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Decomposition of 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane and its use in polymerization of styrene and methyl methacrylate

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Abstract

A new radical initiator, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane (DMDEHPH), has been used to initiate styrene (ST) and methyl methacrylate (MMA) polymerization in the temperature range of 50–80 °C and DMDEHPH concentration range of 0.005–0.100 mol/L. The effects of initiator concentration, monomer concentration and reaction temperature on the polymerization rate were investigated in details. The increase of these three parameters will all increase the polymerization rate. The orders of polymerization rate to peroxide group concentration and monomer concentration were found to be 0.5 and 1.0, respectively, which validates the correctness of kinetic model derived from the mechanism of polymerization. The activity energy obtained from the polymerization rate constants at various temperatures is 92.0 kJ/mol for ST and 81.4 kJ/mol for MMA. The initiator efficiency is in the range of 0.55 ± 0.03 for ST and 0.43 ± 0.02 for MMA under the experiment conditions. And the initiator efficiency decreases with the increase of initiator concentration.

Keywords: Initiator efficiency; Modeling; Polymerization kinetics

1. Introduction

The free radical polymerization is usually carried out in the presence of monofunctional initiator. The kinetics and mechanism have been investigated more deeply. The polymerization rate is of one order with respect to the monomer concentration and half order with respect to the initiator concentration, while the degree of polymerization is inversely proportional to the initiator concentration. It is the feature of traditional radical polymerization that higher polymerization rate and larger molecular weight cannot be obtained simultaneously [1,2]. The initiator concentration and polymerization temperature are main factors for regulating the polymerization rate and molecular weight of the product. Increase in these factors will increase the polymerization rate, but decrease the molecular weight.

Changing the reactor design and using the finishing initiator to increase conversion were the major possible methods. However, for the former, the capital costs can be too great, with adverse effects on molecular weight and branching, and the latter only produces a marginal increase in production [3]. In the past few years, multifunctional initiators provided a new route as their benefits is that they allow higher polymerization rate while increase or maintaining similar molecular weights in comparison with the conventional monofunctional initiators [4–7] without changing the reactor. It is becoming an interesting field. Although this has been reported, most papers only emphasize their role and comparison with monofunctional initiators. Little information on related mechanisms and their microcosmic kinetic behaviors, especially reaction order, activation energy of polymerization and initiator efficiency, can be found which is very important for a new initiated system. So the objective of this paper is to study the mechanism and kinetics of styrene and methyl methacrylate initiated by a new type of difunctional initiator, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy) hexane (DMDEHPH), including reaction order, activation energy of polymerization and initiator efficiency.

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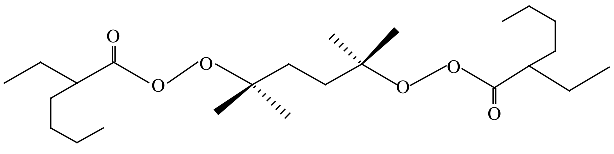
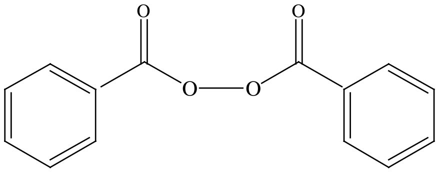
2. Experimental

2.1. Materials

DMDEHPH (I) and benzoyl peroxide (BPO, II) were provided by AKZO NOBEL Co. Styrene (ST) and methyl methacrylate (MMA) monomer were washed with 10% sodium hydroxide solution and then with deionized water several times to remove inhibitor. After drying over anhydrous Na_2SO_4, they were distilled under reduced pressure before use. Benzene (BZ) and ethyl benzene (EB) for analysis were used without any further purification.



I Structure of DMDEHPH



II Structure of BPO

2.2. Polymerization

Bulk and solution polymerization of ST and MMA in the presence of DMDEHPH as initiator were carried out at various temperatures in dilatometers after being swept of oxygen. The conversion was calculated from the change of volume with time. At the end of polymerization, the polymer was cooled down immediately to stop the reaction. Then the product was poured out and precipitated from methanol. The polymer was dissolved in tetrahydrofuran (THF) again, precipitated from a large amount of methanol, filtered, and dried under vacuum at 50 °C.

After it was precipitated, filtered and dried, the bulk polystyrene initiated by DMDEHPH in 0.05 mol/L at 80 °C was dissolve in 20 g solution (MMA:toluene = 3:1), and heated at 80 °C for 8 h. The homopolymers can be removed from the block copolymer with extraction [8] as the following methods. The product was extracted with cyclohexane for 80 h in Soxhlet extractor to remove PS. The residue after dried under vacuum was extracted with acetonitrile for 80 h to remove PMMA. The residue is P(ST-*b*-MMA).

2.3. Analytical techniques

Differential scanning calorimeter (DSC) analyses were performed on a Perkin–Elmer DSC-7 at a certain heating rate in a flowing nitrogen (30 cm^3/min) atmosphere. The number-average molecular weight ($\bar{M}_n$), weight-average molecular weight ($\bar{M}_w$) and polydispersity index ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) of Waters 1525/2414 GPC with three ultrastyragel columns from Waters (10^3, 10^4, and 10^5). The mobile phase used was THF at a flow rate of 0.1 mL/min and the temperature is 25 °C. Six narrow polystyrene (PS) standards were used to calculate the molecular weight of polymer. The ^{1}H NMR spectra in $CDCl_3$ were recorded on a Bruker Advance 500 MHz spectrometer using tetramethylsilane as an internal standard.

3. Results and discussion

3.1. Undecomposed peroxide groups analysis

In the present paper, several studies were carried out to demonstrate the gradual decomposition of DMDEHPH and the reinitiation of the undecomposed peroxides in polymer chain.

3.1.1. DSC study

In order to verify the existence of the O–O bonds in the polymers initiated by DMDEHPH, the polymers were thermally decomposed with scanning rate of 10 °C/min by DSC. As shown in Fig. 1, an exothermic peak corresponding to the characteristic decomposition of peroxy groups in DMDEHPH emerges around 130 °C on the DSC curves of the styrene polymerization product. The locus of exothermic peak is the same as pure peroxide, but no such peak was found in PS initiated by thermal initiation and by conventional monofunctional organic peroxide. There is also no peak in every sample for the second heating, because the peroxide group has been decomposed during the first heating course. This means that some O–O bonds remains in PS chains initiated by DMDEHPH and decompose again to give DSC exotherm. It firmly validates the decomposition of DMDEHPH is not simultaneous. There was no substantial

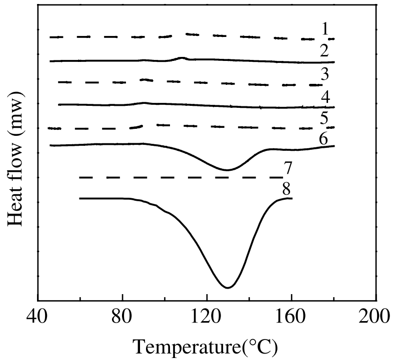


Fig. 1. Differential scanning calorimetry analysis curves of PS by different initiation methods (solid line: the first heating, and dash line: the second heating). 1, PS by thermal initiation; 2, PS by thermal initiation; 3, PS by BPO initiation; 4, PS by BPO initiation; 5, PS by DMDEHPH initiation; 6, PS by DMDEHPH initiation; 7, DMDEHPH in EB; 8, DMDEHPH in EB.

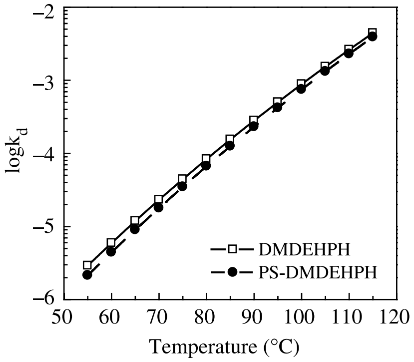


Fig. 2. Comparison of the activity of the peroxide group in DMDEHPH and in PS initiated by DMDEHPH.

difference in the reactivity of the two peroxide groups in initiator molecules under isothermal conditions, because there was only one exothermic peak when heating peroxide from 40 to 180 °C using DSC. From the DSC curves, the decomposition parameter (k_d) of [O–O] bonds can be obtained at various temperatures (T) [9]. Fig. 2 showed the relationship of k_d and T of [O–O] bonds in both DEDMHPH and PS chains which are $k_d = 1.137 \times 10^{15}\exp(-1.294 \times 10^5/RT)$ and $k_d = 1.196 \times 10^{15}\exp(-1.301 \times 10^5/RT)$, respectively. From the above, we can conclude that the O–O bonds in DMDEHPH and in polymers are of the same activity.

3.1.2. Molecular weight

On the other hand, to confirm the position of the peroxy segments in the backbone of polymers initiated by DMDEHPH, the polymer chains with peroxide groups obtained at 70 °C and at the DMDEHPH concentration of 0.100 mol/L were decomposed at 100 °C for 20 h in chlorobenzene to thermally destroy the O–O bonds in polymer chains. The molecular weights of polymers, before and after thermal decomposition, are listed in Table 1.

From the tabulated data, it was observed similar molecular weights of polymers before and after thermal degradation. It is suggested that the O–O bonds in the polymers initiated by DMDEHPH may be probably located in the end of the polymer chains. However, the significant reduction in the molecular weight under thermal decomposition would be observed in the case of the [O–O] bonds located in the middle of the polymer chains initiated by cyclic trifunctional peroxide initiator [10].

3.1.3. Reinitiation validation of polymer with undecomposed peroxide group

In order to have the better insight into decomposition of the peroxy, the bulk polystyrene (after it was precipitated, filtered and dried) initiated by DMDEHPH in 0.05 mol/L at 80 °C was dissolve in 20 g solution (MMA:toluene = 3:1), and heated at 80 °C for 8 h. The products were extracted to remove the homopolymers, then a block copolymer P(ST-*b*-MMA) would be obtained. The percent of block copolymer in the mixture is 31%. The molecular weight of P(ST-*b*-MMA) is 253,000 g/mol. The ^{1}H NMR spectrum of the block copolymer showed the characteristics signals of PS [1.43 (–CH_2–), 1.84 (>CH–), 6.4–6.8 (*o*-protons), and 6.9–7.2 ppm (*p*- and *m*-protons)] and PMMA [0.8–1.1 (–CH_3), 1.89 (–CH_2–), and 3.65 ppm (–OCH_3)], thereby confirming the formation of P(ST-*b*-MMA). In the block copolymer, the mol ratio of PS:PMMA is 0.11:0.89 from the H NMR spectra. All these above shows that the O–O bonds in polymer chains can reinitiate the polymerization of monomer.

3.2. Mechanism of polymerization

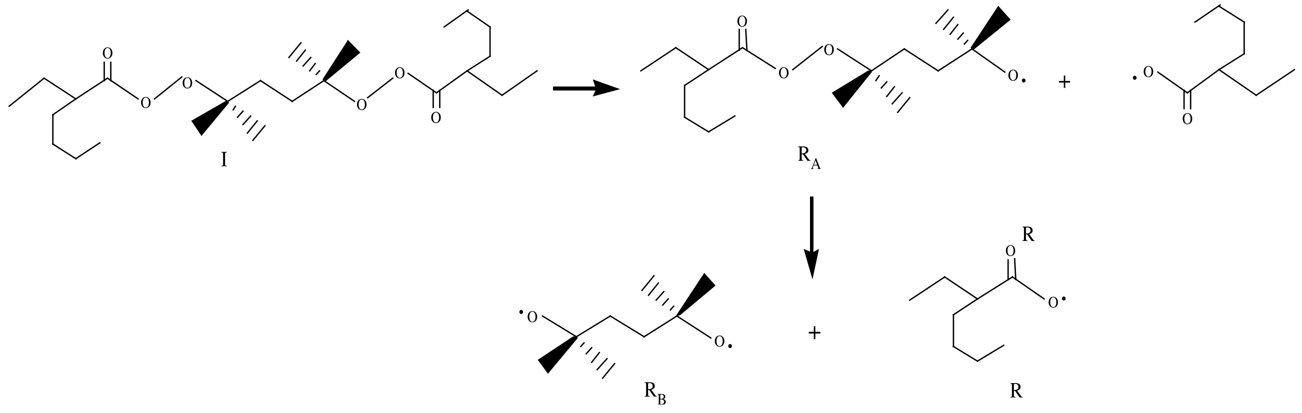
From the above, DMDEHPH decomposed (Scheme 1) thermally to generate two different primary radical species (R_A and R). The route of the peroxyester decomposition depends on the stability of each radical species produced by the above homolytic cleavage reaction. The radical species R_A containing an undecomposed peroxide may decompose further to yield R and R_B.

The primary radical species R and R_A may also undergo decarboxylation and β-scission reaction, respectively. However, there will be no net change in the radical concentration as a result of such reactions. The peroxide groups are separated by a fairly long hydrocarbon segment so that the inductive effect may be negligible. The decomposition rate constant is unaffected by whether the neighboring peroxide groups has decomposed or not. The peroxide groups in the polymer chain ends have the same decomposition rate constant as the peroxide groups in the original difunctional initiator, and may decompose to generate new radical species during the course of polymerization.

The ratio of monoradical concentration to the diradical concentration may be expressed as $(k_d[\mathrm{O{-}O}] - k_dQ_n)/k_dQ_n$, whose magnitude is 10^4–10^8. It means that most of polymer

Table 1
Molecular weight before and after thermal treatment of polystyrene initiated by DMDEHPH

NO	Conversion (%)	Before			After		
		$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	9.87	20,300	33,900	1.67	20,100	35,200	1.76
2	19.8	20,500	34,700	1.69	20,000	34,600	1.73
3	32.4	22,200	38,700	1.75	20,600	37,400	1.82
4	40.6	23,600	41,400	1.76	22,500	41,300	1.84



Scheme 1. DMDEHPH decomposition route.

Table 2
Elementary reactions of radical polymerization initiated by mono- and di-functional initiator

Polymerization with monofunctional peroxide	Polymerization with difunctional peroxide
Peroxide decomposition	
$I\xrightarrow{k_d}2R^\bullet$	$I\xrightarrow{2k_d}R^\bullet+R_A^\bullet$
	$R_A^\bullet\xrightarrow{k_d}R^\bullet+R_B^\bullet$
	$Q_n^\bullet\xrightarrow{k_d}S_n^\bullet+R^\bullet(n\geq 2)$
	$T_n\xrightarrow{2k_d}Q_n^\bullet+R^\bullet(n\geq 2)$
	$Z_n\xrightarrow{k_d}P_n^\bullet+R^\bullet(n\geq 1)$
Initiation	
$R^\bullet+M\xrightarrow{k_i}P_1^\bullet$	$R^\bullet+M\xrightarrow{k_i}P_1^\bullet$
	$R_A^\bullet+M\xrightarrow{k_i}Q_1^\bullet$
	$R_B^\bullet+M\xrightarrow{2k_i}S_1^\bullet$
Propagation: for $n=1$ to N	
$P_n^\bullet+M\xrightarrow{k_p}P_{n+1}^\bullet$	$P_n^\bullet+M\xrightarrow{k_P}P_{n+1}^\bullet$
	$Q_n^\bullet+M\xrightarrow{k_P}Q_{n+1}^\bullet$
	$S_n^\bullet+M\xrightarrow{2k_P}S_{n+1}^\bullet$
Termination: for n, $m=1$ to $N+1$	Combination termination: for n, $m=1$ to $N+1$
$P_n^\bullet+P_m^\bullet\xrightarrow{k_t}D_{n+m}$	$P_n^\bullet+P_m^\bullet\xrightarrow{k_{tc}}D_{n+m}$
$P_n^\bullet+P_m^\bullet\xrightarrow{k_t}P_n+P_m$	$P_n^\bullet+Q_m^\bullet\xrightarrow{k_{tc}}Z_{n+m}$
	$P_n^\bullet+S_m^\bullet\xrightarrow{2k_{tc}}P_{n+m}$
	$Q_n^\bullet+Q_m^\bullet\xrightarrow{k_{tc}}T_{n+m}$
	$Q_n^\bullet+S_m^\bullet\xrightarrow{2k_{tc}}Q_{n+m}$
	$S_n^\bullet+S_m^\bullet\xrightarrow{4k_{tc}}S_{n+m}$
	Disproportionation termination: for n, $m=1$ to $N+1$
	$P_n^\bullet+P_m^\bullet\xrightarrow{k_{td}}P_n+P_m$
	$P_n^\bullet+Q_m^\bullet\xrightarrow{k_{td}}P_n+Q_m$
	$P_n^\bullet+S_m^\bullet\xrightarrow{2k_{td}}P_n+P_m^\bullet$
	$Q_n^\bullet+Q_m^\bullet\xrightarrow{k_{td}}Q_n+Q_m$
	$Q_n^\bullet+S_m^\bullet\xrightarrow{2k_{td}}Q_n+P_m^\bullet$
	$S_n^\bullet+S_m^\bullet\xrightarrow{4k_{td}}S_n+S_m$

Where $P_n^\bullet$, •—]; $Q_n^\bullet$, •—CO–OOR$_1$; $S_n^\bullet$, •—•; $D_n^\bullet$, [—]; $Z_n^\bullet$, [—CO–OOR$_1$; $T_n^\bullet$, R$_1$–OO–CO—CO–OOR$_1$; M, monomer; •, free radical; —], polymer chain with inactive chain end.

chains with undecomposed peroxide group are dead chain, i.e. the concentration of diradical is so tiny comparing to the monoradical concentration that the contribution of diradical to the polymerization rate can be neglected. The active group concentration in propagating chains may also be neglected comparing with those in DMDEHPH molecules and inactive polymer chains.

On the basis of the NMR and DSC studies, the elementary reactions of polymerization initiated by difunctional initiator were presented as shown in Table 2 and compared with that initiated by monofunctional initiator.

With the equal reactivity and long chain assumptions under the quasi steady state, the overall polymerization rate is equal to the propagation constant multiplied by the monomer concentration and by the total concentration of radicals:

$$R_{\mathrm{p}} = -\left(\frac{\mathrm{d}[M]}{\mathrm{d}t}\right)_{\mathrm{p}} = \Sigma k_{\mathrm{p}}[M][R^{\cdot}]_i$$

$$= k_{\mathrm{p}}[M](P^{\cdot} + Q^{\cdot} + 2S^{\cdot}) \tag{1}$$

In radical polymerization, there are several features as follows:

(1) The radical life is very short.
(2) The radical concentration is extremely low (10^{-9}–10^{-7} mol/L).
(3) The concentration of peroxide groups is much higher (10^{-3}–10^{-1} mol/L).
(4) The change of the active group concentration is extraordinary small during the radical living course.

Based on the above, the materials balance to P^* and Q^* are made, respectively:

$$\frac{\mathrm{d}P^{\cdot}}{\mathrm{d}t} = 2k_{\mathrm{d}}I + 2k_{\mathrm{d}}T + 2k_{\mathrm{d}}Z - (k_{\mathrm{tc}} + k_{\mathrm{td}})P^{\cdot 2} - (k_{\mathrm{tc}} + k_{\mathrm{td}})P^{\cdot}Q^{\cdot} = 0 \tag{2}$$

$$\frac{\mathrm{d}Q^{\cdot}}{\mathrm{d}t} = 2k_{\mathrm{d}}I + 2k_{\mathrm{d}}T - (k_{\mathrm{tc}} + k_{\mathrm{td}})Q^{\cdot 2} - (k_{\mathrm{tc}} + k_{\mathrm{td}})P^{\cdot}Q^{\cdot} = 0 \tag{3}$$

And for O–O bonds in system, there is the following relational expression:

$$2I + 2T + Z = [\text{–O–O–}] \tag{4}$$

Considering Eqs. (2)–(4), and assuming that all radicals are of the same initiating efficiency:

$$(k_{\mathrm{tc}} + k_{\mathrm{td}})(P^{\cdot} + Q^{\cdot})^2 = 2fk_{\mathrm{d}}[\text{–O–O–}] \tag{5}$$

Eq. (5) can be arranged as:

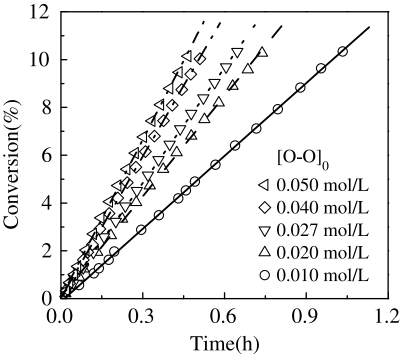


Fig. 3. Conversion vs. time for bulk polymerization of MMA with various DMDEHPH concentration at 60 °C.

$$P^{\cdot} + Q^{\cdot} = \sqrt{\frac{2fk_{\mathrm{d}}[\text{–O–O–}]}{(k_{\mathrm{tc}} + k_{\mathrm{td}})}} \tag{6}$$

Substituting the value of $[P^{\cdot} + Q^{\cdot}]$, we get:

$$R_{\mathrm{p}} = k_{\mathrm{p}}[M](P^{\cdot} + Q^{\cdot}) = k_{\mathrm{p}}[M]\sqrt{\frac{2fk_{\mathrm{d}}[\text{–O–O–}]}{(k_{\mathrm{tc}} + k_{\mathrm{td}})}}$$

$$= k_{\mathrm{p}}\left(\frac{2fk_{\mathrm{d}}}{(k_{\mathrm{tc}} + k_{\mathrm{td}})}\right)^{1/2}([\text{–O–O–}])^{1/2}[M] \tag{7}$$

It is found that the polymerization rate initiated by difunctional initiator is proportional to the square root of the unstable groups (not initiator concentration or two times of initiator concentration) and monomer concentration in one order.

3.3. Kinetics of polymerization

3.3.1. Polymerization rate

To study the polymerization of MMA and ST using DMDEHPH as an initiator, bulk and solution polymerization were carried out using various initiator concentrations and at different reaction temperatures. All conversion was kept below 10% for reliable kinetic analysis. The rate of

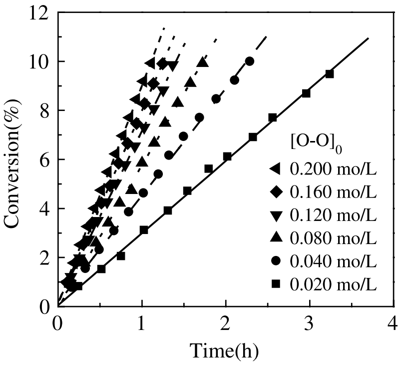


Fig. 4. Conversion vs. time for bulk polymerization of ST with various DMDEHPH concentration at 60 °C.

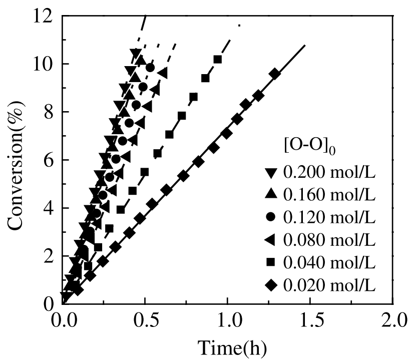


Fig. 5. Conversion vs. time for bulk polymerization of ST with various DMDEHPH concentration at 70 °C.

polymerization was determined from the plots of the conversion (%) vs. time.

Figs. 3 and 4 show the plots of conversion vs. time for homopolymerization of ST and MMA with various peroxide group concentration at 60 °C. And Fig. 5 shows the plot of ST at 70 °C. From these date, the overall homopolymerization rate can be determined. A plot of $\ln R_p$ of MMA vs. ln[O–O] shown as Fig. 6 yields a straight line and the slope gives the order of 0.497 with respect to [O–O]. For the ST polymerization the slope are 0.493 at 60 °C and 0.497 at 70 °C. Both show that the polymerization rate is proportional to $[O\text{–}O]^{1/2}$ and the way of the radical termination is diradical-coupling.

Fig. 7 shows the plot of R_p vs. $[M][I]^{0.5}$ for ST and MMA at different conditions. From the plot, it can be confirmed that the rates of polymerization of MMA and ST are given by Eq. (8), for the existence of solution does not affect the total amount of radicals, even the chain transfer to solution will occur, which shows the correct elemental reaction and the kinetics equation. So based on the kinetics expression:

$$R_p = K[M][O\text{–}O]^{1/2} \qquad (8)$$

where $K = k_p(fk_d/k_t)^{1/2}$ is the overall rate constant, and [M], [O–O] are monomer concentration and peroxide group concentration (not initiator concentration), the values of K was calculated from the slops of the plots and listed in Table 3.

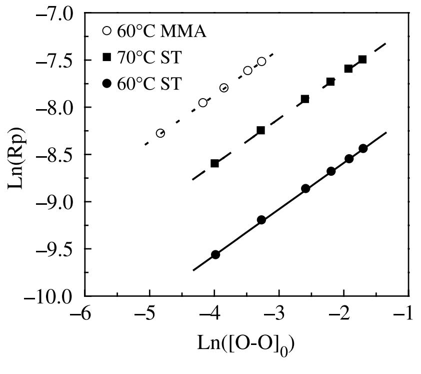


Fig. 6. Dependence of R_p on $[O\text{–}O]_0$ concentration for MMA and ST polymerization.

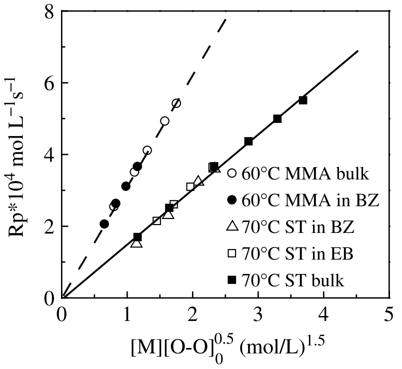


Fig. 7. Conversion vs. time for MMA and ST polymerization at various concentration. MMA bulk: [O–O] = 0.010–0.050 mol/L, [M] = 8.99 mol/L; MMA in BZ: [O–O] = 0.021, [M] = 4.50–8.99 mol/L; ST bulk: [O–O] = 0.020–0.200 mol/L, [M] = 8.26 mol/L; ST in BZ and EB: [O–O] = 0.040 mol/L, [M] = 4.93–8.26 mol/L.

3.3.2. Activation energy of polymerization

The conversion-time curves of MMA and ST polymerization at different reaction temperatures are given in Figs. 8 and 9, respectively, and the polymerization rate thus derived are listed in Table 4. The overall rate constant can be obtained from the polymerization rate, monomer concentration and peroxide concentration. The overall activation energy (E_a) of the polymerization was determined from the Arrhenius equation using experimental K data at different temperatures. Fig. 10 displays the polymerization rates for MMA and ST at different temperatures. From the plots of $\ln K$ vs. $1/T$, the overall activation energies for MMA and ST are 81.4 and 92.0 kJ/mol. Tobolsky reported the values in MMA and styrene polymerization initiated by BPO which yield the value of 83.0 and 90.3 kJ/mol [11], while Redington reported this value in styrene polymerization was from 83.7 to 100 kJ/mol [12]. So it seems that the difference is not very obvious in the overall activation energy between the systems initiated by these two peroxides.

The relationships of the overall rate constant and the reaction temperatures are as follows:

$$K = 2.53 \times 10^9 \exp(-8.14 \times 10^4/RT)$$

for MMA at [O–O] = 0.027 mol/L and

$$K = 2.31 \times 10^{10} \exp(-9.20 \times 10^4/RT)$$

for ST at [O–O] = 0.080 mol/L.

By taking the reported activation energies [13] of propagation (E_p) and termination (E_t) as 123.7 and 29.35 kJ/mol for ST, as well as 76.23 and 12.27 kJ/mol for MMA, respectively, the activation energy for the initiation (E_i) can be calculated as following: $E_i = 2E_a + E_t - 2E_p$. The results are 131.9 kJ/mol for ST and

Table 3
Effect of DMDEHPH concentration on R_p and initiator efficiency

Monomer type	T (°C)	$[O–O]_0$ (mol/L)	R_p (mol/L s)	K (L/mol s)	f
MMA	60	0.010	2.82×10^{-4}	3.15×10^{-4}	0.439
MMA	60	0.020	3.50×10^{-4}	3.13×10^{-4}	0.433
MMA	60	0.027	4.10×10^{-4}	3.12×10^{-4}	0.430
MMA	60	0.040	4.92×10^{-4}	3.11×10^{-4}	0.428
MMA	60	0.050	5.41×10^{-4}	3.08×10^{-4}	0.419
ST	60	0.020	7.11×10^{-5}	8.79×10^{-5}	0.560
ST	60	0.040	1.01×10^{-4}	8.77×10^{-5}	0.558
ST	60	0.080	1.41×10^{-4}	8.69×10^{-5}	0.548
ST	60	0.120	1.69×10^{-4}	8.57×10^{-5}	0.532
ST	60	0.160	1.94×10^{-4}	8.52×10^{-5}	0.526
ST	60	0.200	2.15×10^{-4}	8.48×10^{-5}	0.522
ST	70	0.020	1.84×10^{-4}	1.63×10^{-4}	0.572
ST	70	0.040	2.61×10^{-4}	1.63×10^{-4}	0.568
ST	70	0.080	3.64×10^{-4}	1.61×10^{-4}	0.558
ST	70	0.120	4.38×10^{-4}	1.59×10^{-4}	0.544
ST	70	0.160	5.03×10^{-4}	1.59×10^{-4}	0.543
ST	70	0.200	5.54×10^{-4}	1.57×10^{-4}	0.532

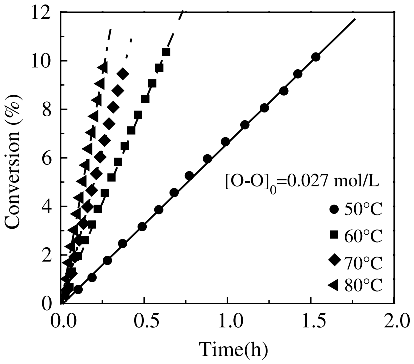


Fig. 8. Conversion vs. time for bulk polymerization of MMA at various temperature.

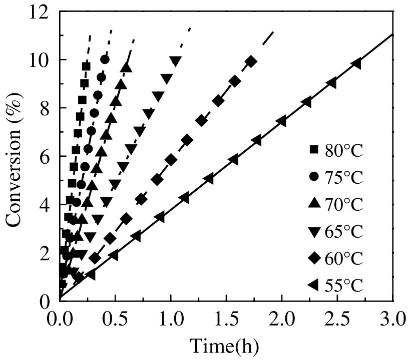


Fig. 9. Conversion vs. time for bulk polymerization of styrene at various temperatures ($[O–O]_0 = 0.080$ mol/L).

129.2 kJ/mol for MMA, which are close to the 129.4 kJ/mol from DSC methods in Section 3.1.

3.3.3. Initiator efficiency

During the course of polymerization, the initiator efficiency, f, may vary in particular as the viscosity of the reaction mixture increases with monomer conversion. But at the beginning, f, k_p and k_t may be regarded as constant [14–19]. So the following equation can be used to estimate f:

$$f = \frac{R_{p0}^2}{2[\text{–O–O–}]_0[M]_0^2}\left(\frac{k_t}{k_d k_p^2}\right) \tag{9}$$

The results are listed in Tables 3 and 4. It is found that f is 0.43 ± 0.02 for MMA and 0.55 ± 0.03 for ST. The initiator efficiency decreases with an increase in the initiator concentration for the range of initiator concentrations considered in this study. The similar result was also

Table 4
Effect of reaction temperature on R_p and initiator efficiency

Monomer type	$[O–O]_0$ (mol/L)	T (°C)	R_p (mol/L s)	K (L/mol s)	f
MMA	0.027	50	1.69×10^{-4}	1.79×10^{-4}	0.435
MMA	0.027	60	4.10×10^{-4}	4.41×10^{-4}	0.430
MMA	0.027	70	6.47×10^{-4}	7.01×10^{-4}	0.446
MMA	0.027	80	9.40×10^{-4}	1.03×10^{-3}	0.422
ST	0.080	50	8.48×10^{-5}	5.19×10^{-5}	0.530
ST	0.080	60	1.41×10^{-4}	8.69×10^{-5}	0.548
ST	0.080	65	2.25×10^{-4}	1.40×10^{-4}	0.537
ST	0.080	70	3.66×10^{-4}	2.29×10^{-4}	0.563
ST	0.080	75	5.67×10^{-4}	3.51×10^{-4}	0.552
ST	0.080	80	8.97×10^{-4}	5.71×10^{-4}	0.578

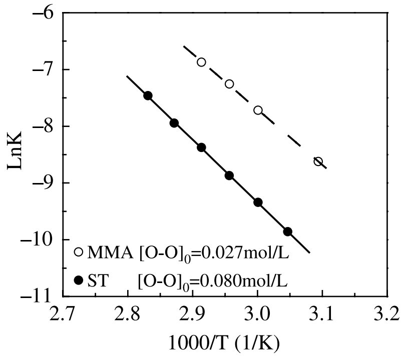


Fig. 10. ln *k* vs. 1/*T* for MMA and ST polymerizations initiated by DMDEHPH.

reported by Heffelfinger and Langsam [20] with *t*-butyl perneodecanoate as an initiator. The initiator efficiency is depended on the radicals number, which escape from the cage, while the diffusion is affected by the temperature [16,17,19]. At the same temperature, the more the initiator concentration is, the more the radicals terminated in cage is. So the initiator efficiency decreases with an increase in the initiator concentration. Although the peroxy groups will undergo more facile degradation to form radicals at higher temperature, the initiator efficiency seems similar for there are more radicals diffused out of the cage.

4. Conclusions

Several studies have demonstrated the gradual decomposition of DMDEHPH and the reinitiation of the undecomposed peroxides in polymer chain. The block copolymer can also be obtained by using this type of peroxide. From these studies, the initiation mechanism and the elementary reaction has been presented. Based on these, the detailed microscopic kinetic model can be deduced. It is the first paper on the microscopic kinetic model of the ST and methyl MMA bulk polymerization initiated by diperoxyester initiator. The model shows the relationships between the polymerization rate and the corresponding concentration with the order of 0.5 to peroxide group concentration (not the initiator concentration or two times of it) and 1.0 to monomer concentration, respectively. The increases of monomer concentration, initiator concentration and reaction temperature will all increase the polymerization rate. And the experimental results validate the correctness of kinetic model presented from the mechanism of polymerization. The activity energy obtained from the polymerization rate constants at various temperatures is 92.0 kJ/mol for ST and 81.4 kJ/mol for MMA. The initiator efficiency is in the range of 0.55 ± 0.03 for ST and 0.43 ± 0.02 for MMA under the experimental conditions. And the initiator efficiency decreases with the increase of initiator concentration.

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