Propagation and Termination Rate Constants of *N*-*tert*-Alkyl- and *N*-Trialkylsilylmaleimides in Radical Polymerization Initiated with 2,2'-Azobisisobutyronitrile

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ABSTRACT: Radical polymerizations of *N*-*tert*-alkylmaleimide (tRMI) and *N*-trialkylsilylmaleimide (RSiMI) were investigated kinetically by means of electron spin resonance (ESR) spectroscopy. By the use of the steady-state concentrations of the polymer radicals determined by ESR, the propagation and termination rate constants (k_p and k_t) were evaluated. k_t was also determined by analysis of the non-steady state. tRMI and RSiMI were revealed to have similar k_p depending on the bulkiness of the *N*-substituents, while k_t for RSiMI were about ten times larger than those for tRMI. The relationships between k_p and k_t values and the structure of the *N*-substituents were discussed.

KEY WORDS *N*-Substituted Maleimide / Radical Polymerization / Electron Spin Resonance / Propagation / Termination / Rate Constant /

In the previous papers, we reported radical polymerization of various *N*-substituted maleimides and some properties of the resulting polymers.¹⁻⁶ The synthesis and polymerizations of *N*-trialkylsilylmaleimides (RSiMI) and thermal properties and hydrolysis of the polymers obtained were also reported.⁶ It was pointed out that the introduction of the bulky alkyl groups into the *N*-substituent induced the reduced polymerization reactivity, *i.e.*, decreases in the yield and molecular weight of the polymers in the polymerization of RSiMIs as well as *N*-*tert*-alkylmaleimides (tRMI)³ and some *N*-(alkyl-substituted phenyl)maleimides (RPhMI).^{1,7}

Recently, the kinetic studies on radical polymerization by means of electron spin resonance (ESR) spectroscopy have intensively been carried out.⁸ In the polymerizations of some 1,2- and 1,1-disubstituted ethylenes such as dialkyl fumarates⁹ and dialkyl itacon-

nates,^{10,11} the steady-state radical concentrations are higher than those for ordinary polymerizations, being very advantageous for determination of the radical concentration. In those reports, the propagation and termination rate constants (k_p and k_t) were determined and the effects of the structures of the ester alkyl groups on the constants were discussed. In 1989 Sato *et al.* reported¹² an ESR study on the polymerization of *N*-cyclohexylmaleimide (CHMI). We reported the determination of k_p and k_t for RPhMI and revealed the great effects of the ortho substitution resulting in the decrease in k_p .⁷

In this paper, we describe the determination of the rate constants of *N*-*tert*-butylmaleimide (tBMI), *N*-*tert*-amylmaleimide (tAMI), *N*-*tert*-octylmaleimide (tOMI), *N*-(trimethylsilyl)maleimide (MSiMI), and *N*-(*tert*-butyldimethylsilyl)maleimide (BSiMI) (Scheme 1), in the radical polymerization initiated with

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Monomer	R ¹	R ²	R ³
tBMI	CH ₃	CH ₃	CH ₃
tAMI	CH ₃	CH ₃	C ₂ H ₅
tOMI	CH ₃	CH ₃	C(CH ₃) ₂ CH ₂ C(CH ₃) ₃
MSiMI	CH ₃	CH ₃	CH ₃
BSiMI	CH ₃	CH ₃	C(CH ₃) ₃

Scheme 1.

2,2'-azobisisobutyronitrile (AIBN) in benzene at 60°C.

EXPERIMENTAL

tRMIs and RSiMIs were prepared by the methods described previously.^{3,6} AIBN and 2,2'-azobis(2,4,4-trimethylpentane) (ATMP) (Scheme 2) were recrystallized twice from methanol. Benzoyl peroxide (BPO) was reprecipitated from chloroform and methanol. 1,3,5-Triphenylverdazyl (Scheme 3) was synthesized and purified by the method in literature.¹³ Other reagents and solvents were used after ordinary purification.

Radical polymerization was carried out in benzene at 60°C in the presence of AIBN in a sealed glass tube. The polymerization mixtures were poured into methanol to isolate a polymer. In the polymerization of MSiMI, the resulting polymer was isolated as poly-maleimide after quantitative hydrolysis.⁶ The conversion was determined gravimetrically.

ESR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. The typical operation conditions are as

Scheme 2.

Scheme 3.

follows: modulation amplitude, 1.0 G; conversion time, 41 ms; time constant, 164 ms; sweep time, 42 s; power, 10.0 mW; scan number 50—100. For determination of the radical concentration, 10-G modulation amplitude was employed to get a good signal to noise ratio, and the spectrum was not accumulated. Intensity of the spectra was determined from a double integration of the spectra. The radical concentration was calibrated by using 1,3,5-triphenylverdazyl dissolved in the monomers and benzene in the ESR tube at 60°C. For analysis of the non-steady state, the photopolymerization systems with ATMP as an initiator was employed at 60°C ([ATMP] = 0.02 mol l⁻¹). In the case of tBMI, the ATMP concentration was reduced to 0.01 mol l⁻¹ because of the fast polymerization. After the measurements, all polymer yields were less than 10%. Intensity of the spectrum was evaluated from the height of the peak at the lowest magnetic field, and the steady state concentration of the radical under UV irradiation was determined with the verdazyl similarly to the method described above.

UV-vis spectra were recorded on a Shimadzu UV-160 spectrometer with a 1-cm quartz cell maintained at 60°C. For the determination of the initial rate of polymerization, a decay of the absorbance of the verdazyl at 720 nm

($\epsilon=4370$) was recorded.

RESULTS AND DISCUSSION

The time-conversion relationships are shown in Figure 1 for the radical polymerization of tRMIs and RSiMIs initiated with AIBN in benzene at 60°C. Linear relationships were

Figure 1. Time-conversion relationships for radical polymerization of RSiMIs and tRMIs in benzene at 60°C: [Monomer] = 1 mol l⁻¹; [AIBN] = 0.005 mol l⁻¹. (○) tBMI; (●) tAMI; (◐) tOMI; (△) MSiMI; (▲) BSiMI.

obtained not only at an initial stage but also even at a higher conversion region as shown in Figure 1(a), although the polymerization rate should decrease along with a consumption of the monomer. It suggests that the radical concentration of these polymerization systems increases during polymerization because of the formation of a polymer, which increases the viscosity of the polymerization medium. Therefore the initial polymerization rate (R_p) was determined from an initial slope of the plot of $\ln([M]/[M]_0)$ versus the polymerization time (Figure 1(b)). R_p were in the following order: tBMI > tAMI > MSiMI > BSiMI > tOMI as listed in Table I. In the polymerization of tRMIs, R_p decreased by the introduction of bulky substituents. In these polymerization systems, ESR spectra of the propagating radicals are detectable with a certain intensity under the polymerization conditions identical to those in Figure 1. As shown in Figure 2, all of the spectra analogous to the spectrum of CHMI reported by Sato *et al.*¹² However, the spectra obtained in this work have a weaker central line, and small peaks were obviously observed at the both outer sides of the two strong peaks. The spectra included no significant change when the polymerization temperature was increased from 60°C to 100°C, as shown in Figure 3. This result suggests that the change of the intensity of the central peak is not attributed

Table I. Propagation and termination rate constants for tRMIs and RSiMIs at 60°C^a

Monomer	$R_p \times 10^5$ mol l ⁻¹ s ⁻¹	$[P^\cdot] \times 10^7$ mol l ⁻¹	$k_p \times 10^{-1}$ l mol ⁻¹ s ⁻¹	$k_d f \times 10^6$ s ⁻¹	$k_t^b \times 10^{-4}$ l mol ⁻¹ s ⁻¹	$k_t^c \times 10^{-4}$ l mol ⁻¹ s ⁻¹
tBMI	13.6	13.3	10	3.61	2.1	2.3
tAMI	6.25	9.1	6.9	3.96	4.8	1.7
tOMI	2.69	11.8	2.3	3.76	2.7	1.5
MSiMI	5.55	4.7	12	3.48	15	23
BSiMI	5.00	4.1	12	3.41	20	—

^a Polymerization conditions: [Monomer] = 1 mol l⁻¹, [AIBN] = 0.005 mol l⁻¹ in benzene at 60°C.

^b Determined from the steady-state equation: $k_t = (2k_d f [I]) / [P^\cdot]^2$.

^c Determined from the second-order plot of the decay curve of the radical concentration. [Monomer] = 1 mol l⁻¹, [ATMP] = 0.02 mol l⁻¹. For tBMI, [ATMP] = 0.01 mol l⁻¹.

Figure 2. ESR spectra of propagating radicals: [Monomer] = 1 mol l^{-1} , [AIBN] = 0.005 mol l^{-1} in benzene at 60°C . (a) tBMI; (b) tAMI; (c) tOMI; (d) MSiMI; (e) BSiMI. Modulation amplitude 1.0 G . For the other measurement parameters, see the experimental section.

to an exchange broadening, which may give a wrong conclusion for the determination of radical concentration, and that the spectrum had better be interpreted as an overlapping of two or more conformation. In fact, these spectra might be obtainable by the superposition of a doublet and a triplet with a 1:2:1 intensity ratio, which have *ca.* 30 G coupling constants, respectively, from our results of preliminary simulation. The change in the shape of the spectra depending on the structure of the *N*-substituents in Figure 2 might be due to the difference of the conformation of the polymer chain end. The conformational study of the polymer radicals from these monomers is now in progress.

By the use of the solution of the verdazyl as a stable radical for calibration, we determined the concentration of the polymer radical

Figure 3. ESR spectra of propagating radical of poly(tOMI) observed at various temperatures: (a) [tOMI] = 1 mol l^{-1} , [BPO] = 0.01 mol l^{-1} , in benzene at 80°C . Modulation amplitude 1 G and (b) [tOMI] = 1 mol l^{-1} , [ATMP] = 0.01 mol l^{-1} , in toluene at 100°C . Modulation amplitude 5 G .

Figure 4. ESR spectra used for determination of the concentration of the propagating radicals of tAMI: (a) poly(tAMI) radical and (b) verdazyl as a calibration. Modulation amplitude 10 G , a single scan.

($[\text{P}\cdot]$) in these polymerization systems. Typical spectra for the determinations are depicted in Figure 4, which were taken by a single scan with a higher modulation amplitude (10 G). It

reflects an initial region of the polymerization, *i.e.*, a few per cent conversion region, since the ESR measurement could be completed within several minutes. $[P\cdot]$ are $9\text{--}13 \times 10^{-7}$ and $4\text{--}5 \times 10^{-7} \text{ mol l}^{-1}$ for the tRMIs and RSiMI polymerizations, respectively, as shown in Table I, from which termination may be supposed to occur more frequently in the polymerization of RSiMIs than tRMIs.

By the following equation, k_p can be estimated;

$$k_p = R_p / ([P\cdot][\text{Monomer}]) \quad (1)$$

The k_p values determined were $2\text{--}12 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$, being comparable to that reported for CHMI ($65 \text{ l mol}^{-1} \text{ s}^{-1}$).¹² It has been found that k_p of tBMI, MSiMI, and BSiMI are resemble to each other, but tAMI and tOMI bearing bulkier *N*-substituents have smaller k_p .

For the determination of k_t , we can adopt two methods, *i.e.*, analyses of a steady state and a non-steady state. The change of the radical concentration in polymerization is represented by the difference of the rates between formation and consumption of the radical (eq 2).

$$d[P\cdot]/dt = 2k_d f[I] - k_t[P\cdot]^2 \quad (2)$$

where k_d and f are the decomposition rate constant and the efficiency of the initiator, respectively.

From a steady-state assumption of the radical concentration during polymerization, *i.e.*, $d[P\cdot]/dt = 0$, k_t may be estimated.

$$k_t = (2k_d f[I]) / [P\cdot]^2 \quad (3)$$

The initiation rate ($2k_d f[I]$) is determined by means of the primary radical trapping with the verdazyl.¹⁴ Figure 5 shows the decay of the concentration of the verdazyl in the polymerization system of tRMI. The $k_d f$ values were determined from the slope of the straight lines. As shown in Table I, $k_d f$ are $3.4\text{--}4.0 \times 10^{-6} \text{ s}^{-1}$, from which f is calculated to be 0.35–0.40 by using the reported k_d

Figure 5. Determination of the initiation rate for the tRMI polymerization systems: $[\text{Monomer}] = 1 \text{ mol l}^{-1}$, $[\text{AIBN}] = 0.005 \text{ mol l}^{-1}$ in benzene at 60°C . (○) tBMI; (●) tAMI; (◐) tOMI.

value ($9.8 \times 10^{-6} \text{ s}^{-1}$).¹⁵ Subsequently k_t was estimated from the values of $k_d f[I]$ and $[P\cdot]$. It has been revealed that k_t are $2.1\text{--}4.8 \times 10^4$ and $1.5\text{--}2.0 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ for tRMIs and RSiMIs, respectively. The k_t values for tRMI are slightly smaller than $9 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ for CHMI,¹² of which *N*-substituent is secondary alkyl.

In the analysis of a non-steady state radical concentration, pre- and post effects are available. In the latter, the propagating radical is entirely consumed by bimolecular termination because a primary radical is not supplied. As a result of it, we can analyze readily the decay curve of the propagating radicals after the interrupt of UV irradiation for the photopolymerization in the presence of ATMP at 60°C , according to the following equation;

$$-d[P\cdot]/dt = k_t[P\cdot]^2 \quad (4)$$

This equation is rewritten as follows;

$$[P\cdot]_0/[P\cdot]_t = 1 + k_t[P\cdot]_0 t \quad (5)$$

where $[P\cdot]_0$ and $[P\cdot]_t$ are the radical concentration at a steady state and after t second from the UV interception.

Figure 6 shows the change of the intensity

Figure 6. Intensity change of ESR spectra of the propagating radicals: (a) poly(tOMI) radical and (b) poly(MSiMI) radical. Polymerization conditions, $[\text{Monomer}] = 1 \text{ mol l}^{-1}$; $[\text{ATMP}] = 0.02 \text{ mol l}^{-1}$.

of the ESR spectra of the polymer radicals from tOMI and MSiMI after the turning on and off of the UV irradiation. These curves indicate that the radical concentrations reach a steady state within a few minutes and several ten seconds for the tOMI and MSiMI systems, respectively. It was also confirmed that these polymerization systems did not give any polymer without UV irradiation, *i.e.*, the radical concentration in dark was zero. The increase in the radical concentration after the UV irradiation at the pre-effect, which is represented by eq 2, suggests that k_t of tOMI is much less than that of MSiMI, if the both systems are assumed to have same initiation rate. Similar behavior was also observed in the post effect, *i.e.*, decay after the UV interception. Subsequently quantitative analysis of the decay curves was carried out.

The second-order plots of the radical concentration (eq 5) obtained from the decay curves are shown in Figure 7. The straight relationship obtained evidences bimolecular termination, and therefrom k_t was calculated by the combination with $[\text{P}\cdot]_0$ under the UV irradiation, *i.e.*, 1.1, 1.0, and $2.8 \times$

Figure 7. Second-order plot of decay of the propagating radicals: (○) tBMI; (●) tAMI; (◐) tOMI; (△) MSiMI.

$10^{-6} \text{ mol l}^{-1}$ for tBMI, tAMI, and tOMI, respectively. The k_t values determined from the analysis of these non-steady states are $1.5\text{--}2.3 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ for tRMIs and $2.3 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ for MSiMI, which consistent quite with the values from a steady state mentioned above.

It is very interesting that k_t of RSiMI is much larger than those of tRMI. In general, a termination process is related with mobility of the segments in a polymer chain, because the termination is a diffusion-controlled reaction and segmental diffusion has been pointed out to be important.¹⁶ The chain mobility of poly(RSiMI) is expected to be much high on account of the silyl substituents in the side chain. The fact that the glass transition temperatures (T_g) of poly(RSiMI)s are lower than those of poly(tRMI)s might support the active mobility of the chain, *e.g.*, T_g is 261°C for poly(MSiMI) and 216°C for poly(BSiMI),⁶ while T_g is not observed for poly(tRMI)s below their onset temperature of decomposition.³

In conclusion, k_p and k_t values for tRMIs and RSiMIs are summarized in Table II, which involves those of other monomers reported previously.^{12,17} These *N*-substituted

Table II. k_p and k_t for *N*-substituted maleimides at 60°C

Monomer	k_p	$k_t \times 10^{-4}$	$k_p k_t^{-0.5}$	Reference
	$\text{l mol}^{-1} \text{s}^{-1}$	$\text{l mol}^{-1} \text{s}^{-1}$	$(\text{l mol}^{-1} \text{s}^{-1})^{0.5}$	
tRMI	23—100	2—5	0.15—0.76	This work
RSiMI	120	15—20	0.27—0.28	This work
CHMI	65	9	0.22	12
DtBF	0.46	0.00112	0.14	17

maleimides have k_p slightly smaller than those of typical vinyl monomers¹⁸ such as methyl methacrylate and styrene, but k_t are much smaller, resulting in a high polymerization reactivity of the maleimides, *i.e.*, large $k_p k_t^{-0.5}$ values. In the comparison with di-*tert*-butyl fumarate (DtBF)¹⁷ as a 1,2-disubstituted ethylene with a high polymerization reactivity, both k_p and k_t of the maleimides are greater than those of DtBF. It is interpreted as a result of the evasion of steric interactions in propagation and termination by the cyclic structure of the maleimides. For the larger k_p of the maleimides than DtBF, reduction of an internal strain in the five-membered ring of the monomers may be also one of important factors.¹⁹ The lower R_p of RSiMIs than tBMI has been revealed to be due to large k_t , but not decrease in k_p , while the decrease in the polymerization reactivity of tAMI and tOMI are concluded to be due to reduced k_p by the steric hindrance in propagation.

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