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# Detailed Kinetic Analysis of the Radical Polymerization of *trans*-4-*tert*-Butylcyclohexyl Methacrylate in Benzene Based on the Rate Constants Determined by Electron Spin Resonance Spectroscopy

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ABSTRACT: The radical polymerization of *trans*-4-*tert*-butylcyclohexyl methacrylate (4BCHMA) in benzene at 60 °C was kinetically analyzed in detail. The propagation and termination rate constants ($k_p$ and $k_t$) were determined by means of electron spin resonance spectroscopy in several polymerization systems, at various initiator and monomer concentrations in the absence or presence of a viscosity modifier and a chain transfer agent. The aftereffect was also analyzed during the polymerization with a photoinitiator to evaluate $k_t$. We obtained a constant $k_p$ (570 ± 10 L/(mol·s)) irrespective of the polymerization conditions, whereas $k_t$ was (0.5–2.3) × $10^6$ L/(mol·s) depending on the viscosity of the polymerization medium and the chain length of the propagating radical. It has been revealed that $k_t$ is proportional to the −0.28 power of the chain length when it was evaluated in the polymerization systems including negligible viscosity effects. The reaction orders with respect to monomer and initiator concentrations in the polymerization rate equation are discussed.

## Introduction

In radical polymerization an overall polymerization rate is determined as a balance of several elementary reactions, which consist of initiation, propagation, termination, and chain transfer reactions (Scheme 1), where I, M, P, and X-A are the initiator, monomer, polymer, and substances to which a chain transfer occurs (e.g. solvent, monomer, initiator, polymer, and others involved in the polymerization system) and R$^\bullet$, P$^\bullet$, and A$^\bullet$ are the primary radical, the propagating radical, and the radical produced from XA, respectively. $k_d$, $k_{add}$, $k_p$, $k_t$, $k_{tr}$, and $k_{prt}$ represent the rate constants for decomposition of the initiator, addition of the primary radical to the monomer, propagation, bimolecular termination including recombination and disproportionation, chain transfer, and primary radical termination, respectively.

The rates of initiation, propagation, and bimolecular termination are given as follows:

$$R_i = R_d = 2k_d f[\mathrm{I}] \quad (1)$$

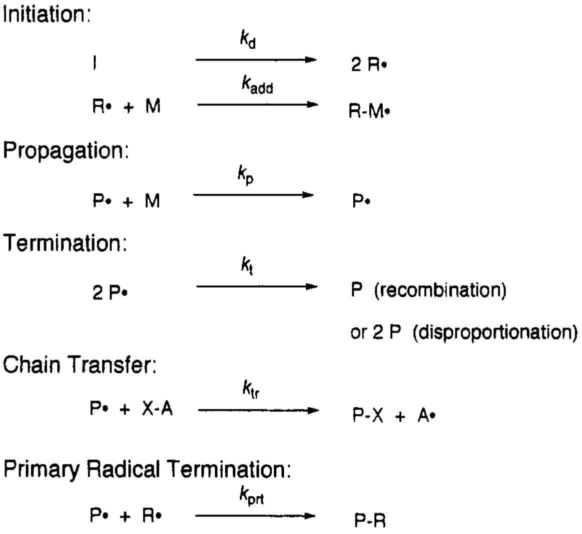
$$R_p = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p[\mathrm{P}^\bullet][\mathrm{M}] \quad (2)$$

$$R_t = -\mathrm{d}[\mathrm{P}^\bullet]/\mathrm{d}t = k_t[\mathrm{P}^\bullet]^2 \quad (3)$$

where $f$ is the initiator efficiency. Since the addition of the primary radical to the monomer is much faster than the primary radical formation, $R_i$ is represented as being equal to the rate of decomposition of the initiator ($R_d$) (eq 1). Under appropriate polymerization conditions, the chain transfer reactions are negligible and the bimolecular termination predominantly occurs rather than the primary radical termination.

In ordinary radical polymerization in a homogeneous system, the concentration of the propagating radicals increases initially and then instantaneously reaches a constant value, i.e. a steady state, within a very short time. This steady state has been classically regarded as an assumption, but recent research developments have discounted this view. The propagating radicals can directly be observed and applied to kinetic studies in many polymerization systems by means of electron spin resonance (ESR) spectroscopy.[1-11] The ESR method is the most useful and convenient method for evaluation of [P$^\bullet$] at a steady state because it enables direct observation of the propagating species. It provides the most reliable values of $k_p$ and $k_t$ by utilizing eqs 2 and 3, independently.

**Scheme 1**



From the steady state of [P$^\bullet$], eq 4 is given

$$\mathrm{d}[\mathrm{P}^\bullet]/\mathrm{d}t = R_i - R_t = 2k_d f[\mathrm{I}] - k_t[\mathrm{P}^\bullet]^2 = 0 \quad (4)$$

and can be rearranged to

$$[\mathrm{P}^\bullet] = (2k_d f[\mathrm{I}]/k_t)^{0.5} \quad (5)$$

By substitution of eq 5 into eq 2, the most well-known rate expression for an ideal free radical polymerization is obtained.

$$R_p = (2k_d f/k_t)^{0.5} k_p[\mathrm{M}][\mathrm{I}]^{0.5} \quad (6)$$

However, some deviations from eq 6 are observed in actual

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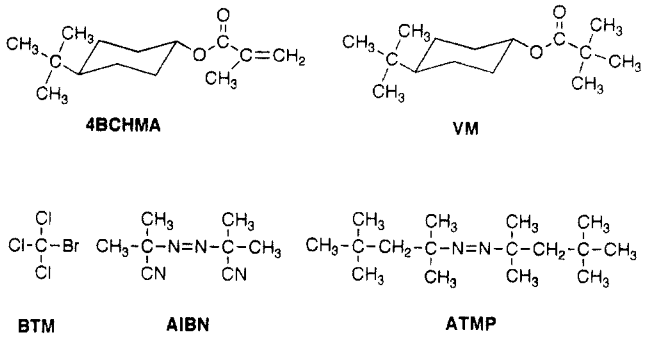
Chart 1



polymerizations and these have been discussed with regard to the effects of chain-length dependence of the rate parameters, as well as the primary radical termination, variation of $f$, and participation of M in the initiation.[12]

In a previous paper,[13] we reported the determination of $k_p$ and $k_t$ in the radical polymerization of *trans*-4-*tert*-butylcyclohexyl methacrylate (4BCHMA) initiated with 2,2′-azobis(isobutyronitrile) (AIBN) in benzene at 60 °C, by using ESR spectroscopy. Moreover, we recently revealed the chain-length dependence of $k_t$ in the polymerization, and the preliminary results have been reported.[14] In this article, we deal with the polymerization kinetics of 4BCHMA in detail on the basis of $k_p$ and $k_t$ being determined by the ESR spectroscopy. The following polymerization systems of 4BCHMA initiated with AIBN in benzene at 60 °C were examined: polymerization at various monomer and initiator concentrations in the absence of any additives, polymerization at various monomer concentrations in the presence of *trans*-4-*tert*-butylcyclohexyl pivarate as a viscosity modifier (VM), polymerization in the presence of bromotrichloromethane (BTM) as a chain transfer agent (Chart 1). The aftereffect in the photopolymerization with 2,2′-azobis(2,4,4-trimethylpentane) (ATMP) was also analyzed. The purpose of this work is to evaluate $k_p$ and $k_t$ in the methacrylate polymerization in solution using the ESR method, and subsequently to clarify the effects of polymerization conditions on these rate constants, especially the chain-length dependence of $k_t$.[15,16] For discussion of chain-length dependence, the acquisition of reliable experimental data in real polymerization systems under ideal conditions is indispensable. We discuss the rate equation of the polymerization on the basis of $k_p$ and $k_t$ determination.

## Experimental Section

**Materials.** 4BCHMA was synthesized and purified by the method described previously.[13] *trans*-4-*tert*-Butylcyclohexyl pivarate (VM) was synthesized from pivaric acid and 4-*tert*-butylcyclohexanol (a cis/trans mixture) in the presence of $p$-toluenesulfonic acid in benzene under reflux and the azeotropic removal of water. The crude VM as a cis/trans mixture was recrystallized from either hexane or methanol to isolate the trans isomer, and then passed through an alumina column with benzene as an eluent. The pure trans isomer was obtained with 48% yield: mp 72 °C; $^1$H NMR ($CDCl_3$) $\delta$ 4.59 (dd, $J$ = 11.2 and 4.4 Hz, 1H, OCH), 1.17 (s, 9H, $OCOC(CH_3)_3$), 0.96–2.00 (m, 9H, others), 0.85 (s, 9H, $CHCC(CH_3)_3$); $^{13}$C NMR ($CDCl_3$) $\delta$ 178.1 (C=O), 73.2 (OCH), 47.2 ($CHC(CH_3)_3$), 38.6 ($OCOC(CH_3)_3$), 32.2 ($CHC(CH_3)_3$), 31.9 ($OCHCH_2$), 27.6 ($CHC(CH_3)_3$), 27.1 ($OCOC(CH_3)_3$), 25.4 ($CH_2CHC(CH_3)_3$). The isomeric purity was determined to be 99.4% from the ratio of the peak intensities of methine protons at 4.59 and 4.96 ppm for the trans and cis isomers, respectively, by analogy to 4BCHMA purity evaluation.[13] BTM was used after distillation under a reduced pressure. AIBN and ATMP were recrystallized from methanol and hexane, respectively. Other reagents and solvents were used with prior purification.

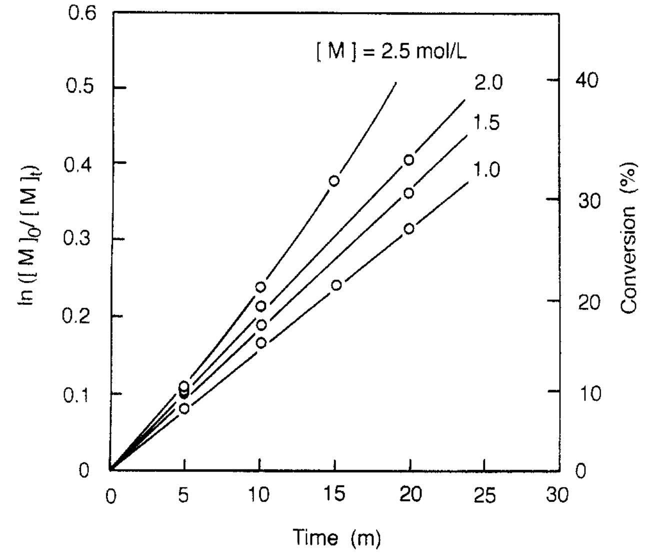


**Figure 1.** First-order plots of time–conversion relationship for polymerization of 4BCHMA in benzene at 60 °C: [4BCHMA] = 1–2.5 mol/L; [AIBN] = 5 × $10^{-2}$ mol/L.

**Polymerizations.** Polymerization was carried out in a sealed glass tube. The resulting polymer was isolated with aqueous methanol, and the polymer yield was determined gravimetrically. Photopolymerization was carried out under UV irradiation with a xenon lamp (500 W).

**ESR Measurements.** ESR spectra were recorded on a Bruker ESP 300 spectrometer with a 5-mm-diameter tube as described in the previous paper.[13] The radical concentration was determined in a low conversion region (below ca. 10%) without any corrections with respect to the sensitivity change associated with the conversion.

**Other Measurements.** The number-average molecular weight ($M_n$) and polydispersity ($M_w/M_n$) were determined by gel permeation chromatography (GPC) with a Tosoh 8000 series GPC system equipped with TSK-gel columns and calibrated with standard polystyrenes (Tosoh). The UV–visual spectrum of 1,3,5-triphenylverdazyl (TPV) was recorded on a Shimadzu UV-160 photometer with a 1-cm quartz cell maintained at 60 °C to determine the initiation rate. NMR spectra were recorded on a JEOL JNM-A400 spectrometer. Viscosity was determined at 30 °C from a flow time and a density by using a Ubbelohde type viscometer and a pycnometer, where benzene was used as a standard.

## Results and Discussion

**1. Polymerization Profile.** Figure 1 shows a first-order plot of the time–conversion relationships for polymerization of 4BCHMA in benzene at various initial monomer concentrations. A linear relationship was observed in a wide range of conversions (0–60%) at [M] = 1 mol/L,[13] while the gel effect was observed from an earlier stage of polymerization at a higher monomer concentration, e.g. [M] = 2.5 mol/L, because of the decrease in $k_t$ with conversion.[3–6,17,18] $R_p$ was determined from an initial slope of the curves in Figure 1. In Figures 2 and 3, the dependence of [M] and [I] on $R_p$ are shown, respectively. From slopes of the lines in these figures, the apparent kinetic orders in eq 7, $m$ and $n$, were determined

$$R_p = k'[M]^m[I]^n \qquad (7)$$

to be 1.38 and 0.451, respectively. The $m$ observed is higher than the value expected from eq 6, i.e. unity. The $n$ is slightly smaller than 0.5, and the deviation of the experimental points was found in the high [I] region; the slope decreases slightly as [I] increases.

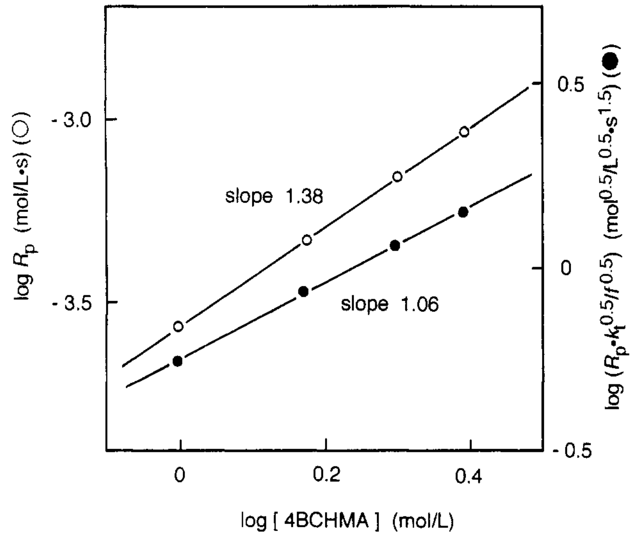


**Figure 2.** Monomer concentration dependences of $R_P$ for polymerization of 4BCHMA in benzene at 60 °C: [AIBN] = 5 × $10^{-2}$ mol/L. (○) log [M] versus log $R_P$; (●) log [M] versus log $[R_P(k_t/f)^{0.5}]$.

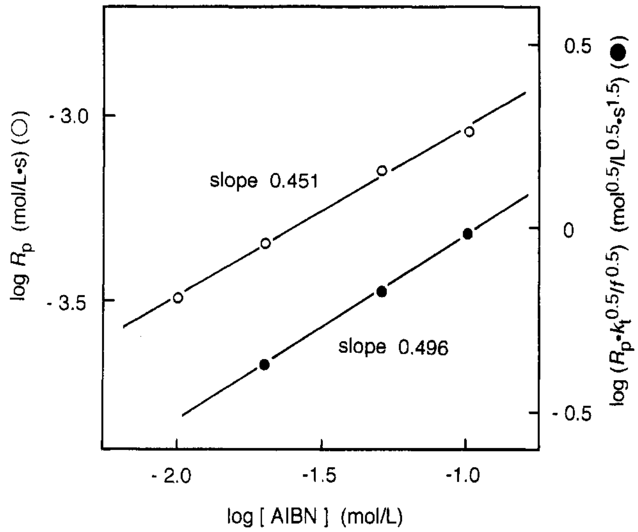


**Figure 3.** Initiator concentration dependences of $R_P$ for polymerization of 4BCHMA in benzene at 60 °C: [4BCHMA] = 2 mol/L. (○) log [I] versus log $R_P$; (●) log [I] versus log $(R_P k_t^{0.5})$.

The deviation of these kinetic orders from an ideal equation (eq 6) is considered to be due to variable rate parameters, $k_p$, $k_t$, and $f$, which depend on the polymerization conditions, i.e. [M] and [I]. Therefore we evaluated $k_p$ and $k_t$ for each polymerization by the ESR method. ESR spectra due to the propagating radical of 4BCHMA were observed as shown in Figure 4a. The [P•] at a steady state was determined to be (4.0–8.0) × $10^{-7}$ mol/L within 10% error by comparison with the spectrum from a standard solution of a stable radical. The results obtained are shown in Table 1.

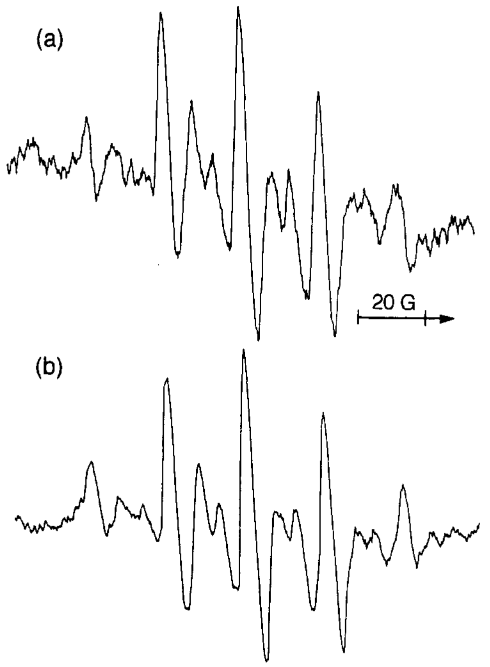
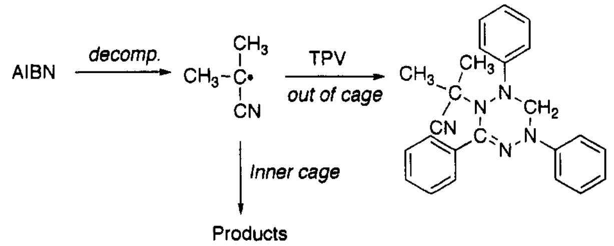


**Figure 4.** ESR spectra of propagating radicals observed in the polymerization of 4BCHMA in benzene at 60 °C. (a) [4BCHMA] = 2 mol/L, [AIBN] = 5 × $10^{-2}$ mol/L; (b) [4BCHMA] = 2 mol/L, [ATMP] = 5 × $10^{-2}$ mol/L under UV irradiation.

**Scheme 2**



With the [P•] and $R_p$ determined, eq 2 yielded $k_p$ irrespective of [I] and [M] (570 ± 10 L/(mol•s)). It has been established that $k_p$ is independent of its chain length except for very short chain regions.[19-21] The value for 4BCHMA is comparable to those for other methacrylates, e.g. octadecyl (530 L/(mol•s)),[22] cyclohexyl (510),[23] bornyl (580),[23] 1-adamantyl (530),[24] and 3,5-dimethyl-1-adamantyl (570)[24] determined by our ESR experiments and others in the literature determined by several methods.[25,26]

$k_t$ was evaluated by the steady-state equation with respect to the radical concentration (eq 4). $R_i$ ($=2k_d f$[I]) was determined according to eq 8 by using the decay of

$$-\mathrm{d[TPV]}/\mathrm{d}t = 2k_d f[\mathrm{I}] \qquad (8)$$

the concentration of TPV, which traps a primary radical diffusing out of the cage in the polymerization system (Scheme 2).[27] The decay curves are depicted in Figure 5.

**Table 1. Polymerization of 4BCHMA with AIBN in Benzene at 60 °C in the Absence of Any Additives**

| [M], mol/L | $10^{-2}$[I], mol/L | $10^4 R_p$, mol/(L·s) | $10^{-4}$, $M_n$ | $M_w/M_n$ | $10^{-4}X_n$ | $10^7$[P•], mol/L | $10^{-2}k_p$, L/(mol·s) | $10^7 R_i$, mol/(L·s) | $f$ | $10^{-6}k_t$, L/(mol·s) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1.0 | 5 | 2.67 | 7.5 | 2.1 | 5.9 | 4.9 | 5.5 | 4.53 | 0.46 | 1.9 |
| 1.5 | 5 | 4.64 | 16.4 | 2.0 | 12.8 | 5.5 | 5.6 | 4.23 | 0.43 | 1.4 |
| 2.0 | 5 | 7.11 | 30.6 | 1.7 | 23.9 | 6.2 | 5.7 | 3.41 | 0.35 | 0.89 |
| 2.5 | 5 | 9.33 | 38.5 | 1.7 | 30.1 | 6.5 | 5.7 | 2.19 | 0.22 | 0.52 |
| 2.0 | 1 | 3.26 | 50.6 | 1.6 | 39.5 | a | a | b | b | a |
| 2.0 | 2 | 4.54 | 49.5 | 1.6 | 38.7 | 4.0 | 5.7 | b | b | 0.87 |
| 2.0 | 10 | 9.08 | 14.1 | 1.9 | 11.0 | 8.0 | 5.7 | b | b | 1.1 |

[a] Not determined. [b] Assumed to be equal to that at [M] = 2 mol/L, [I] = 5 × $10^{-2}$ mol/L.

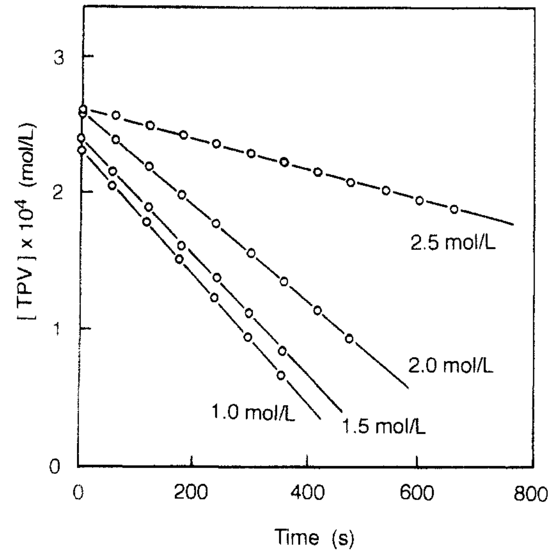


**Figure 5.** Decay curves of TPV concentration in the polymerization system of 4BCHMA with AIBN ($5 \times 10^{-2}$ mol/L) in benzene at 60 °C: [4BCHMA] = (a) 2.5, (b) 2.0, (c) 1.5, (d) 1.0 mol/L.

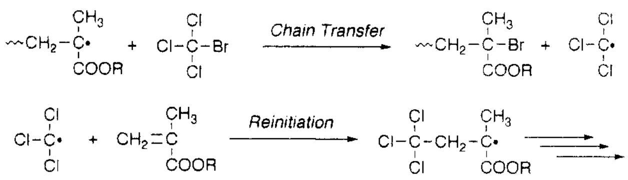
**Table 2. Viscosity of 4BCHMA and VM in Benzene at 30 °C**

| | concn, mol/L | density, g/cm$^3$ | viscosity, cP |
|---|---|---|---|
| 4BCHMA | 0 | 0.868 | 0.562 |
| | 1.0 | 0.875 | 0.726 |
| | 1.5 | 0.884 | 0.913 |
| | 2.0 | 0.891 | 1.17 |
| | 2.5 | 0.901 | 1.47 |
| VM | 2.0 | 0.887 | 1.24 |

$f$ was calculated with the $k_d$ reported in the literature ($9.8 \times 10^{-6}$ s$^{-1}$ at 60 °C).[28] Contrary to $k_p$ being irrespective of [M] and [I], $k_t$ strongly depended on [M], resulting in the large $m$ (Figure 2). This [M] dependence of $k_t$ involves both chain-length dependence and viscosity effects. Here the viscosity also influences $f$; $f$ changed from 0.46 to 0.22 by the increase in the viscosity of the polymerization medium along with the increase in [M].[29,30] Table 2 summarizes the viscosities with [M] at 30 °C. The viscosity varied from 0.726 to 1.47 cP at [M] = 1.0–2.5 mol/L. The change of $f$ with [M] tends to diminish the $m$ apparently observed, in a reverse fashion to the effect of $k_t$ on $m$.

In the polymerizations at constant [M] (i.e. at various [I]) $k_t$ reflects the effect of the chain length without the influence of viscosity effects, but we could not overcome an experimental limitation of the variable range of [I]; we obtained appropriate experimental data in the range 0.02–0.1 mol/L of [I]. Outside this range we could not obtain any data because of the difficulty of precise estimations of [P$^\bullet$] and $R_p$. The contribution of primary radical termination might also be unavoidable at a higher [I]. In addition $M_n$ is less sensitive to [I] rather than [M]; i.e. $M_n$ is roughly proportional to [I]$^{-0.5}$, this being disadvantageous for elucidation of the chain-length dependence.

### Scheme 3



Therefore, we selected the following two systems in which the chain length of the propagating radicals can be easily varied independent of the viscosity effect: the polymerizations in the presence of a viscosity modifier and a chain transfer agent.

**2. Polymerization in the Presence of a Viscosity Modifier or a Chain Transfer Agent.** We carried out the polymerization at various [M] in the presence of a viscosity modifier (VM) under constant viscosity conditions. We used the pivarate (Chart 1), which is a model compound of the polymer repeating unit. The viscosity change accompanied by the varying [M] is compensated for by an addition of VM, whose solution has a viscosity similar to that of the 4BCHMA solution (Table 2). The results of polymerization in the presence of VM are shown in Table 3. In this work the combined concentration of 4BCHMA and VM was 2 mol/L. When [M] varied from 0.25 to 2 mol/L, $M_n$ changed from $2.7 \times 10^4$ to $30.6 \times 10^4$. In the presence of VM, [P$^\bullet$] was higher than that in the absence of VM; e.g. [P$^\bullet$] was $5.8 \times 10^{-7}$ and $6.0 \times 10^{-7}$ mol/L at [M] = 1.0 and 1.5 mol/L, respectively, in the presence of VM, whereas [P$^\bullet$] was $4.9 \times 10^{-7}$ and $5.5 \times 10^{-7}$ mol/L in the absence of VM. This is ascribed to the difference in $k_t$, because $k_p$ is the same as that in the absence of VM and independent of [M] and [VM]. In these polymerizations $f$ did not alter as [M] varied, supporting the constant viscosity of the polymerization solutions.

Subsequently, we examined the polymerization system in the presence of BTM as a chain transfer agent. BTM is an effective chain transfer agent for methacrylate polymerization;[31] the chain transfer constant ($C_{tr}$) is $4.5 \times 10^{-2}$ for the polymerization of methyl methacrylate (MMA) at 30 °C. In the polymerization with BTM, reinitiation in Scheme 3 would occur quantitatively because of the high reactivity of the trichloromethyl radical; i.e. the reinitiation efficiency is close to unity. The results of the polymerization are shown in Table 4. The $M_n$ decreased by the addition of BTM, as was expected.

$R_p$ was found to decrease slightly as [BTM] increased, as depicted in the time–conversion relationships (Figure 6). The ESR measurements of this system revealed that [P$^\bullet$] decreases with an increasing [BTM] (Figure 7b). It has been found that $k_t$ increases by the shortened chain length of the propagating species through chain transfer, whereas $k_p$ is independent of [BTM] (Figure 7c,d). The detail of the chain-length dependence of $k_t$ is discussed later.

**3. Analysis of the Aftereffect of Polymerization.** $k_t$ is also obtained by the analysis of a non steady state of

**Table 3. Polymerization of 4BCHMA with AIBN in Benzene at 60 °C in the Presence of VM**

| [M], mol/L | [VM], mol/L | $10^2$[I], mol/L | $10^4R_p$, mol/(L·s) | $10^{-4}M_n$ | $M_w/M_n$ | $10^{-4}X_n$ | $10^7$[P$^\bullet$], mol/L | $10^{-2}k_p$, L/(mol·s) | $10^7R_i$, mol/(L·s) | $f$ | $10^{-6}k_t$, L/(mol·s) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.25 | 1.75 | 5 | 0.565 | 2.7 | 1.9 | 2.1 | 3.9 | 5.8 | *a* | *a* | 2.3 |
| 0.5 | 1.5 | 5 | 1.54 | 4.9 | 2.2 | 3.8 | 5.2 | 5.8 | 3.66 | 0.37 | 1.4 |
| 0.75 | 1.25 | 5 | 2.36 | 8.4 | 2.0 | 6.6 | 5.4 | 5.8 | *a* | *a* | 1.2 |
| 1.0 | 1.0 | 5 | 3.35 | 10.1 | 2.0 | 7.9 | 5.8 | 5.8 | 3.50 | 0.36 | 1.1 |
| 1.5 | 0.5 | 5 | 5.18 | 17.0 | 2.1 | 13.3 | 6.0 | 5.7 | *a* | *a* | 0.96 |
| 1.75 | 0.25 | 5 | 6.00 | 18.3 | 1.8 | 14.3 | 6.1 | 5.6 | *a* | *a* | 0.92 |

[a] Assumed to be equal to that at [M] = 2 mol/L in the absence of VM.

**Table 4. Polymerization of 4BCHMA with AIBN in Benzene at 60 °C in the Presence of BTM**

| [M], mol/L | $10^2$[BTM], mol/L | $10^2$[I], mol/L | $10^4R_p$, mol/(L·s) | $10^{-4}M_n$ | $M_w/M_n$ | $10^{-4}X_n$ | $10^7$[P•], mol/L | $10^{-2}k_p$, L/(mol·s) | $10^{-6}k_t$, L/(mol·s) |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 1 | 2 | 4.35 | 11.7 | 2.1 | 11.0 | 3.8 | 5.7 | 0.94 |
| 2 | 2 | 5 | 6.06 | 7.9 | 2.0 | 7.4 | 5.3 | 5.8 | 1.2 |
| 2 | 10 | 5 | 5.56 | 2.9 | 1.8 | 2.8 | 4.9 | 5.6 | 1.4 |
| 2 | 20 | 5 | 5.03 | 1.7 | 1.6 | 1.7 | 4.4 | 5.8 | 1.8 |
| 2 | 40 | 5 | 4.71 | 1.0 | 1.6 | 1.0 | 4.1 | 5.7 | 2.0 |

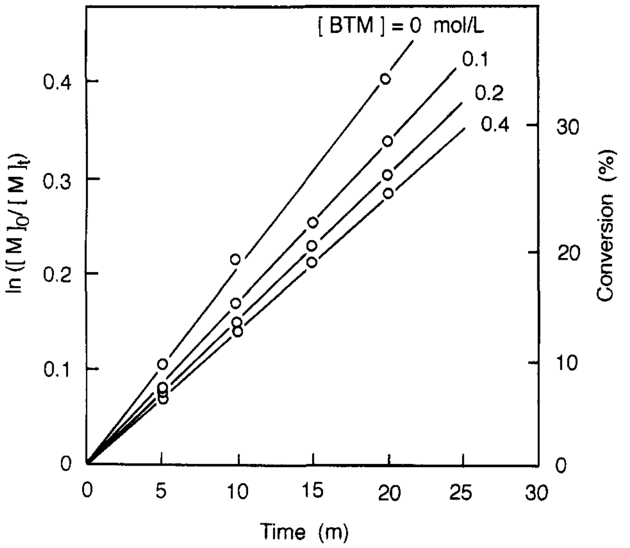


**Figure 6.** First-order plots for time–conversion relationship for polymerization of 4BCHMA in the presence of BTM in benzene at 60 °C: [4BCHMA] = 2 mol/L; [AIBN] = $5 \times 10^{-2}$ mol/L; [BTM] = 0–0.4 mol/L.

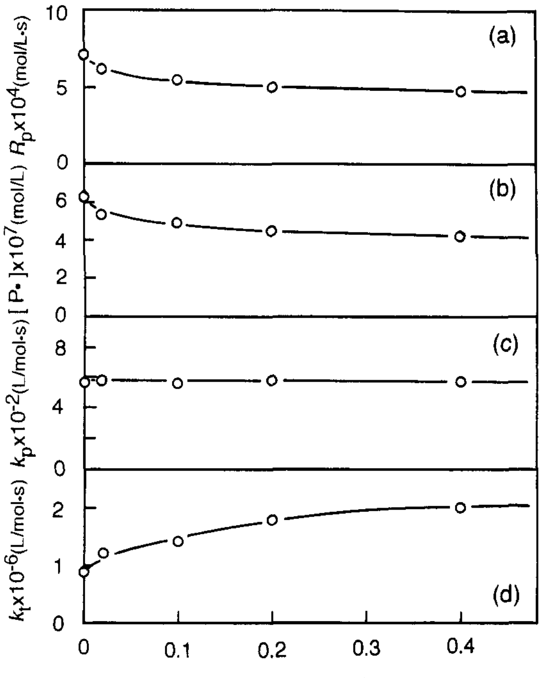


**Figure 7.** BTM concentration dependence on (a) $R_P$, (b) [P•], (c) $k_P$, and (d) $k_t$ for polymerization of 4BCHMA in benzene at 60 °C. Polymerization conditions: see Figure 6 and Table IV.

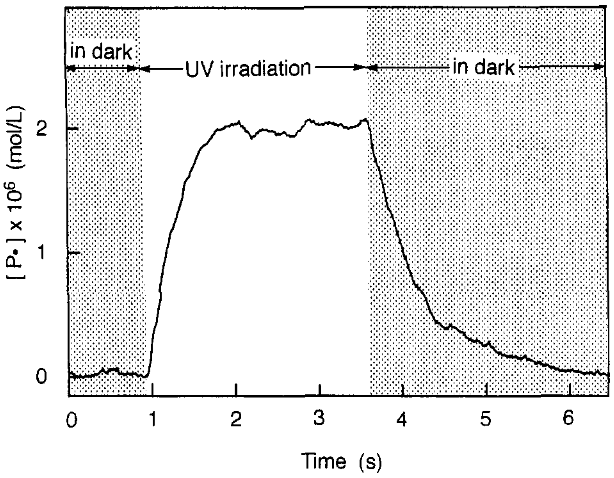


**Figure 8.** Aftereffect of photopolymerization of 4BCHMA in benzene at 60 °C by using ATMP as a photoinitiator: [4BCHMA] = 2 mol/L; [ATMP] = $5 \times 10^{-2}$ mol/L.

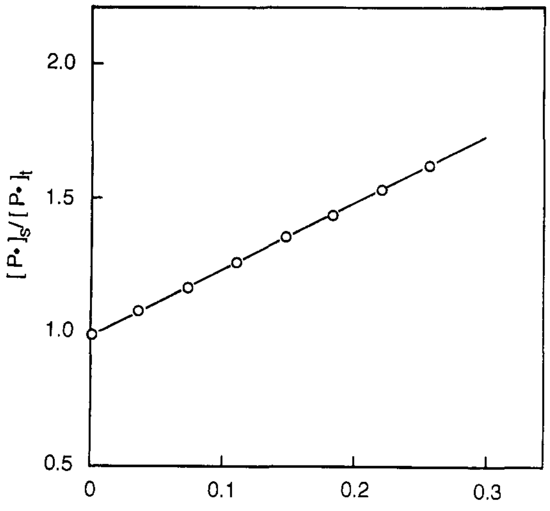


**Figure 9.** Second-order plot for termination of poly(4BCHMA) radicals after interception of UV irradiation in benzene at 60 °C.

polymerization. Integration of eq 3 gives eq 9, where $[P^\bullet]_s$ and $[P^\bullet]_t$ represent [P•] at a steady state and after $t$ seconds, respectively.

$$[P^\bullet]_s/[P^\bullet]_t = k_t[P^\bullet]_s t + 1 \qquad (9)$$

Figure 8 illustrates the change in [P•] for the photopolymerization at 60 °C with ATMP as a photoinitiator. ATMP hardly initiated polymerization of 4BCHMA at 60 °C without UV irradiation, and the propagating radical could not be observed by ESR in the dark conditions. By irradiation, [P•] increased and reached a steady state within a very short period (<ca. 1 s), giving an ESR spectrum as illustrated in Figure 4b, which is identical to that observed in the thermal polymerization (Figure 4a). We analyzed the decay of the spectrum after the interception of irradiation according to eq 9. From the slope of the line for the second-order plot in Figure 9, $k_t$ was evaluated. $k_t$ was $1.4 \times 10^6$ and $1.2 \times 10^6$ L/(mol·s) for the experiments at [I] of $5 \times 10^{-2}$ and $1 \times 10^{-2}$ mol/L, respectively, as shown in Table 5. Here $M_n$ was determined by the polymer produced under continuous photoirradiation.

**4. Chain Length of Propagating Radicals.** For evaluation of the chain-length dependence, we should deal with the chain length of the propagating radical, but not

**Table 5. Determination of $k_t$ from Analysis of the Aftereffect in Photopolymerization of 4BCHMA with ATMP in Benzene at 60 °C**

| [M], mol/L | $10^2$[I], mol/L | $10^{-4}M_n$ | $10^{-4}X_n$ | $10^7$[P•], mol/L | $10^{-6}k_t$, L/(mol·s) |
|---|---|---|---|---|---|
| 2 | 5 | 2.7 | 2.7 | 20.1 | 1.4 |
| 2 | 1 | 5.4 | 5.4 | 16.7 | 1.2 |

the molecular weight of the resulting polymer. Therefore, we estimated the chain length of the propagating radical ($X_n$) from $M_n$ of the resulting polymer by using the ratio of disproportionation and recombination during termination.

If termination occurs only through either disproportionation or recombination, $M_n$ is equal to $X_n$ or $2X_n$, respectively. In many cases, however, both terminations occur simultaneously and $M_n$ is represented as follows:

$$M_n = [2p/\{2p + (1-p)\}]X_n + [(1-p)/\{2p + (1-p)\}]2X_n \quad (10)$$

where $p$ is the probability for disproportionation termination (i.e. $1 - p$ is for recombination). It may be rewritten in the form

$$X_n = \{(1+p)/2\}M_n \quad (11)$$

In the case of chain transfer polymerization, one primary radical from the initiator produces a certain number of polymer chains respective to the magnitude of chain transfer ability. The number of the polymer chains produced per primary radical ($N_{CT}$) is given by

$$N_{CT} = X_{n,0}/X_{n,CT} \quad (12)$$

where $X_{n,0}$ and $X_{n,CT}$ are the number-average chain length of the propagating radical in the absence and presence of a chain transfer agent, respectively. In this case, the number of polymers having a chain length of $X_{n,CT}$ is $2(N_{CT} - 1) + 2p$, and that of $2X_{n,CT}$ is $1 - p$. Therefore, the number-average molecular weight in the presence of a chain transfer agent ($M_{n,CT}$) is represented as follows:

$$\begin{aligned} M_{n,CT} &= [\{2(N_{CT} - 1) + 2p\}X_{n,CT} + (1-p)2X_{n,CT}]/\{2(N_{CT} - 1) + 2p + (1-p)\} \\ &= 2N_{CT}X_{n,CT}/\{2N_{CT}(1-p)\} \quad (13) \end{aligned}$$

We have eq 14 from eqs 11–13, where $M_{n,0}$ is the number-average molecular weight in the absence of a chain transfer agent.

$$X_{n,CT} = \{(1+p)/2\}M_{n,0}[\{(1+p)/2\}(M_{n,0}/M_{n,CT}) + \{(1-p)/2\}]^{-1} \quad (14)$$

In the photopolymerization in this work, primary radical termination occurs predominantly because of a high concentration of the primary radical. Therefore $X_n$ is regarded as being equal to $M_n$.

We assumed that the bimolecular termination of poly(4BCHMA) radicals occurred in a fashion similar to that of poly(MMA) radicals; i.e. a frequency factor of disproportionation to recombination is 0.36 to 0.28.[32] The results of calculation are shown in the tables for each polymerization system.

As the reacting propagating radicals have a chain length distribution, then strictly speaking eq 3 should be described as follows:

$$R_t = \sum_i \sum_j k_{t,ij}[P_i^\bullet][P_j^\bullet] \quad (15)$$

where $[P_i^\bullet]$ and $[P_j^\bullet]$ are the concentrations of $i$- and $j$-meric radicals. However, we deal with $k_t$ and [P•] as average values in this work.

**5. Chain-Length Dependence of $k_t$.** Figure 10 shows the relationship between $X_n$ and $k_t$, which were determined in the polymerization systems in the absence of additives at [M] = 2 mol/L, in the presence of VM or BTM, and in the photopolymerization by using the aftereffect analysis. All plots give a linear relationship reflecting chain-length dependence of $k_t$ except for the points in the higher $X_n$ region.

In the region $10^4 < X_n < 10^5$, $k_t$ is represented as follows:

$$k_t = AX_n^{-0.28} \quad (16)$$

where $A$ is the constant.

The order −0.28 is close to the values reported for termination in the polymerizations of MMA and St and for the diffusion-controlled polymer–polymer reactions between poly(St) chain ends or poly(oxyethylene) chains as follows: Mahabadi et al.[33,34] reported the slopes of −0.15 and −0.24 for bulk polymerizations of MMA and St, respectively, by utilizing the spatially intermittent polymerization technique.[35] Their analytical expression for $R_p$ recognizing the chain-length dependence of $k_t$ also gave similar results for both polymerizations. The difference in their and our values for the methacrylates might be due to the difference in the molecular weight range used in the experiments; i.e. the lower value for the MMA polymerization was determined from the data in a molecular weight range ($M_n = 1.3 \times 10^4$–$1.4 \times 10^6$) higher than ours. The chain-length dependence of $k_t$ becomes less sensitive in a high molecular weight region, as described later. In 1969, Schnabel and co-workers[36] reported the chain-length dependent rate constant of the reactions between polymer radicals from poly(ethylene oxide), which was generated by pulse radiolysis. Later, Horie et al.[15,37] investigated the diffusion-controlled reactions between polymer chain ends in a dilute solution by using the triplet probe method. They examined the chain-length dependence of the rate constants for quenching of phosphorescence of poly(styrylbenzyl) by poly(styrylanthracene) in several solvents and proposed a model for the diffusion-controlled polymer–polymer reactions. The constant in benzene was inversely proportional to the 0.29 power of the degree of polymerization for the range 23–3900. This −0.29 order is very close to that obtained in this work. A similar value was reported for the triplet–triplet annihilation rate constant, which was measured for a pyrenyl group at the poly(St) chain end.[38]

In $X_n > 10^5$, the experimental points deviate from the linear relationship given by eq 16 to an upper side. The chain-length dependence of $k_t$ becomes weaker in this greater $X_n$ region. Benson and North[39] proposed in 1962 a model for the segmental diffusion-controlled termination. According to the model, $k_t$ is expected to be independent of the chain length of the polymer radical when the chainlength is sufficiently large. In this work we could observe no constant value as $k_t$ because of the experimental limit of determination of [P•] at the present conditions and apparatus. The critical point around $10^5$ of $X_n$ may be correlated with the expansion of a random coil of a polymethacrylate chain and entanglement between the segments of the chain.[40–42] The molecular characteristics of the poly(4BCHMA) chain in solutions are further investigated at the present time to discuss the effect of

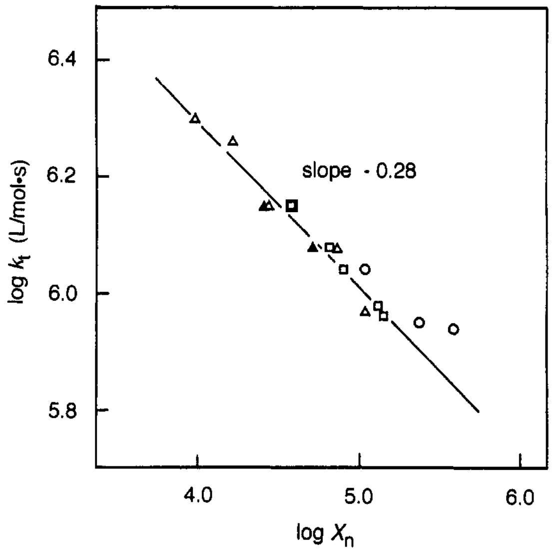


**Figure 10.** Relationship between log $X_n$ and log $k_t$ in radical polymerization of BCHMA at 2 mol/L in benzene at 60 °C; (○) in the absence of any additives: [□] in the presence of VM ([4BCHMA] + [VM] = 2 mol/L); (△) in the presence of BTM; (▲) from aftereffect.

**Table 6. Kinetic Orders in the Radical Polymerization Equation of 4BCHMA with AIBN in Benzene at 60 °C: $R_p = k[M]^m[I]^n$**

at [M] = 1.0–2.5 mol/L, [I] = 5 × $10^{-2}$ mol/L:

$m = 1.38\ (r = 0.9992)^a \xrightarrow{\text{modified with } k_t \text{ and } f} m = 1.06\ (r = 0.999\ 98)$

at [M] = 2 mol/L, [I] = (1–10) × $10^{-2}$ mol/L:

$n = 0.451\ (r = 0.998) \xrightarrow{\text{modified with } k_t} n = 0.496\ (r = 0.999\ 95)$

at [M] + [VM] = 2 mol/L ([M] = 0.5–2 mol/L), [I] = 5 × $10^{-2}$ mol/L:
$m = 1.10\ (r = 0.9995)$

[a] $r$ is the correction factor.

the chain conformation on the diffusion-controlled termination reaction in radical polymerization.

**6. Effects of Chain-Length Dependent $k_t$ and Viscosity on the Polymerization Rate Equation.** As described in section 1, the apparent $m$ and $n$ values in eq 7 involve the effects of both the chain-length dependence of $k_t$ and the viscosity. The increase in viscosity along with [M] influences both initiation and termination processes. In the initiation $f$ (i.e. $R_i$) decreases as the viscosity increases to result in an increase in the apparent $R_p$, whereas $k_t$ decreases. This change in $k_t$ cannot be discussed apart from the chain-length dependence. In this work, the $m$ and $n$ values were recalculated after considering varying $k_t$ and $f$ values, as summarized in Table 6. The plots of log [M]–log $[R_p(k_t/f)^{0.5}]$ and log [I]–log $(R_pk_t^{0.5})$ are shown in Figures 2 and 3, respectively. The relationships indicated with closed circles in Figures 2 and 3 exhibit a linearity greater than those of the unmodified ones shown with open circles, and their slopes were 1.06 and 0.496, which agree well with the expected values for the ideal polymerization equation in eq 6. Figure 11 shows the [M] dependence of $R_p$ for the polymerization system in the presence of VM. In this system, we can evaluate only the chain-length dependence of $k_t$ on $R_p$ because the viscosity effects on $k_t$ and $f$ are negligible. The slope ($m$ = 1.10) indicates the contribution of the chain length on $k_t$. Thus, it has been revealed that $R_p$ is influenced by the viscosity more importantly than the chain-length dependence in this polymerization.

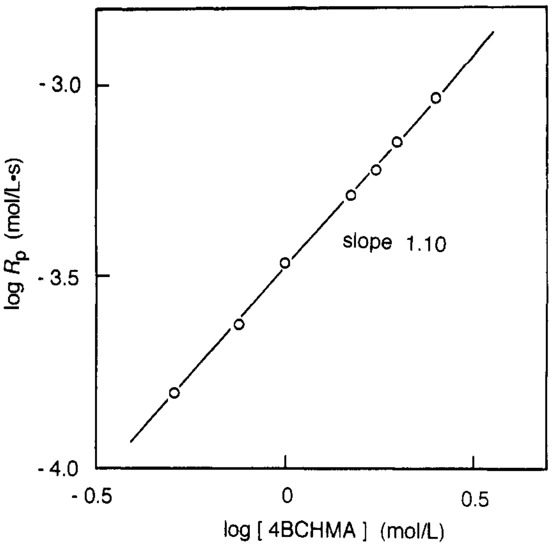


**Figure 11.** Monomer concentration dependence on $R_P$ for polymerization of 4BCHMA in benzene in the presence of VM at 60 °C: [4BCHMA] + [VM] = 2 mol/L; [AIBN] = 5 × $10^{-2}$ mol/L.

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