

THE EFFECTS OF HINDERED AMINES ON METHYL METHACRYLATE POLYMERIZATION*

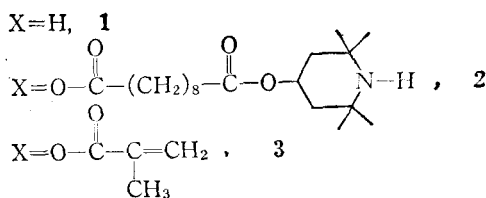
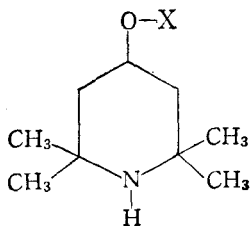
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ABSTRACT

The effects of hindered amines, such as TMP, TPM, TUV-770, on MMA and St homopolymerization have been studied. It was found that in the MMA polymerization initiated with BPO or AIBN, the presence of TPM, TUV-770 prolonged the induction period and a little change on R_p was observed. However, in the presence of TMP R_p increased slightly. The activation energy of polymerization and polymerization rate equation were determined.

Hindered amines such as 2,2,6,6-tetramethyl-4-hydroxy-piperidine (TMP, **1**), bis (2,2,6,6-tetramethylpiperidinyl-4) sebacate (TUV-770, **2**) are used as antioxidant and light stabilizer. Few papers^[1-4] reported that homopolymerization and copolymerization of 2,2,6,6-tetramethylpiperidinyl-4-methacrylate (TPM, **3**) were carried out in the presence of 2,2'-azobis-isobutyronitrile (AIBN). However, it could not copolymerize with styrene (St) using benzoyl peroxide (BPO) initiator, because the imino group of TPM was oxidized by BPO to its corresponding N-oxyl radical, which would inhibit the polymerization^[3]. In order



to study the structure effects of hindered cyclic secondary amines on radical polymerization, three kinds of hindered amines such as TMP, TUV-770 and TPM and its reference piperidine (PD) were used as cyclic secondary amine component and the effects of these amines on methyl methacrylate (MMA) and St polymerization initiated with BPO or AIBN were investigated.

EXPERIMENTAL

Polymerization

The monomers, amines, BPO, AIBN, tetracyanoethylene (TCNE) and the others were

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chemical reagents, and purified by usual methods. The rate of polymerization was determined by dilatometric method.

Molecular weight of polymer and end-group analysis

The molecular weight of polymethyl methacrylate (PMMA) was determined from the intrinsic viscosity of the polymer solution by Ubbelohde viscometer, and then calculated according to the following equation^[5]:

$$[\eta] = 8.68 \times 10^{-5} M^{0.76} \quad (\text{dl/g, } C_6H_6, 30^\circ\text{C})$$

The end-group of polymer is determined by UV-VIS spectrometer using the "CTC Spectrum Method"^[6]. This method is based on an amine donor molecule can react with a strong electron acceptor TCNE to form a charge transfer complex (CTC) which exhibits a characteristic absorption in UV or visible band. The polymer was purified by dissolving and precipitating for several times until its filtrate was free from amine, and then it was dissolved in 0.01 M TCNE methylene chloride solution, the CTC formed from amine moiety and TCNE showed a characteristic absorption band at 400–430 nm.

RESULTS AND DISCUSSION

1. Effects of hindered amines on radical polymerization

(1) Effects of hindered amines on MMA or St polymerization initiated with BPO

Table 1 showed the effects of amines, such as PD, TMP, TUV-770 and TMPM, on the bulk polymerization of St and MMA at 50°C. It showed that although PD and hindered amines exhibited cyclic secondary amine structure, the effects on MMA polymerization were different. In the presence of PD, it prolonged the induction period, decreased the polymerization rate R_p , and reduced the molecular weight of polymer formed. The decomposition rate R_d of BPO in benzene was determined by iodometry. The value of R_d is 2.8×10^{-7} mol/l·s at 70°C, while the R_d for BPO-PD system is 1.6×10^{-4} mol/l·s at 30°C^[7]. Although the R_d for BPO-PD is faster than the R_d of BPO alone, the polymerization rate R_p initiated with BPO-PD system is much slower. This may be due to the non-radical decomposition of BPO with cyclic secondary amine PD^[8], or through the chain transfer reaction of PD and then terminates the propagation chain.

Different effects of hindered amines on St, MMA homopolymerization were observed. In the presence of TMP, it could promote the polymerization, i.e. shortened the induction period and enhanced the R_p . However, TUV-770 and TMPM prolonged the induction period, the effect of TUV-770 on R_p was small, while the R_p descended as the concentration of TMPM increased. The molecular weight of polymer formed was reduced in the presence of TMP, TUV-770 and TMPM, but its decrease was not so obvious as the effect of PD. It revealed that a chain transfer between a propagation chain and the imino group of hindered amine molecule would take place.

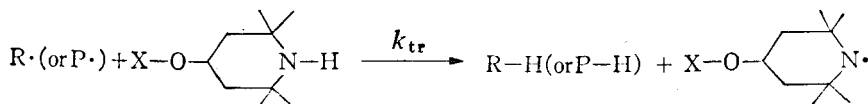


Table 1 The effects of amines on St or MMA bulk polymerization initiated with BPO (50°C)

Monomer	Initiation system	[Amine]/[BPO] (mol ratio)	Induction period (min)	$R_p \times 10^8$ (mol/l·s)	MW (10^{-4})
St	BPO	0	16	1.58	
	BPO-TMP	1	14	1.60	
	BPO-TUV-770	1	24	1.41	
	BPO-TMPM	1	25	1.48	
MMA	BPO	0	6	7.80	
		0	5	7.22	78.4
	BPO-PD	1	28	7.21	35.2
		2	29	6.20	30.0
	BPO-TMP	1	4	7.42	67.8
		2	4.5	8.39	58.8
		5	5	8.93	44.8
	BPO-TUV-770	0.5	4	7.30	
		1	7	7.50	71.6
		2	6	7.12	70.0
		5	8	7.14	51.3
		10	21	7.50	37.0
	BPO-TMPM	1	8	7.48	74.1
		2	10	7.00	65.6
		5	18.5	7.21	39.6
		10	28	7.40	37.6
		20	42	7.04	24.1

[BPO] = 1.0×10^{-2} mol/l.

$R\cdot$ and $P\cdot$ are primary radical and propagation chain respectively, k_{tr} is rate constant of chain transfer. Because the steric effect of hindered amines, the rate of chain transfer of hindered amine is slower than that of PD. This is verified also by the decomposition rate of BPO, the R_d for BPO-TMP is 4.2×10^{-6} mol/l·s at 70°C, which is smaller than the R_d for BPO-PD, i.e. 1.6×10^{-4} mol/l·s at 30°C.

In our experiment the polymerization is performed under nitrogen, even if we use BPO as initiator it can not oxidize the hindered amine to form the N-oxyl radical which would inhibit the polymerization. While through the chain transfer the hindered amines can reduce the molecular weight of polymer formed and even somewhat retard the polymerization.

(2) Effects of hindered amines on MMA polymerization using AIBN initiator

Table 2 showed the effects of PD and hindered amines on the MMA bulk polymerization using AIBN initiator. It showed that in the presence of PD, although it prolonged the induc-

Table 2 The effects of amines on MMA polymerization initiated with AIBN (50°C)

Initiation system	[Amine] $\times 10^3$ (mol/l)	Induction period (min)	$R_p \times 10^4$ (mol/l·s)	MW (10^{-4})
AIBN	0	1.7	1.08	60.7
	0	1.3	1.10	56.4
AIBN-PD	1	20	1.20	51.1
	2	33	1.24	52.2
AIBN-TMP	0.5	2	1.09	56.7
	1	2	1.12	58.5
	2	4.5	1.06	62.0
	5	7.5	1.11	54.4
AIBN-TUV-770	0.5	2.4	1.06	49.0
	2	2.9	1.05	63.0
	5	4.7	1.04	57.3
AIBN-TMPM	0.5	2	1.11	61.9
	2	5.5	1.11	64.0
	5	8.8	1.10	58.0
	10	21	1.13	56.0

$$[\text{AIBN}] = 1.0 \times 10^{-3} \text{ mol/l.}$$

tion period, the values of R_p were substantially equal and the molecular weight of polymer decreased slightly. While in the presence of TMP, TUV-770 and TMPM, these hindered amines had little effects on induction period as well as molecular weight of PMMA and did not promote or retard the polymerization. It revealed that the chain transfer reaction to imino group of hindered amine was much slower than that of PD.

According to the data in Table 1 and 2, the behaviour of functional monomer containing hindered amine group, i.e. TMPM, is different from the other hindered amines. In the MMA polymerization initiated with AIBN, the R_p did not change until the concentration of TMPM increased to 0.1 mol/l, while in the polymerization using BPO as initiator, as the concentration of TMPM increased to 0.2 mol/l, the R_p decreased. When the polymerization of MMA was performed in a sealed tube using either BPO or AIBN as initiator, and the concentrations of initiator and TMPM were 0.01 and 0.5 mol/l respectively, in the case of BPO initiated polymerization only 5% polymer conversion was obtained during 7 hrs reaction period at 50°C, while using AIBN as initiator the conversion for 4 hrs reaction was 16%. Accordingly, the higher conversion was obtained using AIBN as initiator.

2. Activation energy of polymerization

When the fixed concentration of BPO was 1.0×10^{-2} mol/l, the rate of polymerization R_p for MMA bulk polymerization at different temperatures was determined and the k_M

was calculated according to the following equation^[9]:

$$R_p = k_M [I]^{1/2} [M]$$

k_M includes the ratio of various rate constants, I is initiator and M is monomer. The values of k_M were compiled in Table 3. The overall activation energy of polymerization E_a was calculated from the slope of Arrhenius plot as shown in Fig. 1 and 2. The values of E_a were compiled in Table 4. It showed that the value of E_a for MMA polymerization initiated with BPO alone was 20.5 Kcal/mol, while in the presence of hindered amines such as TUV-770, TPM and TMP little change of E_a was observed. Although the value of E_a for BPO-TMP system decreases to 17.9 Kcal/mol^[7], it is still higher than the E_a for BPO-DMA (Dimethylaniline) system, i.e. $E_a = 10.7$ Kcal/mol. Therefore, BPO-TMP, BPO-TUV-770 and BPO-TMPM systems are not redox initiation systems, and it is verified also from the results of kinetic study.

Table 3 k_M of MMA polymerization at different temperatures

Initiator	Temperature (°C)	k_M (1/mol·s)	Ref.
BPO	30	9.91×10^{-6}	[9]
	40	2.91×10^{-5}	
	45	4.71×10^{-5}	
	50	7.94×10^{-5}	
	55	1.41×10^{-4}	
	60	2.14×10^{-4}	
	60	2.23×10^{-4}	[9]
	90	2.71×10^{-4}	[9]

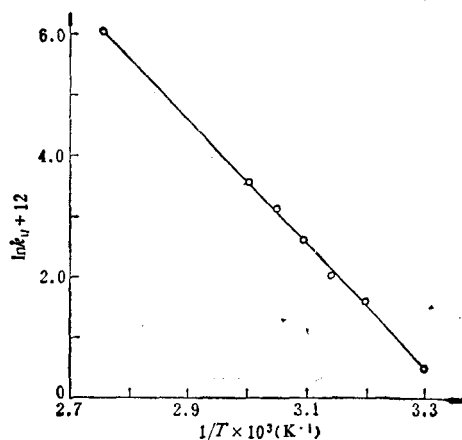


Fig. 1 Correlation between $\ln k_M$ and $1/T$ (BPO initiator)

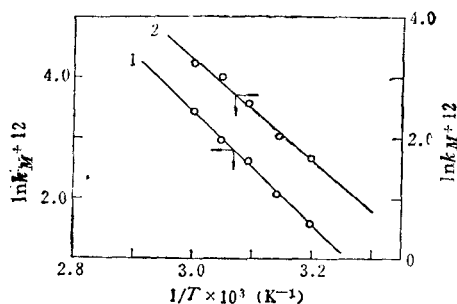


Fig. 2 Correlation between $\ln k_M$ and $1/T$
1 BPO-TUV-770; 2 BPO-TMPM.

Table 4 The overall activation energy of polymerization

Initiation system	E_a (Kcal/mol)	Temperature ($^{\circ}\text{C}$)
BPO	20.5	30—90
BPO-TUV-770	19.4	40—60
BPO-TMPM	18.5	40—60
BPO-TMP	17.9	45—60

3. Kinetics of polymerization

In the case of MMA polymerization initiated with BPO-TMPM system, the fixed concentration of TMPM was 1.0×10^{-2} mol/l, and the concentration of BPO varied at a range of 0.5 — 1.5×10^{-2} mol/l, then the polymerization curves for MMA bulk polymerization at 50°C were drawn as in Fig. 3 and the values of R_p were calculated from the slopes of these straight lines. A plot of R_p versus $[\text{BPO}]^{0.5}$ gave a straight line as shown in Fig. 4 line 1. When benzene was used as solvent, the R_p of solution polymerization was determined by similar method, plotted the R_p versus $[\text{MMA}]$ a straight line was given too (Fig. 4 line 2). However, the independence of R_p on concentration of TMPM was obtained from the double logarithmic plot of R_p versus concentration of TMPM. So the polymerization rate equation could be expressed as follows:

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

Similarly, from Fig. 5 the following rate equation of the MMA polymerization initiated with BPO-TUV-770 system was obtained

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

In the case of MMA polymerization initiated with BPO-TMP system, the dependence of R_p on the concentration of BPO was 0.5 order and on the concentration of TMP was 0.14 order as shown in Fig. 6.

According to the E_a values and polymerization rate equations, it revealed that BPO and hindered amines are not redox initiation systems.

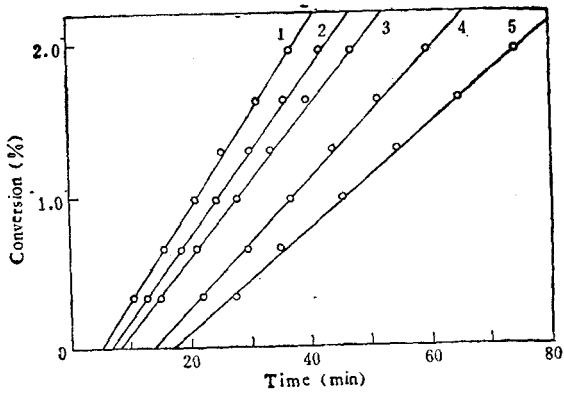


Fig. 3 Correlation between conversion of MMA polymerization and time (55°C) [TMPM]= 1.0×10^{-2} mol/l, [BPO] $\times 10^2$ mol/l (1) 1.5; (2) 1.25; (3) 1.0; (4) 0.75; (5) 0.50.

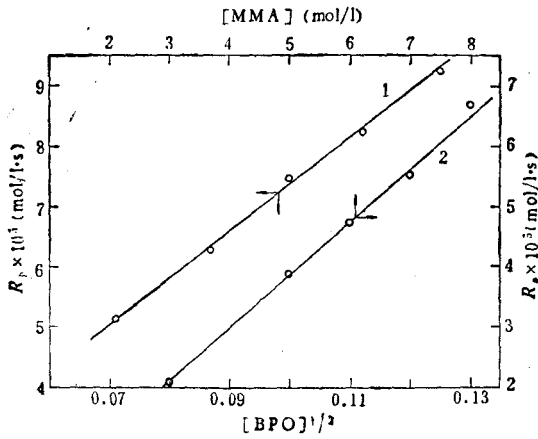


Fig. 4 A plot of R_p versus concentration of BPO or MMA BPO-TMPM initiation system, 1 R_p vs. $[BPO]^{1/2}$; 2 R_p vs. [MMA].

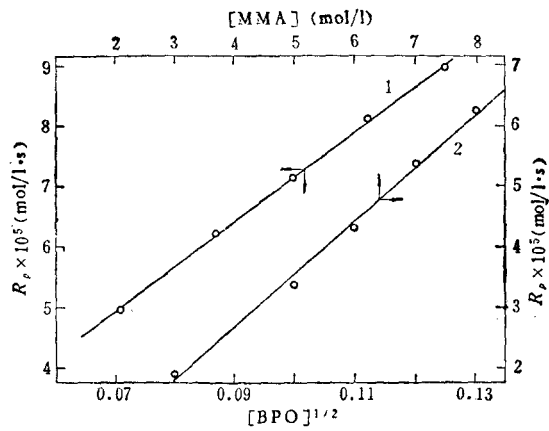


Fig. 5 A plot of R_p versus concentration of BPO or MMA BPO-TUV-770 initiation system, 1 R_p vs. $[BPO]^{1/2}$; 2 R_p vs. [MMA].

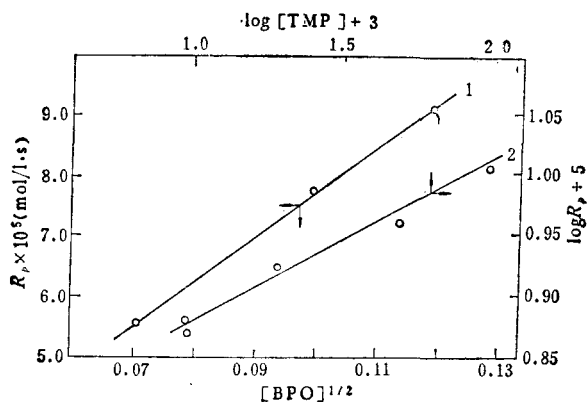


Fig. 6 A plot of R_p versus concentration of BPO or TMP
BPO-TMP initiation system, 1 R_p vs. $[BPO]^{1/2}$; 2 $\log R_p$ vs. $\log [TMP]$.

4. Analysis of the end-group of PMMA

The amino-end group of PMMA can be determined by UV-VIS spectrometer using

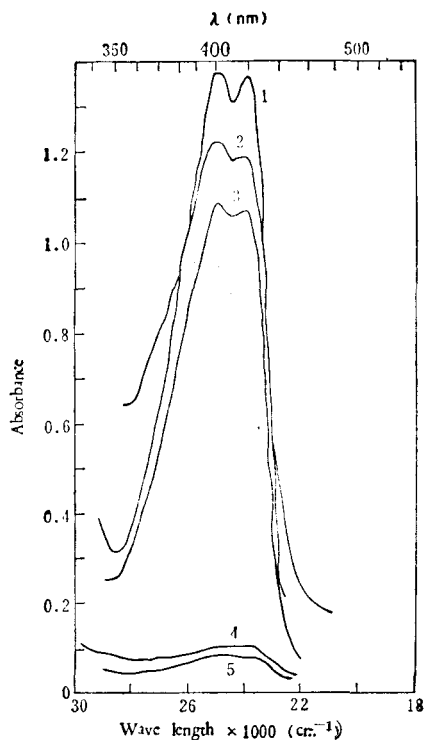


Fig. 7 The spectra of the CTC (TMPM, PMMA treated with $TCNE-CH_2Cl_2$)
1 TMPM; 2 PMMA (BPO-TMPM initiation system); 3 PMMA (AIBN-TMPM initiation system); 4 PMMA (BPO-TMP initiation system); 5 PMMA (AIBN-TMP initiation system).

"CTC Spectrum Method" as reported in our previous paper^[6]. In the MMA polymerization using BPO-TMPM or AIBN-TMPM as initiation system, when the concentration of BPO or AIBN was 0.01 mol/l and the concentration of TMPM was 0.5 mol/l, and then polymerization maintained at 50°C. The polymer formed after purified by dissolving and precipitating several times until its filtrate was free from amine, and then it was dissolved in TCNE-CH₂Cl₂ solution, its spectrum was detected by UV-VIS spectrometer and the absorption band at 400—430 nm was observed, this is similar to characteristic absorption band of CTC from hindered amine and TCNE, so it revealed the polymer containing amino-end group. So far, it is difficult to distinguish the CTC spectrum of TCNE and hindered secondary cyclic amine or of TCNE and hindered tertiary cyclic amine, e.g. both show the absorption band at 400—430 nm.

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