

STUDIES ON ORGANIC PEROXIDE / N,N-DI (2- α -METHYL-ACRYLOYLOXY PROPYL) -PARA-TOLUIDINE BINARY SYSTEMS

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ABSTRACT

The polymerization of methyl methacrylate (MMA) initiated by organic peroxide and polymerizable aromatic tertiary amine such as N,N-di (2- α -methylacryloyloxy propyl) -p- toluidine (MP)₂PT binary system has been studied. It was found that the (MP)₂PT promotes MMA polymerization, and the kinetics of MMA polymerization fits the radical polymerization rate equation. Based on the ESR studies and the end-group analysis the initiation mechanism is proposed.

INTRODUCTION

In our previous paper^[1] we reported that a new functional monomer N,N-di (2- α -methylacryloyloxy propyl) -p- toluidine, ((MP)₂PT), can be polymerized by using organic peroxide initiators. This kind of functional monomer having tertiary aromatic amine group also belongs to polymerizable aromatic tertiary amine. When conjunction with organic peroxide it forms an organic redox initiator^[2]. In this paper polymerization of MMA initiated by organic peroxides such as bis (2-phenoxyethyl) peroxydicarbonate (BPPD), benzoylperoxide (BPO) and lauroyl peroxide (LPO) in conjunction with (MP)₂PT binary systems were investigated. The overall activation energies and the rate equations of MMA polymerization were determined respectively. The initiation mechanism is proposed based on the ESR studies and the end group analysis of the polymers formed.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was chemical reagent and purified by usual method. Functional monomer (MP)₂PT was synthesized from the reaction of α -methylacryloyl chloride with N,N-di (2-hydroxypropyl) -p- toluidine (DHPT) as described in reference^[1], mp. 40.5 — 41.5 °C. Elemental analysis, calculated for C₂₁H₂₉NO₄: C % 70.17; H % 8.13; N % 3.90; Found: C % 70.11; H % 8.18; N % 3.66.

Organic peroxides BPPD, BPO, LPO were purified by usual methods. The organic solvents such as toluene, methanol, chloroform, benzene were used as received.

Spin trap 2-methyl-2-nitroso propane (MNP) was synthesized according to the method in Ref. [3].

Polymerization

The polymerization of MMA in bulk or in toluene solution was carried out in a dilatometer at a constant temperature. Conversion of polymerization was calculated by the volume change of the polymerization system. The PMMA was precipitated from methanol. Molecular weight of PMMA were determined by viscometry method and calculated according to the following equation^[4],

$$[\eta] = 8.68 \times 10^{-5} \bar{M}^{0.76} \quad (\text{Benzene, } 30^\circ\text{C, dL/g})$$

ESR study

A MNP solution (0.04 mol/L in benzene) and an organic peroxide in benzene solution were added into a test tube, and finally a (MP)₂PT benzene solution. Then nitrogen was bubbled through the solution for 5 min in order to remove the oxygen. ESR spectra of organic peroxide-(MP)₂PT-MNP system in benzene solution were taken with a Bruker ER 200D-SRC ESR spectrometer using a TM cavity at X band (microwave power: 19.9 mW, modulation frequency: 100 kHz at room temperature). The hyperfine splitting constants were observed directly from the ESR spectra.

End group analysis

The polymer used for end group analysis were prepared in a polymerization tube using various organic peroxides and (MP)₂PT initiation systems at 40 °C for 3.5 hrs. The polymer obtained were treated by dissolved in chloroform and precipitated by methanol for several times until free of (MP)₂PT. Then the purified polymer samples were dissolved in chloroform and the UV spectra were taken with Shimadzu UV-250 Spectrometer.

RESULTS AND DISCUSSION

1. Effects of organic peroxide and (MP)₂PT systems in MMA polymerization

In the presence of organic peroxide initiator, addition of (MP)₂PT promotes

Table 1 Effects of (MP)₂PT on the bulk polymerization of MMA (50 °C)

Initiation system	BPPD	BPPD-(MP) ₂ PT	BPO	BPO-(MP) ₂ PT	LPO	LPO-(MP) ₂ PT
$R_p \times 10^4$ (mol/L.s)	4.65	10.7	0.73	3.56	1.06	1.36

[BPPD] = 1.0×10^{-2} mol/L; [(MP)₂PT] = 0.25×10^{-2} mol/L;

[BPO] = [LPO] = [(MP)₂PT] = 1.0×10^{-2} mol/L

Table 2 Effects of organic peroxides on the bulk polymerization

Initiation systems	I.P. (min)	$R_p \times 10^4$ (mol/L.s)	^{a)} MW ($\times 10^{-4}$)	I.P. (min)	$R_p \times 10^4$ (mol/L.s)	^{b)} MW ($\times 10^{-4}$)
BPPD-(MP) ₂ PT	0.1	13.9	2.70	1.8	4.30	8.32
BPO-(MP) ₂ PT	0.90	6.28	8.95	5.7	1.84	31.4
LPO-(MP) ₂ PT	2.0	2.68	24.3	8.7	0.72	42.7

I.P. = Induction period

a) [Peroxide] = 4.0×10^{-2} mol/L; [(MP)₂PT] = 1.0×10^{-2} mol/L

b) [Peroxide] = 1.0×10^{-2} mol/L; [(MP)₂PT] = 0.25×10^{-2} mol/L

the polymerization of MMA and enhances the rate of polymerization R_p as shown in Table 1. In case of MMA polymerization by organic peroxide and $(MP)_2PT$ initiator system, the structure of organic peroxide also affect the R_p , as can be seen from the data of Table 2, the order of activities of organic peroxides is as follows $BPPD > BPO > LPO$. However, the order of molecular weights of polymers is reversed.

2. Overall activation energy of MMA polymerization

The polymerization of MMA was carried out at different temperatures and the values of R_p were compiled in Table 3. From the Arrhenius plot, i.e. $\ln R_p$ versus $1/T$ as shown in Fig. 1, the values of overall activation energy (E_a) of MMA polymerization were evaluated to be 44.5, 69.4 and 46.2 KJ/mol for $BPO-(MP)_2PT$, $LPO-(MP)_2PT$ and $BPPD-(MP)_2PT$ initiating systems respectively.

Table 3 R_p of MMA at different temperatures

Initiation system	$R_p \times 10^4 \quad (\text{mol/L} \cdot \text{s})$							E_a (KJ/mol)
	60	55	50	45	40	35	30 (°C)	
$BPO-(MP)_2PT^a)$	5.85 (18.5)	4.88 21.6	3.56 22.4	2.74 24.8	2.04 26.1	/	/	44.5
						/	c)	
$LPO-(MP)_2PT^a)$	3.01 (28.4)	2.00 34.4	1.37 38.4	0.89 43.7	0.55 49.0	/	/	69.4
						/	c)	
$BPPD-(MP)_2PT^b)$	/	/	10.7	7.54	5.31	4.64	2.55	46.17
	(/	/	6.12	6.35	6.92	7.76	8.79) ^{c)}	

a) $[BPO] = [LPO] = [(MP)_2PT] = 1.0 \times 10^{-2} \text{ mol/L}$;

b) $[BPPD] = 2.0 \times 10^{-2} \text{ mol/L}$, $[(MP)_2PT] = 0.25 \times 10^{-2} \text{ mol/L}$;

c) Data in parentheses are the values of molecular weight of the polymers.

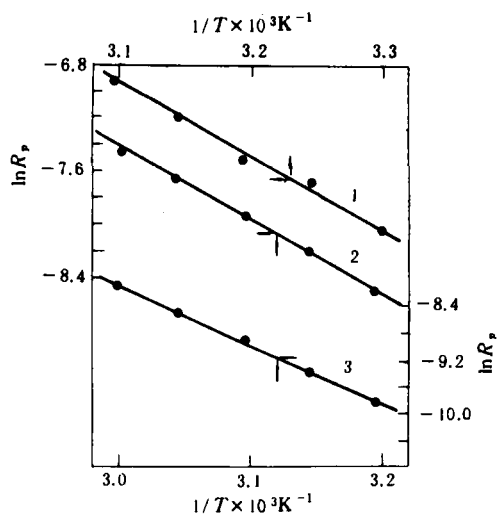


Fig. 1. Relations between $\ln R_p$ and $1/T$

1, $BPPD-(MP)_2PT$ initiation system; 2, $BPO-(MP)_2PT$ initiation system;

3, $LPO-(MP)_2PT$ initiation system

3. Kinetics of polymerization

The kinetic equation of MMA polymerization using BPO- $(MP)_2PT$ initiation system was obtained by usual experimental methods. Under a fixed concentration condition, the concentrations of BPO, $(MP)_2PT$ and monomer were varied respectively and then the R_p was measured. The values were shown in Table 4. The dependence of R_p on concentrations of BPO and $(MP)_2PT$ and MMA monomer was obtained from the slopes of these curves of double logarithmic plots as shown in Fig. 2. The rate equation is expressed as the following:

$$\text{BPO-}(MP)_2PT \text{ system: } R_p = K [BPO]^{0.49} [(MP)_2PT]^{0.46} [MMA]^{1.12} \quad (1)$$

Similarly, from the double logarithmic plot as shown in Fig. 3 and the following rate equations were obtained:

$$\text{LPO-}(MP)_2PT \text{ system: } R_p = K [LPO]^{0.52} [(MP)_2PT]^{0.46} [MMA]^{0.98} \quad (2)$$

$$\text{BPPD-}(MP)_2PT \text{ system: } R_p = K [BPPD]^{0.42} [(MP)_2PT]^{0.52} [MMA]^{1.13} \quad (3)$$

These rate equations were found fitting the equation of polymerization with redox initiation system, that is

$$R_p = K [\text{Oxidant}]^{0.5} [\text{Reductant}]^{0.5} [\text{Monomer}]^{1.0} \quad (4)$$

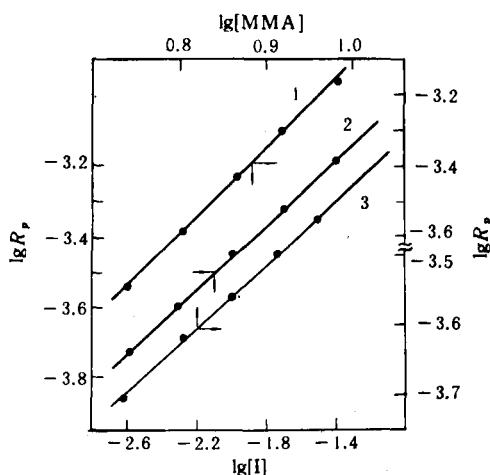


Fig. 2 Double logarithmic plots of $\lg R_p$ vs. $\lg [MMA]$ or $\lg [I]$
1. $[I] = [BPO]$; 2. $[I] = [(MP)_2PT]$;
3. $\lg R_p$ vs. $\lg [MMA]$

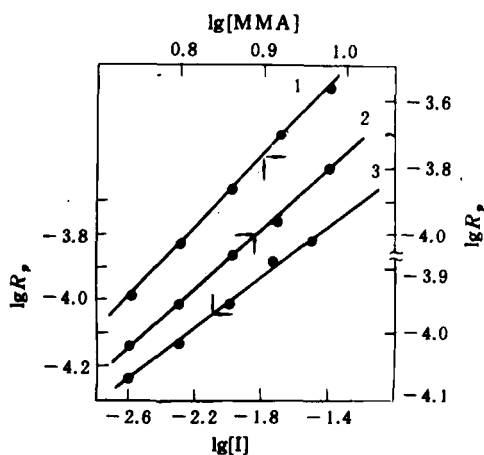


Fig. 3 Double logarithmic plots of $\lg R_p$ vs. $\lg [MMA]$ or $\lg [I]$
1. $[I] = [LPO]$; 2. $[I] = [(MP)_2PT]$;
3. $\lg R_p$ vs. $\lg [MMA]$

The correlation between $\overline{P}_n$ (average degree of polymerization) and R_p in radical polymerization can be expressed as follows:

$$\frac{1}{\overline{P}_n} = \frac{(k_{tc} + 2k_{td})R_p}{k_p[M]^2} \quad (5)$$

Substituting equation (1) to equation (5) gives

$$1/\bar{P}_n = K [BPO]^{0.49} [(MP)_2PT]^{0.46} \quad (6)$$

Table 4 R_p and $\bar{P}_n$ values of MMA polymerization under different concentrations of monomer or initiators (at 50 °C)

$[BPO] \times 10^2$ (mol/L)	$[(MP)_2PT] \times 10^2$ (mol/L)	$[MMA]$ (mol/L)	$R_p \times 10^4$ (mol/L.s)	$1/\bar{P}_n$ ($\times 10^4$)
4.0	1.0	9.07	6.82	11.2
2.0	1.0	9.07	5.06	6.47
1.0	1.0	9.07	3.56	4.47
0.5	1.0	9.07	2.55	3.35
0.25	1.0	9.07	1.79	2.16
1.0	4.0	9.07	6.33	8.84
1.0	2.0	9.07	4.72	7.83
1.0	0.5	9.07	2.51	4.11
1.0	0.25	9.07	1.84	3.19
1.0	1.0	8.16	3.20	5.20
1.0	1.0	7.26	2.76	6.15
1.0	1.0	6.35	2.44	6.65
1.0	1.0	5.44	1.98	7.29

Form the data of Table 4, plotted $1/\bar{P}_n$ versus $[BPO]^{0.49}$ and $1/\bar{P}_n$ versus $[(MP)_2PT]^{0.46}$ which were straight lines as shown in Fig. 4. Therefore, equation (6) can be used to correlate the relation between $1/\bar{P}_n$ and concentrations of initiator.

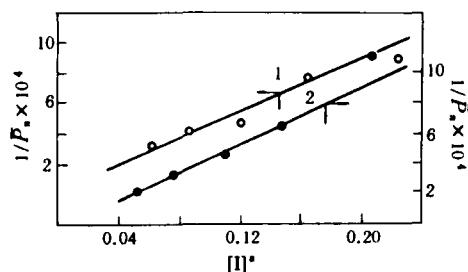


Fig. 4 Correlation between $1/\bar{P}_n$ and $[I]$
 ○ $1/\bar{P}_n$ versus $[BPO]^{0.49}$; ● $1/\bar{P}_n$ versus $[(MP)_2PT]^{0.46}$

4. ESR spectra study

From the above mentioned results, the polymerization of MMA initiated by organic peroxide and $(MP)_2PT$ binary system belongs to radical redox polymerization. In order to determine the free radicals formed from the reaction of organic peroxide with $(MP)_2PT$, MNP was used as spin trap and the adducts of free radicals were observed by means of an ESR spectrometer as shown in Figs. 5–6.

Fig. 5 is the ESR spectrum of BPPD- $(MP)_2PT$ -MNP system. It shows the hyperfine splitting by one α - ^{14}N nucleus, one β -proton and one β - ^{14}N nucleus to form twelve lines in three groups type spectrum each with relative intensity 1:2:2:1. The coupling constants were measured as $a_\alpha^N = 13.60$ G, $a_\beta^H = 3.25$ G, $a_\beta^N =$

3.25G. This result implies the tertiary aromatic amine was oxidized by organic peroxide to form the corresponding free radical I as follows :

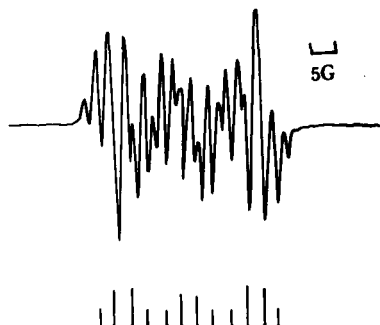
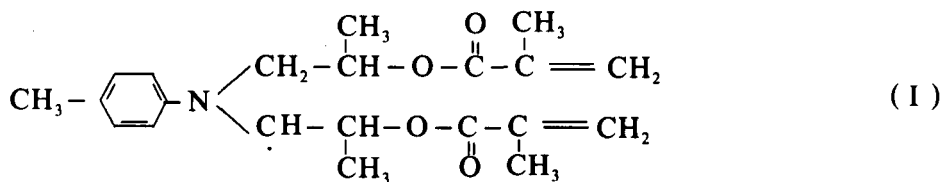


Fig. 5 ESR spectrum of BPPD/(MP)₂PT/MNP system

[BPPD] = 1.67×10^{-2} mol/L ;
 [(MP)₂PT] = 3.33×10^{-2} mol/L ;
 [MNP] = 1.33×10^{-2} mol/L ;

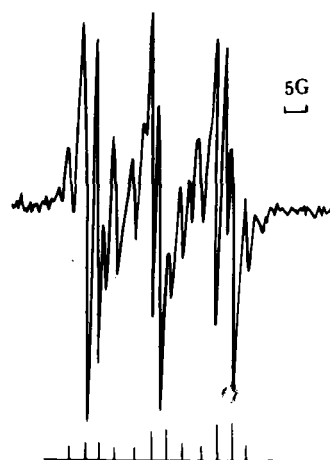


Fig. 6 ESR spectrum of BPO/(MP)₂PT/MNP system

[BPO] = 1.67×10^{-2} mol/L ;
 [(MP)₂PT] = 6.66×10^{-2} mol/L ;
 [MNP] = 1.33×10^{-2} mol/L

Table 5 Hyperfine splitting constants of spin adducts of radicals with MNP

Reaction systems	Radicals trapped by MNP	Hyperfine splitting constants (G)			Ref.
		a_{α}^{N}	a_{β}^{H}	a_{β}^{N}	
BPPD-(MP) ₂ PT ^{a)}	I	13.60	3.25	3.25	Fig. 5
BPO-(MP) ₂ PT ^{b)}	I	13.14	3.20	3.20	Fig. 6
LPO-(MP) ₂ PT ^{c)}	I	13.60	3.24	3.24	[1]
	II	15.20	10.13	$0.75 (a_{\gamma}^{\text{H}})$	[1]

[MNP] $\times 10^{-2}$ mol/L : a) 1.33 ; b) 1.33 ; c) 0.36 .

a) [BPPD] = 1.67×10^{-2} mol/L ; [(MP)₂PT] = 3.33×10^{-2} mol/L ;

b) [BPO] = 1.67×10^{-2} mol/L ; [(MP)₂PT] = 6.66×10^{-2} mol/L ;

c) [LOP] = 1.82×10^{-2} mol/L ; [(MP)₂PT] = 14.5×10^{-2} mol/L .

Similar results are obtained in $\text{BPO}-(\text{MP})_2\text{PT-MNP}$ system (Fig. 6) and in $\text{LPO}-(\text{MP})_2\text{PT-MNP}$ system. In the latter case besides the formation of radical I, the *n*-undecyl radical II, which is formed via decarboxylation of the initial lauroyloxy radical, is obtained as well^[1]. The data of hyperfine splitting constants are compiled in Table 5.

5. End group analysis

The purified samples of polymethyl methacrylate (PMMA) obtained from the MMA polymerization using $\text{BPPD}-(\text{MP})_2\text{PT}$, $\text{BPO}-(\text{MP})_2\text{PT}$, and $\text{LPO}-(\text{MP})_2\text{PT}$ as initiator respectively were dissolved in chloroform and then the polymer solutions were detected by UV spectrometer. The UV spectra were shown in Fig. 7. It shows that all three polymer samples contain the $(\text{MP})_2\text{PT}$ moiety, which exhibited its own characteristic absorption at 254 and 306 nm. Therefore it also confirmed the formation of radical I which can initiate monomer to polymerize and become the end group of polymers. Of course, there may be some $(\text{MP})_2\text{PT}$ moieties present as a pendant group in the polymer formed via copolymerization of $(\text{MP})_2\text{PT}$ and MMA, which might also contribute to the UV absorption.

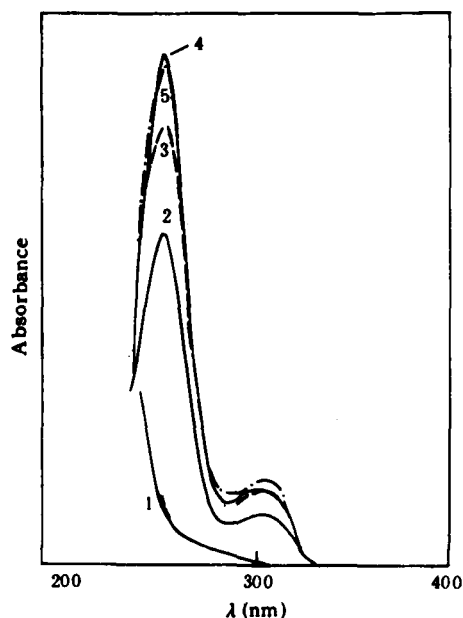
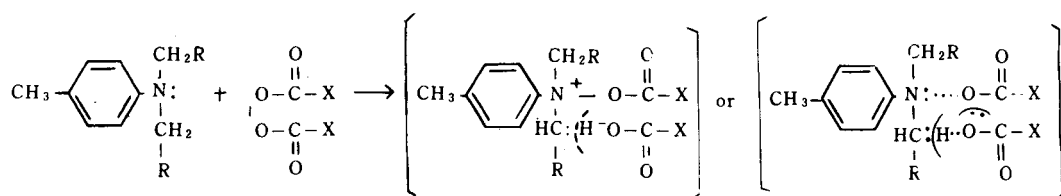


Fig. 7 The UV spectra of PMMA solutions

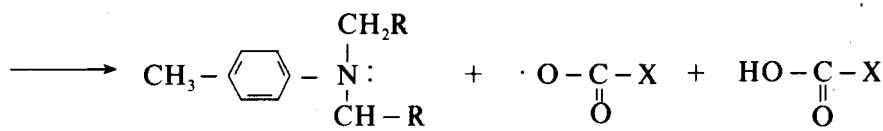
1. PMMA (130 mg / 10 mL, AIBN as initiator);
2. $(\text{MP})_2\text{PT}$ (0.01 mg / 10 mL);
3. PMMA (48 mg / 10 mL, $\text{BPPD}-(\text{MP})_2\text{PT}$ as initiator);
4. PMMA (45 mg / 10 mL, $\text{LPO}-(\text{MP})_2\text{PT}$ as initiator);
5. PMMA (50 mg / 10 mL, $\text{BPO}-(\text{MP})_2\text{PT}$ as initiator)

6. Initiation mechanism

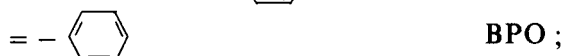
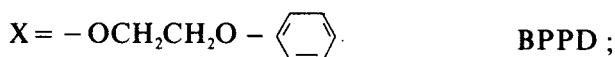
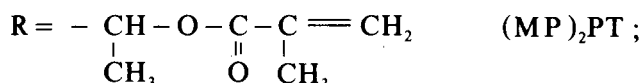
Based on the kinetics studies, ESR spectra and end group analysis, we propose the initiation mechanism of organic peroxide and $(\text{MP})_2\text{PT}$ systems as the following, which is similar to the initiation mechanism of organic peroxide and *N*, *N*-di (2-hydroxyalkyl)- *p*-toluidine systems as described in reference [5].



(Intimate ion pair) (Cyclic transition state)



wherein

**Keywords:**

Organic peroxide; N, N-Di (2- α -methylacryloyloxy-propyl)-p-toluidine; Redox initiation system; MMA polymerization; ESR, End group analysis.

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