Radical Polymerization of 4-*tert*-Butylcyclohexyl Methacrylate: Polymerization Kinetics and Polymer Properties

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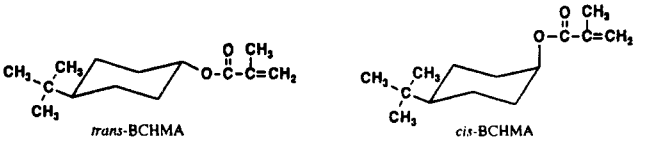
ABSTRACT: Radical polymerizations of *trans*-4-*tert*-butylcyclohexyl methacrylate (*trans*-BCHMA) or mixtures of the trans and cis isomers were carried out with 2,2′-azobis(isobutyronitrile) as an initiator in benzene at 60 °C. The polymerization kinetics were investigated in detail. From electron spin resonance studies, propagation and termination rate constants (k_p and k_t) of *trans*-BCHMA were evaluated to be 550 and 1.9×10^6 L/(mol·s), respectively. This k_p was similar to the values reported for methyl methacrylate and k_t was much smaller, resulting in the high polymerization reactivity of *trans*-BCHMA. From the results of the copolymerization of *trans*- and *cis*-BCHMA, it was clarified that the trans isomer had a slightly higher reactivity than the cis isomer. The solubility, microstructure, and thermal decomposition behavior of the resulting polymers were examined. It was also revealed that the glass transition temperature of poly(BCHMA) varied from 178 to ca. 130 °C depending on the geometric structure, i.e., the trans contents, in the polymer side chain.

Introduction

In radical polymerization an overall polymerization reactivity is dominated by a balance of several elementary reactions, i.e., initiation, propagation, termination, and chain transfer. It may be expected that steric hindrance leads to an increase in the polymerization reactivity if steric effects take a more important role in termination than in propagation. In the radical polymerization of dialkyl fumarates as a sterically hindered 1,2-disubstituted ethylene, it has been reported that the introduction of a *tert*-butyl group into the ester group increases the polymerization reactivity.[1] In our previous papers,[2a] we reported that adamantyl methacrylate (AdMA), which has a bulky ester alkyl group, showed high polymerization reactivities on account of suppressed termination between the polymer radicals. It was also described that the resulting poly(AdMA) had excellent thermal stabilities (i.e., a high glass transition temperature (T_g) and an onset temperature of the decomposition), as did other acrylic polymers containing an adamantyl ester group.[2] Similar polymerization behavior and thermal properties might not only be peculiar to the adamantyl ester but also be expected for other alkyl esters. We considered that bulky cycloalkyl groups with a fixed conformation as an ester alkyl group would be suitable for this purpose, e.g., introduction of a *tert*-butyl group, bridged-ring structure, or fused-ring structure into the ester cycloalkyl groups of cycloalkyl methacrylates. At the outset, we carried out radical polymerization of *cis*- and *trans*-4-*tert*-butylcyclohexyl methacrylates (BCHMA) (Chart I), which have the most simple structure of the ester alkyl groups, and we examined the thermal properties of the resulting polymers as an example of the first case.[3] Some physical properties of poly(BCHMA) on T_g[4] and unperturbed dimensions in dilute solutions[5] were reported by Gargallo et al. in 1975, but they did not mention the effects of the geometrical structure of the side group on the properties at all. Furthermore we cannot see any description which deals with the kinetics of the radical polymerization of *cis*- and *trans*-BCHMA in the literature.

In several recent years, an interest in some fundamental kinetic parameters of radical polymerization, especially propagation and termination rate constants, k_p and k_t, respectively, has been enhanced by the recent applications

Chart I



of newly developed experimental techniques including electron spin resonance (ESR) spectroscopy.[6,7] Radical polymerizations of methyl methacrylate (MMA),[8-11] or other methacrylic esters (RMA),[12] and styrene (St)[13] have been most intensively investigated by means of the ESR methods, as has the polymerization of 1,2- and 1,1-disubstituted ethylenes bearing bulky substituents such as dialkyl fumarates,[1,14] N-substituted maleimides,[15,16] and dialkyl itaconates.[17-19] In the polymerization of the last monomers, high concentrations of the propagating radicals permit an easy ESR observation and determination of the rate constants. Recently, we have found that the ESR spectra of the polymer radicals from RMA bearing bulky cycloalkyl side groups, including BCHMA, are detectable under ordinary polymerization conditions without any special ESR technique and apparatus because of the suppression of termination.

The present paper deals with the results of the detailed kinetic studies of the polymerization of BCHMA by means of ESR spectroscopy, and subsequently, the structure and thermal properties of the resulting polymer were also investigated. We discuss the effects of the geometrical structure, i.e., the trans/cis structure, of the cyclohexyl group on the polymerization kinetics and the properties of the polymer.

Experimental Section

Monomers. BCHMA was synthesized from methacrylic acid and 4-*tert*-butylcyclohexanol (Tokyo Chemical Industry, cis/trans = 30/70) in the presence of *p*-toluenesulfonic acid and 4-*tert*-butylcatechol in benzene with reflux for 30 h on removing water. The crude BCHMA was obtained by distillation under reduced pressure, yield 85%, bp 85 °C (1 mmHg). BCHMA was purified by column chromatography on silica gel with hexane. By repeating recrystallizations from hexane, *trans*-BCHMA was isolated from the mixture. The purity was confirmed by ^{1}H NMR spectroscopy to be more than 99.9%, mp 42 °C. The mixtures of cis and trans isomers consisting of various fractions were obtained from the filtrates, but a pure cis isomer could not be

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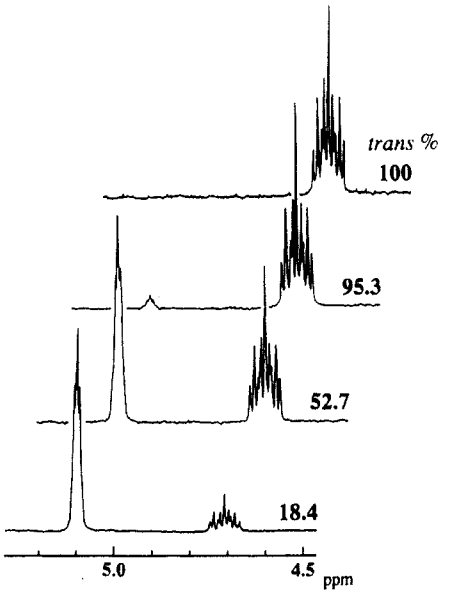

Figure 1. Expanded ^{1}H NMR spectra of BCHMA monomers.

Table I
^{13}C and ^{1}H NMR Spectral Data for *trans*- and *cis*-BCHMA in $CDCl_3$

structure	*trans*-BCHMA	*cis*-BCHMA
	^{13}C NMR Chemical Shifts	
—C(=O)—	166.9	166.6
CH_2=C(—)—	136.9	137.1
CH_2=C(—)—	124.7	124.7
—OCH—	73.8	69.4
—CHC(CH$_3$)$_3$	47.1	47.4
-C(CH$_3$)$_3$	32.2	32.4
—OCHCH_2—	32.0	30.5
-C(CH$_3$)$_3$	27.5	27.5
—CH_2CHC(CH$_3$)$_3$	25.4	27.3
α-CH_3	18.3	21.6
	^{1}H NMR Chemical Shifts	
H, H, C=C(CH$_3$)(COO—)	6.07 (s)	6.11 (s)
H, H, C=C(CH$_3$)(COO—)	5.51 (s)	5.53 (s)
—OCH—	4.69 (tt, J = 11.0 and 4.3 Hz)	5.07 (br)
α-CH_3	1.93 (s)	1.95 (s)
-C(CH$_3$)$_3$	0.86 (s)	0.87 (s)
others	0.94–2.07 (m)	1.01–2.06 (m)

obtained in the present work. ^{13}C and ^{1}H NMR spectral data for *trans*- and *cis*-BCHMA are summarized in Table I. The contents of the mixture were determined from the peak intensities of the methine protons at 4.69 and 5.07 ppm for the trans and cis isomers, respectively,[20] as shown in Figure 1.

Other Materials. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Other reagents and solvents were used after ordinary purifications.

Polymerization. Radical polymerization was carried out in a sealed glass tube in the presence of AIBN in benzene at 60 °C with shaking. The resulting polymer was isolated with methanol and dried under vacuum. The polymer yield was determined gravimetrically. Copolymerization parameters were calculated by the nonlinear least-squares procedure.[21]

Table II
P_n, M_n, and M_w/M_n at the Initial Stage of the Radical Polymerization of *trans*-BCHMA with AIBN in Benzene at 60 °C

monomer	[monomer], mol/L	10^3[AIBN], mol/L	10^5R_p, mol/(L·s)	$10^{-5}M_n$[a]	M_w/M_n[a]
BCHMA	1.0	1.0	3.69	5.25	1.7
	1.0	0.50	2.62	5.51	2.2
	1.0	2.0	6.05	3.03	2.0
	1.0	5.0	8.99	2.58	2.0
	1.0	10.0	12.2	1.75	2.0
	1.0	50.0	26.7	0.750	2.1
	0.20	1.0	2.84	0.877	2.0
	0.50	1.0	3.70	2.02	1.9
	2.0	1.0	4.82	10.4	2.4
AdMA[b]	1.0	1.0	3.52	3.91	1.7
CHMA[b]	1.0	1.0	2.28	2.73	2.2
tBMA[b]	1.0	1.0	1.28	1.29	2.1
MMA[b]	1.0	1.0	1.10	1.04	1.8

[a] By GPC calibrated with standard polystyrenes. [b] Reference 2a.

ESR Measurements. ESR spectra were recorded on a Bruker ESP 300 spectrometer with a 5-mm-diameter ESR tube at 60 °C. The operation conditions were as follows: microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; modulation amplitude, 1 or 5 G; conversion time, 41 ms; time constant, 655 ms; sweep time, 42 s; power, 6.32 mW; receiver gain 1 or 5×10^5 scan number, 1–10. The intensity of the spectra was determined from double integration of the spectra which was recorded at a 5-G modulation amplitude (see Figure 4b). The radical concentration was calibrated by using the spectrum of 1,3,5-triphenylverdazyl[22] under identical circumstances, i.e., dissolved in the monomer and benzene in the ESR tube at 60 °C (see Figure 4c). The second resonance line of manganese from a higher magnetic field side was used for the correction of sensitivity of the spectrometer, which changed corresponding to the conversion.[9b]

Other Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-400 spectrometer in deuteriochloroform at ambient temperature. Gel permeation chromatography (GPC) was performed with a Tosoh 8000 Series GPC system equipped with TSK-gel columns. Number- and weight-average molecular weights (M_n and M_w) were calibrated with standard polystyrenes. UV–vis spectra were recorded on a Shimadzu UV-160 photometer with a 1-cm quartz cell maintained at 60 °C. For the determination of the initiation rate of polymerization, a decay of the absorbance of the verdazyl at 720 nm (ϵ = 4370) was recorded.[23] Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in a nitrogen stream with a heating rate of 10 °C/min by means of Seiko TG-200 and DSC-200, respectively.

Results and Discussion

Polymerization Reactivity of *trans*-BCHMA. Radical polymerization of *trans*-BCHMA was carried out with AIBN in benzene at 60 °C, and the results obtained are summarized in Table II, in which the results of AdMA, cyclohexyl methacrylate (CHMA), *tert*-butyl methacrylate (tBMA), and MMA are included for comparison.[2a] *trans*-BCHMA has a high polymerization reactivity, as does AdMA. The polymerization rate (R_p) of *trans*-BCHMA was found to be 3 or 4 times as large as that of MMA, and a similar result was observed in M_n. It is noted that the polymerization reactivities of CHMA and tBMA are not as high as that of *trans*-BCHMA, suggesting that the cyclohexyl ring substituted with a 4-*tert*-butyl group is important for the enhancement in reactivity.

The polymerization of *trans*-BCHMA was further investigated kinetically. The dependence of the monomer and initiator concentrations on R_p for the polymerization in benzene at 60 °C is shown in Figures 2 and 3, respectively. The slopes of the lines in these figures are 0.50 and 1.22, which represent the kinetic orders with respect to the AIBN and *trans*-BCHMA concentrations; i.e., R_p is represented

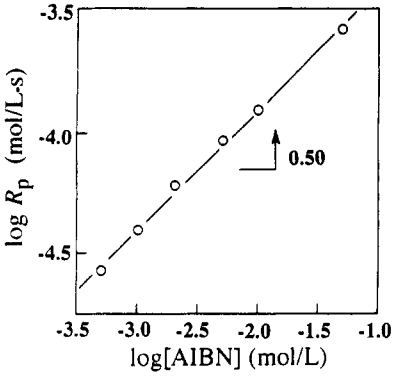

Figure 2. Effect of the AIBN concentration on the rate of polymerization of *trans*-BCHMA in benzene at 60 °C; [*trans*-BCHMA] = 1 mol/L.

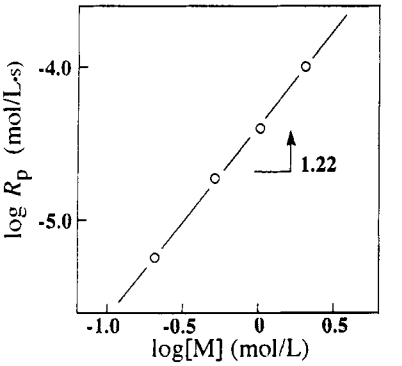

Figure 3. Effect of the monomer concentration on the rate of polymerization of *trans*-BCHMA in benzene at 60 °C; [AIBN] = 1×10^{-3} mol/L.

as follows:

$$R_p = k[\text{AIBN}]^{0.50}[\textit{trans}\text{-BCHMA}]^{1.22} \quad (1)$$

The order 0.5 for AIBN means that bimolecular termination is preferred in the range (5–500) $\times 10^{-4}$ mol/L for the AIBN concentration. The slightly higher order for *trans*-BCHMA might be due to the effects of viscosity of the polymerization system[24] and of the chain-length dependence of termination rate,[25] similar to the polymerization case of AdMA reported previously.[2a]

ESR Spectra of the Poly(*trans*-BCHMA) Radical. The propagating radical of *trans*-BCHMA was detectable under the following polymerization conditions: [*trans*-BCHMA] = 1 mol/L, [AIBN] = 5×10^{-2} mol/L, in benzene at 60 °C. However the spectrum of the poly(MMA) radical was hardly detected with a good signal to noise ratio under identical conditions.[7-10] In Figure 4, the observed ESR spectra of the propagating radical from *trans*-BCHMA are shown. The spectrum in Figure 4a resembles those of AdMA previously reported,[2a] of MMA by Bresler et al.,[8] and of methacrylic esters by Kamachi et al.[12a] Very recently we have also obtained similar spectra of the propagating radicals for other methacrylic esters with bulky cyclic alkyl groups, e.g., bornyl, isobornyl, bicyclodecyl, and tetracyclododecyl esters.[3] The easy observation of the ESR spectrum implied that the steady-state radical concentration ([P•]) in this polymerization was high enough to be quantified. Therefore we carried out quantitative analysis of the ESR spectra. From the intensity of the spectra obtained at a higher modulation amplitude (Figure 4b), [P•] was determined to be 4.85×10^{-7} mol/L within a few percent error by comparison with the spectrum from the standard solution of the verdazyl as a stable radical (Figure 4c), being higher than those for ordinary radical polymerizations.

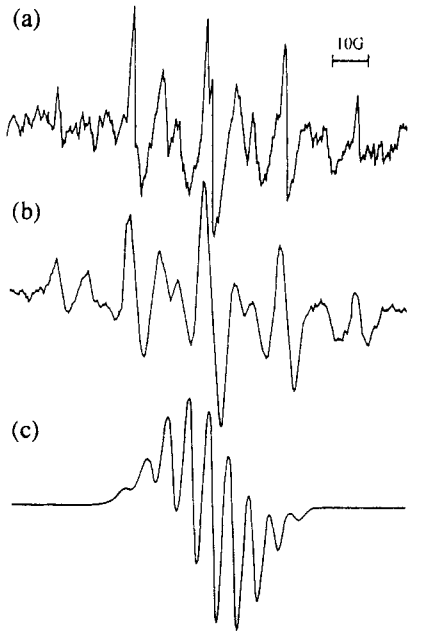

Figure 4. ESR spectra of (a) the propagating radical of poly(*trans*-BCHMA), modulation amplitude 1 G, (b) the propagating radical of poly(*trans*-BCHMA), modulation amplitude 5 G, and (c) verdazyl (2.0×10^{-5} mol/L), modulation amplitude 5 G. For other parameters, see the Experimental Section.

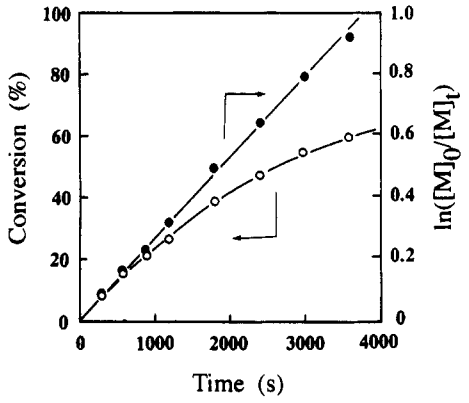

Figure 5. Time–conversion relationship for radical polymerization of *trans*-BCHMA. Polymerization conditions: [*trans*-BCHMA] = 1 mol/L, [AIBN] = 5×10^{-2} mol/L, in benzene at 60 °C.

Propagation and Termination Rate Constants. k_p is determined from [P•] and R_p according to the following equation:

$$k_p = R_p/([\text{P}^\bullet][\text{M}]) \quad (2)$$

In Figure 5, the time–conversion relationship is shown under the polymerization conditions for the ESR measurements, i.e., [*trans*-BCHMA] = 1 mol/L, [AIBN] = 5×10^{-2} mol/L in benzene at 60 °C. R_p was determined from a slope of the first-order relationship as shown in the figure.

k_t was determined on the basis of the steady-state equation with respect to the radical concentration,

$$d[\text{P}^\bullet]/dt = 2fk_d[\text{AIBN}] - k_t[\text{P}^\bullet]^2 = 0 \quad (3)$$

i.e.,

$$k_t = 2fk_d[\text{AIBN}]/[\text{P}^\bullet]^2 \quad (4)$$

where f and k_d are the efficiency and the decomposition rate constant of the initiator, respectively. The bimolecular termination is evidenced by the 0.5-order plot of

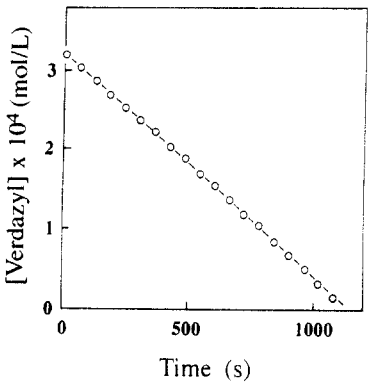

Figure 6. Decay of the concentration of verdazyl in the *trans*-BCHMA polymerization system with AIBN in benzene at 60 °C for determination of the initiation rate; [*trans*-BCHMA] = 1 mol/L, [AIBN] = 5×10^{-2} mol/L.

Table III
Determination of k_p and k_t for BCHMA[a]

% trans	$10^4 R_p$, mol/(L·s)	10^7[P·], mol/L	$10^{-2} k_p$, L/(mol·s)	$2k_d f$[AIBN] $\times 10^7$, mol/(L·s)	f[b]	$10^{-6} k_t$, L/(mol·s)
100	2.67	4.85	5.5	4.53	0.46	1.9
28.9	2.43[c]	4.74	5.1	4.32	0.44	1.9

[a] Polymerization conditions: [BCHMA] = 1 mol/L, [AIBN] = 5×10^{-2} mol/L, in benzene at 60 °C. [b] Calculated with the k_d reported (9.8×10^{-6} s^{-1}).[26] [c] Estimated from the data at [AIBN] = 1×10^{-3} mol/L.

Table IV
k_p and k_t of MMA in the Literature[a]

	temp, °C	k_p, L/(mol·s)	$10^{-7} k_t$, L/(mol·s)	method	ref
Bresler et al. (1974)	60	716		ESR[b]	8
Shen et al. (1991)	60	670	2.2	ESR	10a
Hill et al. (1992)	60	510	4.2	ESR	9c
Matheson et al. (1949)	60	367	1.87	rotating sector	27
Schulz et al. (1961)	60	515	2.55	rotating sector	28
Fukuda et al. (1985)	40	377	3.2	rotating sector	29
Olaj et al. (1988)	40	431	5.0	rotating sector[c]	30
Mahabadi et al. (1977)	30	356	3.06	SIP[d]	31
Kamachi et al. (1981)	30	450	4.20	rotating sector	32

[a] Defined as $-d[P\cdot]/dt = k_t[P\cdot]^2$. [b] With balance resonator. [c] Laser-pulse polymerization. [d] Spatially intermittent polymerization.

[AIBN] on R_p (Figure 2) under the conditions used. The initiation rate, $2fk_d$[AIBN], was determined experimentally by means of the primary radical trapping with the verdazyl.[23] Figure 6 shows the decay of the concentration of the verdazyl in the polymerization system of BCHMA. The slope of the line gives a $2fk_d$[AIBN] value (4.53×10^{-7} mol/(L·s)). Therefrom f was calculated to be 0.46 by using the k_d reported in the literature (9.8×10^{-6} s^{-1}).[26]

Thus, k_p and k_t for *trans*-BCHMA were calculated to be 5.5×10^2 and 1.9×10^6 L/(mol·s), respectively (Table III). The k_p is consistent with the values for MMA reported by several workers with different experimental methods, e.g., Bresler et al. (716 L/(mol·s))[8] by modified ESR, Hill et al. (510 L/(mol·s))[9c] and Shen et al. (670 L/(mol·s))[10a] by ESR, Matheson et al. (367 L/(mol·s)),[27] Schulz et al. (515 L/(mol·s)),[28] Fukuda et al. (377 L/(mol·s) (40 °C)),[29] and Kamachi et al. (450 L/(mol·s) (30 °C))[32] by rotating sector, Mahabadi et al. (356 L/(mol·s) (30 °C))[31] by spatially intermittent polymerization (SIP), and Olaj et al. (431 L/(mol·s) (40 °C))[30] by laser-pulse polymerization, as listed in Table IV. On the contrary, the k_t of *trans*-BCHMA obtained is 10 times as small as those for MMA in these sources.

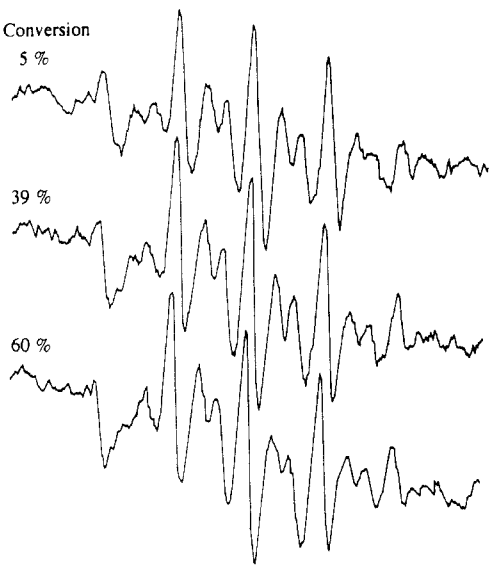

Figure 7. ESR spectra of the poly(*trans*-BCHMA) radical observed during the polymerization at different conversions. Polymerization conditions: [*trans*-BCHMA] = 1 mol/L, [AIBN] = 5×10^{-2} mol/L, in benzene at 60 °C.

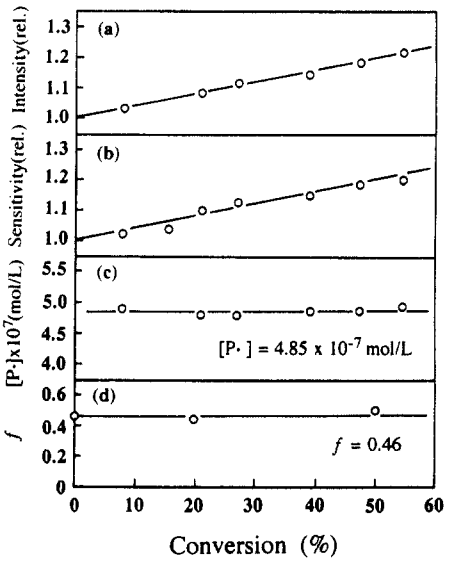

Figure 8. Conversion dependence of (a) the relative spectrum intensity, (b) the relative sensitivity of the spectrometer, (c) the radical concentration, and (d) the initiator coefficient for radical polymerization of *trans*-BCHMA; [*trans*-BCHMA] = 1 mol/L, [AIBN] = 5×10^{-2} mol/L, in benzene at 60 °C.

Conversion Dependence of the Rate Constants. In Figure 7, the ESR spectra of the poly(*trans*-BCHMA) radical at the different conversions from an early stage to 60% are depicted. It was found that the changes in shape and intensity of the spectrum were small even at a high conversion, being utterly different from the results for bulk polymerization of MMA reported by several workers.[9-11] In bulk polymerization of MMA in situ observation (or quantification) of the spectrum is difficult because of the low [P·] (ca. 10^{-7} mol/L or below), and the intensity of the spectrum increases gradually up to 10^{-5} or 10^{-4} mol/L along with the course of polymerization from low-conversion to intermediate and high-conversion regimes.[6b] In such a polymerization system, k_t decreases continuously from the initial regime of the polymerization and consequently [P·] increases.

In the polymerization system in this work, however, an increase was not observed in [P·], as shown in Figure 8c, where the spectrum intensity was corrected by the spectrometer sensitivity, which increases with the con-

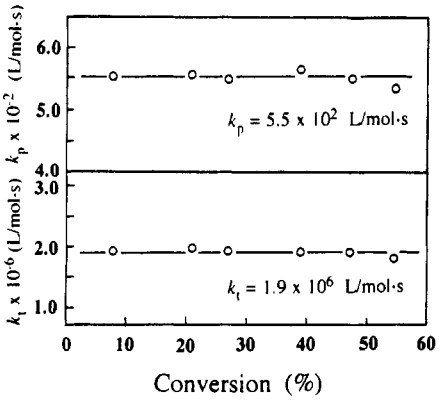

Figure 9. Conversion dependence of k_p and k_t for radical polymerization of *trans*-BCHMA; [*trans*-BCHMA] = 1 mol/L, [AIBN] = 5×10^{-2} mol/L, in benzene at 60 °C.

Table V
Comparison of Radical Polymerization Reactivities of *trans*- and *cis*-BCHMA[a]

% trans in monomer	time, h	conversion, %	$10^{-5}M_n$[b]	% trans in polymer
100	1.5	20.3	5.25	100
82.2	1.5	18.5	4.61	85.9
39.1	1.5	18.9	4.22	43.6
28.9	1.5	17.0	3.94	32.1

[a] [BCHMA] = 1 mol/L, [AIBN] = 1×10^{-3} mol/L in benzene at 60 °C. [b] By GPC calibrated with standard polystyrenes.

version during the course of the polymerization (Figure 8b).[9b] Additionally, the unchanging f value, as shown in Figure 8d, indicates that k_t is independent of the conversion in this system. It might be because of the low initial concentration of *trans*-BCHMA (1 mol/L) and the low molecular weight of the resulting polymer ($M_n = 7.5 \times 10^4$). In this system, the viscosity of the polymerization solution did not change significantly.

It is concluded that the greater polymerization reactivity of *trans*-BCHMA than MMA is due to reduced termination by the introduction of the bulky alkyl side group and that the rate parameters obtained are regarded as those that reflect the polymerization behavior at the low-conversion regime, because both k_p and k_t remained constant in the wide range of the conversion, as depicted in Figure 9. Further investigations of the determination of rate constants of several RMA including BCHMA by ESR methods are now in progress.

Reactivity of *trans*- and *cis*-BCHMA. The effect of the configuration of the methacryloyl group on the cyclohexyl ring of BCHMA toward the polymerization reactivity was examined by using *trans*- and *cis*-BCHMA, of which the methacryloyloxy group is fixed at equatorial and axial positions, respectively.[33] The polymerizations of the BCHMA mixtures consisting of various compositions were carried out. As shown in Table V, the conversion and M_n of the polymer decreased with an increase in the cis content, suggesting that *cis*-BCHMA has a lower reactivity than *trans*-BCHMA and/or the polymer radical terminates more frequently by the introduction of the *cis*-BCHMA unit into the polymer chain. The monomer reactivity ratios, $r_{trans} = 1.11$ and $r_{cis} = 0.83$, which were determined from the comonomer–copolymer composition curve in Figure 10, support that *trans*-BCHMA is slightly more reactive as a monomer than *cis*-BCHMA. These ratios mean that *trans*-BCHMA has 1.1- and 1.2-fold larger reactivities than *cis*-BCHMA toward poly(*trans*-BCHMA) and poly(*cis*-BCHMA) radicals, respectively.

The rate constants were evaluated for the polymerization of a *cis*/*trans*-BCHMA mixture (cis/trans = 71.1/28.9),

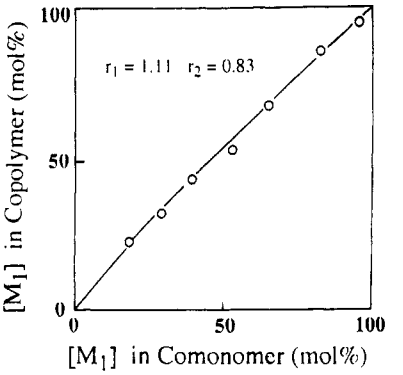

Figure 10. Comonomer–copolymer composition curve for radical copolymerization of *trans*-BCHMA (M_1) and *cis*-BCHMA (M_2) in benzene at 60 °C.

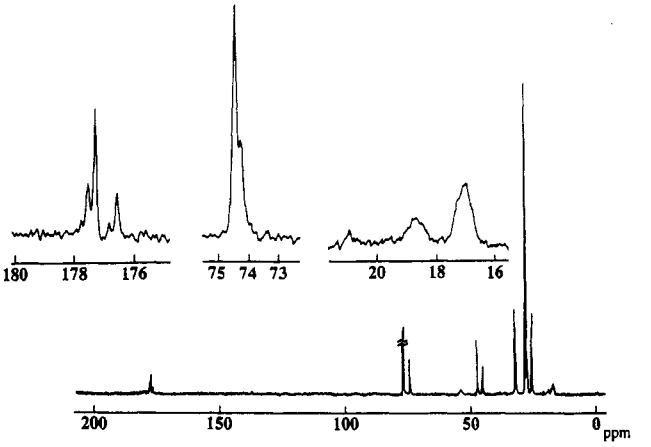

Figure 11. ^{13}C NMR spectra of poly(*trans*-BCHMA) in $CDCl_3$.

similar to the polymerization of *trans*-BCHMA described above. In this system, k_p and k_t were determined to be 510 and 1.9×10^6 L/(mol·s), respectively, as summarized in Table III. The fact that k_p of *trans*-BCHMA is larger than that of the trans/cis mixture is consistent with the results of the copolymerization. The decrease of the propagation rate of *cis*-BCHMA is considered to be due to the steric effect of the ester alkyl group. Similar steric hindrance has also been observed for bornyl and isobornyl methacrylates.[3,34] On the other hand, the agreement of both k_t indicates that the frequency of the occurrence of termination is not affected by the trans and cis structures in the side chain. It is concluded that the lower polymerization reactivity of *cis*-BCHMA originates from the difference in propagation, but not termination.

Structure of Poly(BCHMA). Poly(BCHMA) shows considerable hydrophobicity because of a bulky alkyl group in the side chain. For example, it is soluble in benzene, carbon tetrachloride, chloroform, THF, hexane, cyclohexane, and methyl ethyl ketone and insoluble in dimethyl sulfoxide, dimethylformamide, and methanol. It swells in acetone, which is a good solvent for poly(MMA). The cis/trans configuration had only a negligible effect on solubility.

The ^{13}C NMR spectrum of poly(*trans*-BCHMA) is depicted in Figure 11, in which the splitting of the peaks at 17–21, 74–75, and 176–178 ppm due to the α-methyl, methine adjacent to carbonyl, and carbonyl carbons, respectively, indicates that poly(*trans*-BCHMA) is an atactic polymer with a predominantly syndiotactic structure, as are many other poly(RMA)s. In the spectrum of poly(BCHMA) containing the cis and trans repeating units, a similar tendency was observed, although the less-resolved peaks due to the sequence distribution of the cis and trans

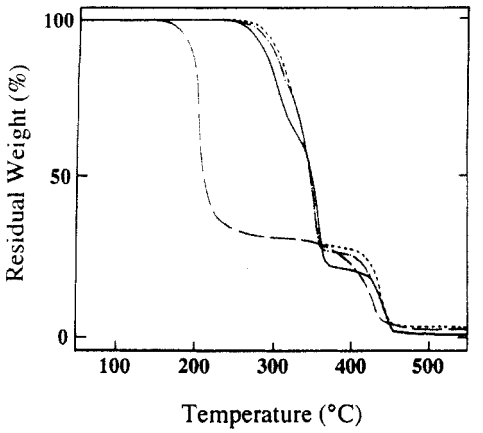

Figure 12. Thermogravimetric analysis of poly(BCHMA)s in a nitrogen stream with a heating rate of 10 °C/min. Trans: (a) 100% (—), (b) 53.6% (- · -), (c) 22.9% (- - -), (d) 100% (in the presence of 5% pTS) (- - -).

Table VI
Thermogravimetric Analysis of Poly(BCHMA) in a Nitrogen Stream with a Heating Rate of 10 °C/min

% trans in polymer	T_{init}, °C	T_{max}, °C
100	243	302, 357, 443
100[a]	148	207, 429
100[b]	140	183, 426
94.8	245	306, 357, 442
53.6	254	302, 351, 441
22.9	265	307, 346, 444

[a] In the presence of pTS (5 wt %). [b] In the presence of pTS (10 wt %).

units made exact assignment and quantification difficult. Triad tacticities were determined from ^{1}H NMR spectra of the poly(MMA)s derived from poly(*trans*-BCHMA) by hydrolysis and methylation; *rr* = 0.687, *rm* = 0.293, and *mm* = 0.020. These values are close to those of poly(AdMA) (*rr* = 0.671, *rm* = 0.300, and *mm* = 0.029),[2a] suggesting that these poly(RMA)s with bulky ester alkyl groups have a slightly predominant syndiotactic structure compared with that of poly(MMA) (*rr* = 0.624, *rm* = 0.341, and *mm* = 0.035).[2a]

Thermal Properties of the Polymer. Thermal stability of poly(BCHMA) was investigated by TGA in a nitrogen stream with a heating rate of 10 °C/min. In Figure 12, TGA thermograms of poly(BCHMA)s with different cis and trans compositions are shown. The initial decomposition temperature (T_{init}) and the maximum decomposition temperature (T_{max}) determined are listed in Table VI. T_{init} increased with the decrease in the trans content, from 243 °C for poly(*trans*-BCHMA) to 265 °C for the 23% trans one. The decomposition of all polymers gave three T_{max} at ca. 300, 350, and 440 °C, which remain constant independent of the side chain structure. The weight-loss curves became flat after the second T_{max}, and the residual weights at 370 °C were 22–30%. These results show that, in the decomposition of poly(BCHMA), side chain scissions occur in addition to the main chain scission leading to depolymerization to produce the monomer,[35] similar to the decomposition of other secondary and tertiary alkyl esters of poly(RMA).[36-39] When the polymer was heated in the presence of *p*-toluenesulfonic acid (pTS), T_{init} decreased to 140–150 °C and the decomposition proceeded clearly via two steps; T_{max} are ca. 200 and 430 °C. The weight loss at the first step was ca. 70%, which agrees with the calculated value on the basis of the formation of the poly(methacrylic anhydride) structure via elimination of the corresponding olefin and dehydration

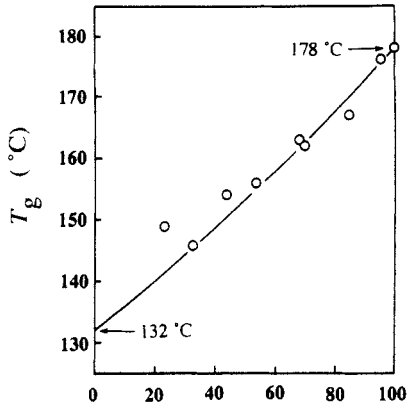

Figure 13. Relationship between T_g of poly(BCHMA) and the trans contents in the side chain of the polymer.

(65.6%), in a way similar to the acid-catalyzed deesterification of some poly(RMA)s.[38]

From DSC measurements, it has been revealed that T_g of poly(BCHMA) depends sensitively on the change of the position of the side group, i.e., T_g varies from 178 to ca. 130 °C corresponding to the trans content in the side chain (Figure 13), being higher than those of many poly(RMA)s including poly(MMA).[40] These T_g values obtained are much higher than the value reported by Gargallo et al. (83 °C),[4] but the values in this work might be correct, judging from the T_g of poly(CHMA) at 111 °C (observed) or 105 °C reported by Wilson et al.[41] and of poly(tBMA) at 113 °C (observed)[2a] or 118 °C (reported).[40]

With the aid of the Fox equation (eq 5),[42] T_g for poly(*cis*-BCHMA) was estimated to be 132 °C

$$1/T_g = w_{trans}/T_{g,trans} + w_{cis}/T_{g,cis} \quad (5)$$

where w_{trans} and w_{cis} are the weight fraction of *cis*- and *trans*-BCHMA units in the polymer and $T_{g,trans}$ and $T_{g,cis}$ are the T_g of poly(*trans*-BCHMA) and poly(*cis*-BCHMA), respectively. The variation of T_g depending on the configuration of the cyclohexyl ring may be interpreted by the difference in the side chain motion; i.e., the rotation of the cyclohexyl ring occupys a larger volume in the cis derivatives than in the trans one because of the fixed COO–C bonds at the axial and equatorial positions, respectively.

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