p*-toluidine (DMT), *p*-hydroxymethyl-N,N-dimethyl aniline (HDMA), *p*-nitro-N,N-dimethyl aniline (NDMA) and *p*-dimethylamino benzaldehyde (DMAB) were used as amine components. It was found that the peroxide-DMT systems give higher rates of bulk polymerization R_p of MMA than the organic hydroperoxide-DMT systems with the following descending order BPO-DMT > LPO-DMT > CHP (cumene hydroperoxide)-DMT > TBH (tert-butyl hydroperoxide)-DMT. The aromatic tertiary amines possess obvious structural effect on the R_p values in the diacyl peroxide-amine system. The overall activation energy of MMA polymerization was determined and the kinetics of polymerization of MMA initiated with BPO-DMT system was investigated.

INTRODUCTION

Organic peroxide and amine initiation system is well-known as an organic redox initiator^[1]. BPO-DMA system is used as an effective initiator in vinyl radical polymerization and has been studied by many researchers. Imoto^[2-5], Horner^[6-7], Lal^[8], O'Driscoll^[9], Walling^[10], Otsu^[11] et al. have studied the reaction mechanism of BPO-DMA system and radical polymerization of vinyl monomers such as styrene, methyl methacrylate, acrylonitrile and vinyl chloride initiated with BPO-DMA system. In our laboratory, Feng et al. have studied the radical polymerization of vinyl monomers initiated with BPO-DMT^[12], CHP-DMT^[13], TBH-TEA (triethanolamine)^[14] and THFHP (tetrahydrofuran hydroperoxide)-DMT^[15] systems. In this paper, we wish to report some results concerning the radical polymerization of MMA initiated with diacyl peroxide-aromatic tertiary amine systems. In order to study the effects of organic peroxide and amine respectively, the polymerizations of MMA were carried out in various initiation systems, including BPO, LPO, TBH and CHP as organic peroxide components, DHET (N,N-di-hydroxyethyl-*p*-toluidine), DMT, HDMA, DMA, NDMA and DMAB as amine components.

EXPERIMENTAL

The monomer, amines and the others were commercial reagents or reagents synthesized in

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our laboratory and purified by usual methods. The rate of MMA polymerization was determined by dilatometric method. The molecular weight of polymer obtained was determined from the intrinsic viscosity of polymer solution by Ubbelohde viscometer, and then calculated according to the following equation

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

RESULTS AND DISCUSSION

1. The effect of organic peroxide on MMA polymerization

At first, we studied the structural effects of organic peroxide, such as BPO, LPO, TBH and CHP, on the R_p of MMA initiated with organic peroxide-DMT systems. The results are listed in Table 1. Although the concentration of organic hydroperoxide (CHP or TBH)-DMT system was used twice as in diacyl peroxide (BPO or LPO)-DMT system, the R_p of MMA initiated with the former system is always lower than that of the latter system by an order of magnitude with the descending order of R_p as BPO > LPO > CHP > TBH. This result showed that the structural effect of diacyl peroxide is more obvious than that of organic hydroperoxide in the peroxide-DMT initiation system. A similar result was obtained in the peroxide-DMA system.

Table 1 Polymerization of MMA initiated with various peroxide-amine systems*

Initiator	Induction period (min)	$R_p \times 10^4$ (mol/l.s)	Initiator	Induction period (min)	$R_p \times 10^4$ (mol/l.s)
BPO-DMT	0.5	71.0	BPO-DMA	2	29.2
LPO-DMT	9.5	21.5	LPO-DMA	11.5	11.7
CHP-DMT	14	7.85	CHP-DMA	11	5.86
TBH-DMT	8	4.36	TBH-DMA	6	3.74

* [BPO] or [LPO]=[DMT] or [DMA]= 1.0×10^{-2} mol/L.

[TBH] or [CHP]=[DMT] or [DMA]= 2.0×10^{-2} mol/L, [MMA]=9.13 mol/L, 45°C .

2. The structural effect of aromatic tertiary amine on MMA polymerization

In order to compare the structural effect of aromatic tertiary amine on the R_p , we selected a varieties of amines, such as DHET, DMT, HDMA, DMA, NDMA and DMAB coupled with BPO, LPO respectively, and used as initiation systems in bulk polymerization of MMA. The relations between the percentage of polymerization and time are shown in Figs. 1, 2, and the values of R_p and relative polymerization rate R_r , and molecular weight of PMMA are listed in Table 2.

In the case of bulk polymerization of MMA using BPO-amine system as initiators, the structural effect of aromatic tertiary amine on the R_p of MMA is distinct. From the data given in Table 2, the order of R_p of MMA descended as follows:



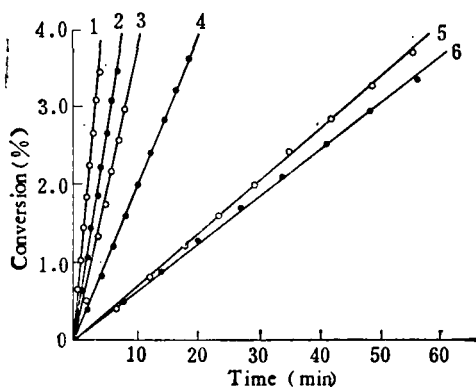


Fig. 1 The relation between conversion and time in bulk polymerization of MMA initiated with BPO-amine system
 $[BPO]=[Amine]=1.0 \times 10^{-2}$ mol/L, 45°C .
 1. DHET; 2. DMT; 3. HDMA; 4. DMA;
 5. NDMA; 6. DMAB.

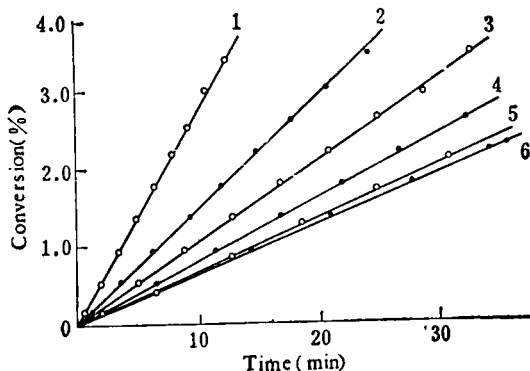


Fig. 2 The relation between conversion and time in bulk polymerization of MMA initiated with LPO-amine system
 $[LPO]=[Amine]=1.0 \times 10^{-2}$ mol/L, 45°C .
 1. DHET; 2. DMT; 3. HDMA;
 4. DMA; 5. NDMA; 6. DMAB.

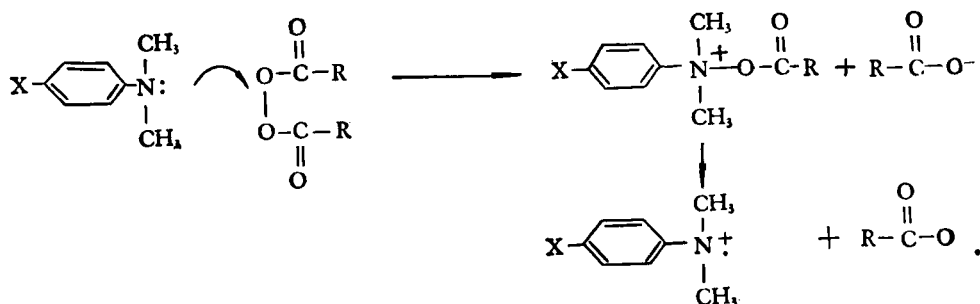
Table 2 Polymerization of MMA initiated with various diacyl peroxide-amine systems*

BPO-amine initiation system				LPO-amine initiation system			
Amine	$R_p \times 10^5$ (mol/l.s)	Relative rate	MW ($\times 10^{-4}$)	Amine	$R_p \times 10^5$ (mol/l.s)	Relative rate	MW ($\times 10^{-4}$)
DHET	130.0	4.45	9.8	DHET	44.4	3.77	28.8
DMT	71.0	2.43	15.8	DMT	21.5	1.84	46.5
HDMA	56.0	1.92	19.2	HDMA	15.8	1.35	67.8
DMA	29.2	1.00	32.8	DMA	11.7	1.00	95.5
NDMA	9.4	0.32	68.6	NDMA	9.8	0.84	98.0
DMAB	9.0	0.31	111.0	DMAB	9.2	0.79	112.0

* $[Diacyl\ peroxide]=[Amine]=1.0 \times 10^{-2}$ mol/L, $[MMA]=9.13$ mol/L, 45°C .

If we took the R_p of MMA in the initiator system containing DMA as 1, the values of relative rate in the presence of DMA derivatives having electron-donating group in the para position such as DMT, HDMA would increase to 1.9–2.4. On the contrary, with an electron-withdrawing group, such as NDMA and DMAB, the R_p would be decreased. This result is similar to that of the work of Lal et al.^[8]

The structural effect of amine on the R_p in the bulk polymerization of MMA initiated with LPO-amine systems were studied also, and similar results were obtained. But the increase on the R_p is somewhat different. The rates in the case of DMT and HDMA are only 1.35–1.8 times as much as that of DMA. The different rates of polymerization may be understood from the initiation reaction mechanism. Decomposition reaction of diacyl peroxide and amine is shown as follows:



The reaction mechanism is somewhat complicated, and the above decomposition reaction is assumed as a nucleophilic displacement reaction. Then the aromatic tertiary amine having electron-rich nitrogen atom enhances the decomposition of diacyl peroxide, with the result in increasing the R_p . Furthermore, as the acidity of benzoic acid (BPO) is stronger than that of lauric acid (LPO), i.e., the benzoyloxy anion is a more reactive leaving group in nucleophilic displacement reaction, hence the rate of decomposition of BPO-DMT is greater than that of LPO-DMT, and the R_p is increased distinctly in the former case.

3. The overall activation energy of polymerization of MMA

When the fixed concentrations of BPO and DMT were 1.0×10^{-2} mol/L, the polymerization of MMA at temperatures of 35, 40, 45, 50 and 55°C gave the results shown in Fig. 3. The values of R_p were obtained from the slopes of these straight lines, and then from $\ln R_p$ versus $1/T$ plot the overall activation energy of polymerization E_a was evaluated. The values of E_a for MMA polymerization initiated with BPO-amine and LPO-amine systems are given in Table 3.

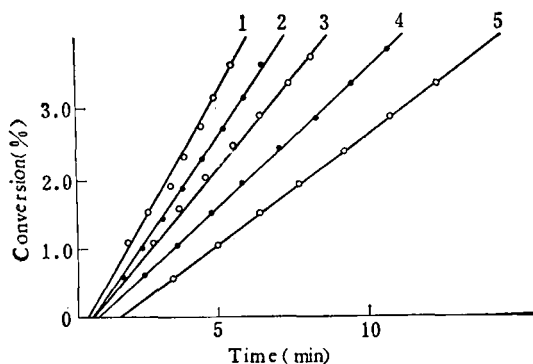


Fig. 3 Polymerization of MMA at different temperatures
 $[\text{BPO}] = [\text{DMT}] = 1.0 \times 10^{-2}$ mol/L.
 °C: 1. 55; 2. 50; 3. 45; 4. 40; 5. 35.

E_a values of MMA initiated with BPO-amine systems were in the range of 35.9–54.4 KJ/mol (8.58–13.0 Kcal/mol), which are much smaller than 78.9 KJ/mol^[16] E_a value of MMA initiated with BPO alone (see Table 3). If we took E_p and E_t of MMA as 26.4 and 11.9 KJ/mol^[17] respectively, we could calculate the E_i of MMA in the BPO-amine systems according to the equation $E_a = E_i/2 + (E_p - E_t)/2$, E_i values in the range of 30.9–67.9 KJ/mol (7.4–16.2 Kcal/mol) were obtained. These values are much smaller than the E_i of MMA

Table 3 Overall activation energy of polymerization of MMA

Initiation system	E_a (KJ/mol)	E_i (KJ/mol)	Initiation system	E_a (KJ/mol)	E_i (KJ/mol)
BPO	79.9*	123.9**	LPO	77.6	114.3
BPO-DMT	35.9	30.9	LPO-DMT	56.1	71.3
BPO-HDMA	39.4	37.9	LPO-HDMA	56.6	72.1
BPO-DMA	44.7	48.5	LPO-DMA	67.0	93.1
BPO-DMAB	50.9	60.9	LPO-DMAB	71.6	102.3
BPO-NDMA	54.4	67.9	LPO-NDMA	71.6	102.3

* From ref. [16], ** From ref. [18].

initiated with BPO alone, $E_i=123.9$ KJ/mol (29.6 Kcal/mol) according to the value of Bawn et al.^[18] The E_i value from our experiment for BPO-DMA initiated MMA polymerization is 48.5 KJ/mol, which is very close to the value of $E_i=53.6$ KJ/mol (12.8 Kcal) determined by O'Driscoll et al.^[9] In contrast to the E_a values in the BPO-amine systems, the E_a values in the range of 56.1–71.6 KJ/mol (13.4–17.1 Kcal/mol) were obtained in the LPO-amine systems, and the E_i values in the range of 71.3–102.3 KJ/mol in these systems were still lower than the $E_i=114.3$ KJ/mol in the LPO alone.

4. The kinetics of MMA polymerization

Imoto et al.^[5] reported the kinetic studies on the polymerization of MMA initiated with the BPO-DMA system. We have studied the polymerization of MMA using BPO-DMT and LPO-DMT as initiator respectively, with the results shown in Fig. 4 and Fig. 5, curve 1 with the slope $0.47 \approx 0.5$ and curve 2 with the slope $0.47 \approx 0.5$. Accordingly, the R_p are proportional both to the 0.5 th power of BPO and DMT concentrations as expressed in the following equation:

$$R_p \propto [\text{BPO}]^{0.5} [\text{DMT}]^{0.5}$$

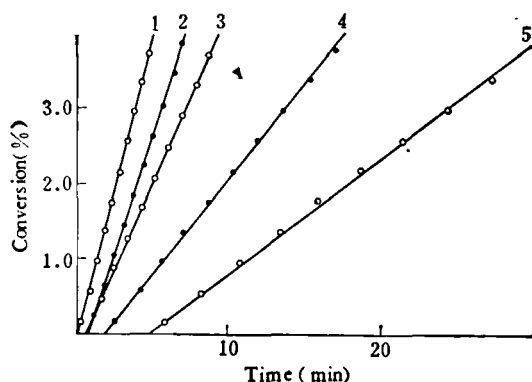


Fig. 4 The effect of concentration of DMT on polymerization
[BPO] = 1.0×10^{-2} mol/L, [MMA] = 9.13 mol/L, 45°C.

[DMT] (mol/L): 1. 4.1×10^{-2} , 2. 2.12×10^{-2} , 3. 1.0×10^{-2} , 4. 0.4×10^{-2} , 5. 0.1×10^{-2} .

Similar results were obtained in LPO-DMT system

$$R_p \propto [\text{LPO}]^{0.5} [\text{DMT}]^{0.5}$$

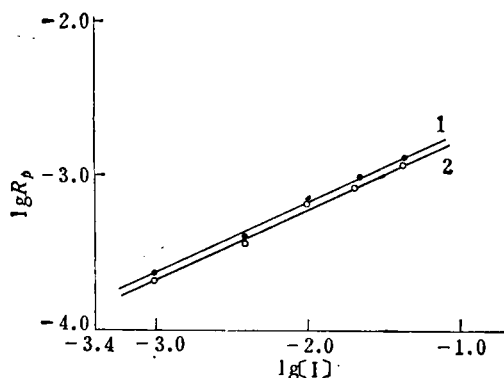


Fig. 5 A plot of $\lg R_p$ versus $\lg [I]$
BPO-DMT initiation system 1. $\lg [I] = \lg [\text{DMT}]$; 2. $\lg [I] = \lg [\text{BPO}]$.

Toluene was used as solvent in the solution polymerization of MMA with different monomer concentrations at 45°C and a fixed concentration of BPO and DMT. The $\lg R_p$ versus $\lg [\text{MMA}]$ plot as shown in Fig. 6 gave a straight line, the slope was $1.07 \approx 1.0$. Hence, the rate equation of MMA polymerization was shown as

$$R_p = K[\text{BPO}]^{0.5} [\text{DMT}]^{0.5} [\text{MMA}]$$

Similar result was obtained in the LPO-DMT system. Therefore, the rate equation obtained in our experiment is in accordance with redox initiated polymerization rate equation^[17]

$$R_p = K[\text{Reductant}]^{1/2} [\text{Oxidant}]^{1/2} [\text{MMA}]$$

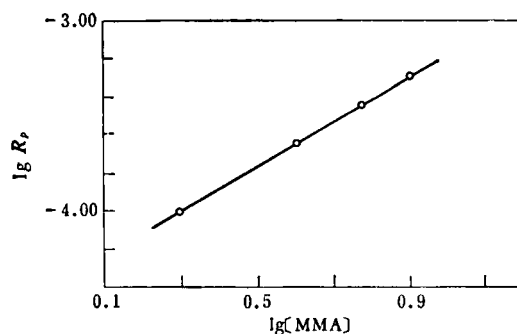


Fig. 6 A plot of $\lg R_p$ versus $\lg [\text{MMA}]$

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