

THE EFFECTS OF MORPHOLINES ON METHYL METHACRYLATE RADICAL POLYMERIZATION

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ABSTRACT

The effects of Morpholine, N-methyl morpholine, and N-ethyl morpholine on methyl methacrylate polymerization initiated with organic peroxides were studied. The polymerization rate R_p , the overall activation energy of polymerization E_a , and the rate equation of polymerization were determined.

Pavlinec et al.^[1] reported briefly on methyl methacrylate (MMA) polymerization using t-butyl hydroperoxide (TBH) and piperidine as a system of initiation. In a Japan patent^[2] TBH and cyclic secondary amine morpholine (MP) was used as anaerobic adhesive initiation system. In order to clarify the effects of MP and its derivatives on radical polymerization, the effects of MP, N-methyl morpholine (NMMP), and N-ethyl morpholine (NEMP) on MMA radical polymerization initiated with benzoyl peroxide (BPO), lauryl peroxide (LPO), TBH, and t-butyl peroxybenzoate (TBPB) have been studied respectively in this work.

RESULTS AND DISCUSSION

1. Effects of MP on MMA polymerization

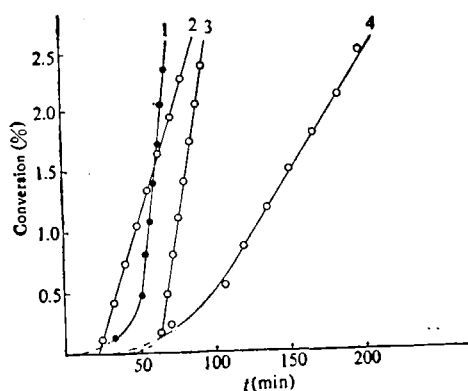
The rate of MMA polymerization R_p was determined by dilatometric method. The molecular weight of polymer obtained was determined viscosimetrically and calculated according to the following equation^[3]

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

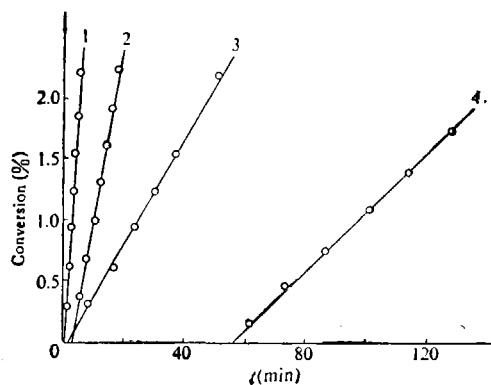
The effects of MP on MMA bulk polymerization initiated with BPO, LPO, TBH and TBPB are varied with the structure of organic peroxide used, the data are listed in Table 1 and Fig. 1.

Table 1 Polymerization rate of MMA (55°C)

Initiation system	[MP]/[Peroxide]* (mol ratio)	Induction period (min)	$R_p \times 10^5$ (mol/l·s)	MW of PMMA (10^{-4})
BPO	0	1	23.0	71.5
BPO-MP	1.2		3.47	10.6
LPO	0	1	33.0	51.7
LPO-MP	1.2		17.3	17.3
TBH	0	18	3.05	
TBH-MP	1.2	23	5.8	29.8
TBPB	0	21	3.1	311
TBPB-MP	1	64	10.4	108

* [Peroxide] = 2.0×10^{-2} mol/l.Fig. 1 Correlation between conversion and time (55°C), [Peroxide] = 2.0×10^{-2} mol/l

1. LPO-MP; 2. TBH-MP;
3. TBPB-MP; 4. BPO-MP.

Fig. 2 Correlation between conversion and time (50°C), [Peroxide] = 2.0×10^{-2} mol/l

1. BPO-NMMP; 2. LPO-NMMP;
3. TBH-NMMP; 4. TBPB-NMMP.

Table 2 Polymerization rate of MMA, (55°C)

Initiation system	[Amine]/[Peroxide] (mol ratio)	Induction period (min)	$R_p \times 10^5$ (mol/l·s)
BPO	0	1	14.3
BPO-NMMP	1	0.5	42.3
BPO-NEMP	1	2	28.6
LPO*	0	1	19.4
LPO-NMMP	1	2	24.5
LPO-NEMP	1	3	23.3

* LPO alone, [LPO] = 0.75×10^{-2} mol/l.

It shows that in the polymerization of MMA using diacyl peroxide BPO or LPO as initiator, MP retards or inhibits the polymerization and decreases both the R_p and molecular weight of polymer formed. While the presence of MP in the polymerization of MMA initiated with TBH initiator, MP prolongs the induction period but enhances the R_p , and similar result is obtained in the polymerization of MMA initiated by TBPB-MP system

2. Effects of *N*-alkyl morpholines on MMA polymerization

The effects of cyclic tertiary amines such as *N*-methyl morpholine (NMMP), and *N*-ethyl morpholine (NEMP) on MMA radical polymerization are different from cyclic secondary amine MP. Either in diacyl peroxide (BPO or LPO)-NMMP systems or in diacyl peroxide (BPO or LPO)-NEMP systems, NMMP and NEMP always enhance the R_p , the data are compiled in Table 2. In the other systems such as TBH-NMMP, TBH-NEMP, TBPB-NMMP and TBPB-NEMP systems, NMMP and NEMP also promote the R_p as shown in Fig. 2 and Table 3. The descending order of R_p for various initiation systems is as follows:



Similar order is observed in the organic peroxide-NEP(*N*-ethyl piperidine initiation systems^[4]). The molecular weight of polymer decreases as the R_p is increased.

Table 3 shows that BPO gives more obvious effect than the other organic peroxide in the peroxide-NMMP or NEMP initiation systems, while the amine component NMMP exhibits more active promoting effect on R_p than NEMP. It reveals that the reaction between the lone pair electrons on nitrogen atom in cyclic amine NEMP molecules and BPO is rather difficult owing to the considerable steric hindrance of the ethyl group, and this is also verified by the higher value of overall activation energy of MMA polymerization for BPO-NEMP initiation system as described in the following section.

According to the results mentioned above, it shows that in BPO-cyclic amine systems, cyclic secondary amine MP retards or inhibits MMA polymerization, prolongs induction period and decreases R_p , however, cyclic tertiary amines NMMP and NEMP promote the polymerization and increase the R_p , similar results are obtained in organic peroxide (LPO, TBH, TBPB)-NMMP initiation systems, and the R_p for BPO-NMMP system is the fastest.

Table 3 Effects of *N*-alkyl morpholines on MMA polymerization

Initiation system	$R_p \times 10^5$ (mol/l·s)	MW^* (10^{-4})	Initiation system	$R_p \times 10^5$ (mol/l·s)	MW^* (10^{-4})
BPO-NMMP	60.8	17.2	BPO-NEMP	35.3	29.1
LPO-NMMP	23.1	55.2	LPO-NEMP	21.9	50.4
TBH-NMMP	6.81	98.6	TBH-NEMP	5.29	43.4
TBPB-NMMP	3.57	259	TBPB-NEMP	3.35	257

* MW : molecular weight of PMMA.

3. Overall activation energy of polymerization

When the concentrations of BPO and NMMP were fixed at 2.0×10^{-2} mol/l respectively, the polymerization of MMA at different temperatures, i.e., 35–50°C, gave different polymerization curves and the values of R_p were obtained from the slopes of these straight lines. The overall activation energy of polymerization E_a was calculated from Arrhenius plot as shown in Fig. 3. From curve 1, the E_a has been found to be 10.2 Kcal/mol. The E_a values for the other systems are compiled in Table 4. It shows that the E_a values for BPO–NMMP and BPO–NEMP systems are much lower than that of BPO alone. Therefore, the R_p increases obviously. The E_a values of LPO–NMMP and LPO–NEMP, however, are very close to that of LPO alone, little effect on the R_p is observed.

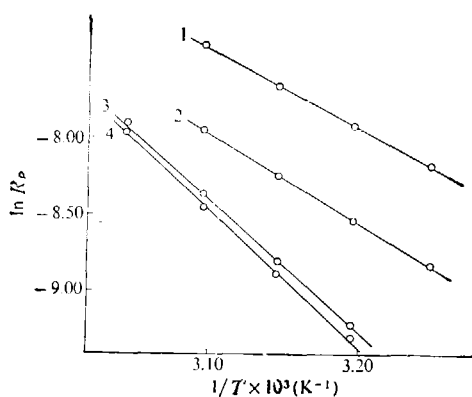


Fig. 3 A plot of $\ln R_p$ versus $1/T$
 1. BPO–NMMP; 2. BPO–NEMP;
 3. LPO–NMMP; 4. LPO–NEMP.

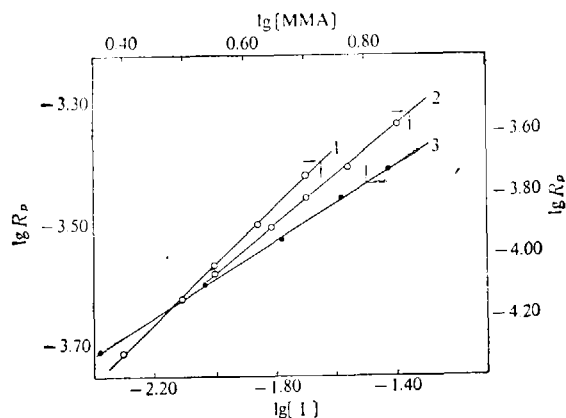


Fig. 4 Double logarithmic plots of R_p versus concentration of initiator and concentration of MMA

1. $\log R_p$ versus $\log [\text{BPO}]$;
2. $\log R_p$ versus $\log [\text{NMMP}]$;
3. $\log R_p$ versus $\log [\text{MMA}]$.

Table 4 Overall activation energy of MMA polymerization

Initiation system	E_a (Kcal/mol)	Temperature ($^{\circ}$ C)
BPO	20.5	30—90 [5]
BPO-NMMP	10.2	35—50
BPO-NEMP	11.6	35—50
LPO	18.4	40—60 [4]
LPO-NMMP	17.1	40—55
LPO-NEMP	17.7	40—55

4. Kinetics of polymerization

In the case of MMA bulk polymerization at 45°C initiated with BPO-NMMP system, the concentration of NMMP was fixed at 1.0×10^{-2} mol/l, and the concentration of BPO varied at a range of 0.50 — 2.0×10^{-2} mol/l, then the values of R_p were calculated from the slopes of polymerization curves, and the data were compiled in Table 5. The double logarithmic plots of R_p versus concentration of BPO and concentration of NMMP were shown in Fig. 4 line 1 and line 2. The orders of dependence of R_p on concentrations of BPO and NMMP were calculated from the slopes to be 0.47 and 0.40 respectively. Therefore,

$$R_p \propto [\text{BPO}]^{0.47} [\text{NMMP}]^{0.40}$$

In benzene solution polymerization of MMA at 45°C , the concentrations of BPO and NMMP were fixed at 1.0×10^{-2} mol/l respectively, and the concentration of MMA varied, then the double logarithmic plot of R_p versus concentration of MMA was obtained as shown in Fig. 4 line 3. The order of dependence of R_p on concentration of MMA was calculated from the

Table 5 Rate of MMA polymerization and molecular weight of PMMA

$[\text{BPO}] \times 10^2$ (mol/l)	$[\text{NMMP}] \times 10^2$ (mol/l)	Induction period (min)	$R_p \times 10^6$ (mol/l·s)	MW of PMMA (10^{-4})	$1/DP \times 10^4$
0.50	1.0	6	19.5	48.6	2.06
0.78	1.0	5	23.9	37.8	2.65
1.00	1.0	3.5	27.0	34.7	2.88
1.39	1.0	2	31.5	27.8	3.60
2.00	1.0	1	37.6	23.4	4.27
1.0	1.56	3.5	31.2	28.9	3.46
1.0	2.00	3.5	34.8	26.9	3.72
1.0	2.79	2.5	39.0	23.5	4.26
1.0	4.02	2.5	45.8	21.7	4.61

slope to be 1.17. The rate equation of the polymerization could be expressed as follows:

$$R_p = K[\text{BPO}]^{0.47}[\text{NMMP}]^{0.40}[\text{MMA}]^{1.17} \quad (1)$$

This rate equation is substantially in accordance with the rate equation of redox polymerization.

The correlation between DP (degree of polymerization) and R_p (rate of polymerization) in radical polymerization can be expressed as follows:

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

Substitution of equation (1) to equation (2) yields

$$\frac{1}{DP} = K'[\text{BPO}]^{0.47}[\text{NMMP}]^{0.40} \quad (3)$$

From the data of Table 5, plotted $1/DP$ versus $[\text{BPO}]^{0.5}$ and $1/DP$ versus $[\text{NMMP}]^{0.4}$ gave straight lines as shown in Fig. 5. Therefore, equation (2) can be used to correlate the relation

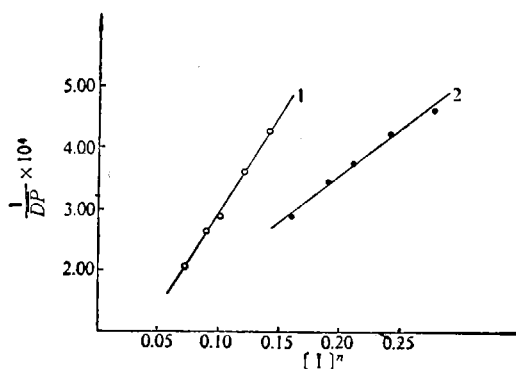


Fig. 5 Correlation between $1/DP$ and $[I]^n$
1. $1/DP$ versus $[\text{BPO}]^{0.5}$; 2. $1/DP$ versus $[\text{NMMP}]^{0.4}$.

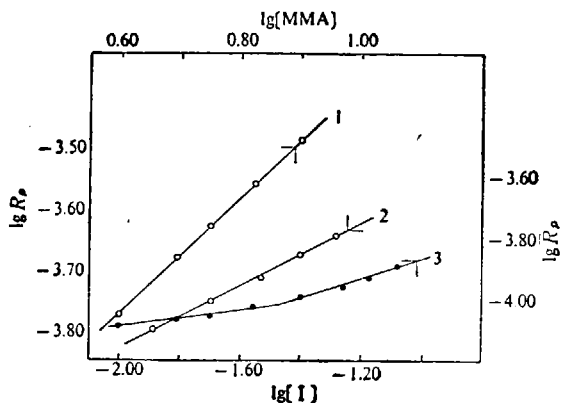


Fig. 6 Double logarithmic plots of R_p versus concentration of initiator and concentration of MMA

1. $\log R_p$ versus $\log [\text{LPO}]$;
2. $\log R_p$ versus $\log [\text{MMA}]$;
3. $\log R_p$ versus $\log [\text{NMMP}]$.

Table 6 Values of R_p and molecular weight of PMMA

$[LPO] \times 10^2$ (mol/l)	$[NMMP] \times 10^2$ (mol/l)	$R_p \times 10^5$ (mol/l·s)	MW of PMMA (10^{-4})	$1/DP \times 10^4$
1.00	1.00	16.8	84.0	1.19
1.56	1.00	20.9	64.6	1.55
2.00	1.00	23.5	60.6	1.65
2.78	1.00	27.5	52.5	1.91
4.00	1.00	32.9	42.9	2.33
1.00	1.01	16.1	88.5	1.13
1.00	1.56	16.5	84.1	1.19
1.00	2.02	16.8	82.5	1.21
1.00	2.79	17.4	79.6	1.26
1.00	4.02	18.1	74.2	1.35
1.00	5.53	18.7	64.6	1.55
1.00	6.64	19.4	61.6	1.62
1.00	8.30	20.3	58.0	1.72

Polymerization temperature = 50°C

between $1/DP$ and concentration of initiator.

In the case of MMA polymerization at 50°C initiated with LPO-NMMP system, the R_p and molecular weight of PMMA were determined respectively. The data were compiled in Table 6.

Fig. 6 shows the double logarithmic plots of R_p versus concentrations of LPO, NMMP and MMA. When the concentration of NMMP is smaller than 2.8×10^{-2} mol/l, the rate equation obtained is as follows:

$$R_p = K[LPO]^{0.48}[NMMP]^{0.07}[MMA]^{1.01} \quad (4)$$

It reveals that in a normal ratio for concentration of NMMP and LPO, i.e., $[NMMP]/[LPO] = 1-2.8$, NMMP has little effect on R_p , in the meantime the molecular weight of PMMA slightly decreases from 885×10^3 to 796×10^3 as the concentration of NMMP increases from 1.00×10^{-2} to 2.78×10^{-2} mol/l (see Table 6). While in higher concentration of NMMP, i.e., $[NMMP] = 4.0-8.3 \times 10^{-2}$ mol/l, NMMP exhibits obvious effect on R_p and the rate equation becomes

$$R_p = K[LPO]^{0.48}[NMMP]^{0.30}[MMA]^{1.02} \quad (5)$$

Meanwhile NMMP has rather profound effect on molecular weight of PMMA, it decreases from 742×10^3 to 580×10^3 .

According to the results mentioned above, the effects of MP and its derivatives, i.e., NMMP, NEMP, on MMA polymerization are summarized as follows:

(1) In BPO-MP or LPO-MP initiation systems, MP can retard or inhibit MMA polymerization, i.e., prolongs the induction period and decreases R_p . However, in TBH-MP or TBPB-MP initiation systems, MP can enhance R_p .

(2) In organic peroxide (BPO, LPO, TBH, TBPB)-NMMP initiation systems, NMMP can promote MMA polymerization, and the BPO-NMMP system is much more active than the other organic peroxide-NMMP systems. While in BPO-amine (NMMP, NEMP) systems, NMMP exhibits more active promoting effect on R_p than NEMP.

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