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Radical polymerization behavior of 2-*tert*-butylcyclohexyl methacrylate

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ABSTRACT

The polymerization of 2-*tert*-butylcyclohexyl methacrylate (2BCHMA) was carried out in benzene at 60 °C. The polymerization reactivity of 2BCHMA decreased due to the steric effect of the ester substituent compared to other alkyl methacrylates (RMA) including 4-*tert*-butylcyclohexyl methacrylate (4BCHMA). The evaluation of propagation and termination rate constants by electron spin resonance spectroscopy revealed that both the propagation and the termination were suppressed by the 2-*tert*-butyl substituent in the cyclohexyl moiety. The microstructure and thermal properties of poly(2BCHMA) were also examined and compared with those of poly(4BCHMA).

INTRODUCTION

We have recently reported that alkyl methacrylates (RMAs) bearing a bulky ester alkyl group show high polymerization reactivity on account of suppressed termination between the polymer radicals.[1-4] The decrease in the termination rate was directly confirmed by the determination of the rate constants by means of electron spin resonance (ESR) spectroscopy.[2-4] In the previous paper,[4] we have also reported that a trans isomer of 4-*tert*-butylcyclohexyl methacrylate (4BCHMA) has a slightly higher reactivity in the radical polymerization than the cis isomer and that the thermal properties of the resulting polymer are affected by the composition of the cis and trans isomers. This paper deals with the radical polymerization of *cis*- and *trans*-2-*tert*-butylcyclohexyl methacrylate (2BCHMA). It is expected that the *tert*-butyl group at the 2-position of the cyclohexyl ester group may exhibit a greater steric effect than in 4BCHMA because the bulky substituent is located near the methacryloyl group as the reactive center. Because *l*-menthyl methacrylate (MEMA) has a 2-*trans*-isopropyl substituent on the cyclohexyl ring in the ester moiety, similar effects are also expected on the polymerization of MEMA. The radical polymerization reactivity of 2BCHMA and MEMA and the structure and thermal properties of the resulting polymers are discussed in comparison with the results of 4BCHMA as well as other RMA bearing *n*- and *sec*-alkyl esters as shown in Scheme I.

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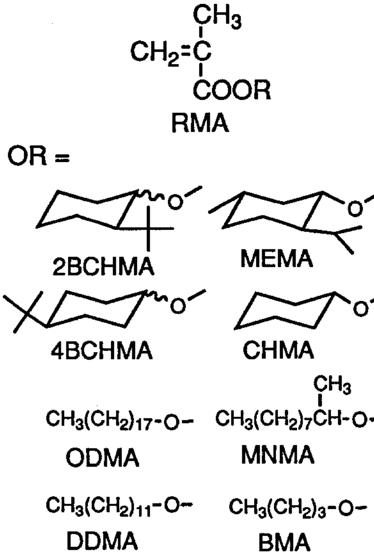

Scheme I

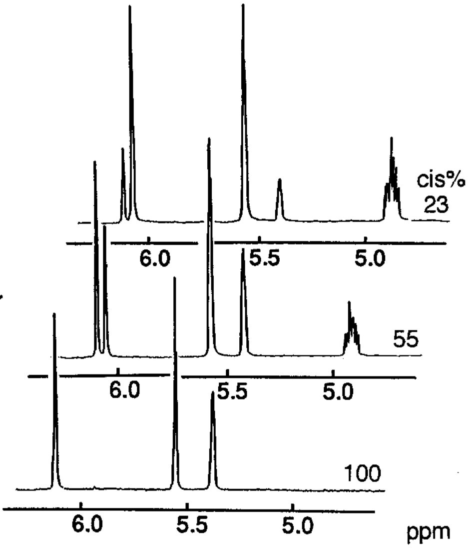

Figure 1. Expanded ^{1}H NMR spectra of 2BCHMA monomers.

EXPERIMENTAL

Materials

2BCHMA was synthesized from methacryloyl chloride and 2-*tert*-butylcyclohexanol (Aldrich, cis/trans = 80/20) in the presence of triethylamine. The crude 2BCHMA was obtained by distillation under reduced pressure, b.p., 75 ℃ (1 mmHg). 2BCHMA was purified by column chromatography on silica gel with hexane. *cis*-2BCHMA was isolated by recrystallization from hexane. The purity was 99.9% as determined by ^{1}H NMR spectroscopy. The melting point was below 25 ℃. *cis*-2BCHMA: ^{1}H NMR ($CDCl_3$) δ 6.12(s, 1H, CH_2=), 5.55(s, 1H, CH_2=), 5.38(b, 1H, OCH), 1.96(s, 3H, α-CH_3), 0.89(s, 9H, $C(CH_3)_3$), 0.91-2.00(m, 9H, CH_2 and CH). ^{13}C NMR($CDCl_3$) δ 166.4(C=O), 137.1(CH_2=$\underline{C}$), 125.1(CH_2=), 71.0(OCH), 50.3($\underline{C}HC(CH_3)_3$), 32.5 ($\underline{C}(CH_3)_3$), 31.5($OCH\underline{C}H_2$), 28.4($C(\underline{C}H_3)_3$), 26.6(CH_2), 22.4(CH_2), 20.8(CH_2), 18.4(α-CH_3). *trans*-2BCHMA: ^{1}H NMR ($CDCl_3$) δ 6.08(s, 1H, CH_2=), 5.54(s, 1H, CH_2=), 4.83(tt, 1H, OCH), 1.94(s, 3H, α-CH_3), 0.91(s, 9H, $C(CH_3)_3$), 1.00-1.99 (m, 9H, CH_2 and CH). ^{13}C NMR($CDCl_3$) δ 166.3(C=O), 137.1(CH_2=$\underline{C}$), 125.1 (CH_2=), 75.4(OCH), 50.4($\underline{C}HC(CH_3)_3$), 32.6($\underline{C}(CH_3)_3$), 32.4($OCH\underline{C}H_2$), 29.0 ($C(\underline{C}H_3)_3$), 26.8(CH_2), 24.6(CH_2), 20.8(CH_2), 25.9(α-CH_3). Mixtures of cis and trans isomers with various compositions were obtained from the filtrates, but a pure trans isomer could not be isolated in this work. The contents of the isomers were determined from the peak intensities of methine protons at 4.84 and 5.38 ppm in the ^{1}H NMR spectra of the trans and cis isomers, respectively (Figure 1). MEMA was synthesized from methacrylic acid and *l*-menthol in the presence of *p*-toluenesulfuric acid and 4-*tert*-butylcatechol in benzene with refluxing for 20 h to remove water. The crude MEMA was obtained by distillation under reduced pressure, b.p., 81 °C (1 mmHg). MEMA was purified by column chromatography on silica gel with hexane. 1-Methylnonyl methacrylate (MNMA) was prepared from methacryloyl chloride and 2-decanol in the presence of triethylamine. MNMA was purified by distillation and column chromatography similarly to MEMA, b.p., 85 °C (1 mmHg). Commercial octadecyl methacrylate (ODMA), dodecyl methacrylate (DDMA), and *n*-butyl methacrylate (BMA) were used after distillation under reduced pressure; b.p., 179 °C (1 mmHg), b.p., 123 °C (1 mmHg), and b.p., 67 °C (25 mmHg), respectively.

2,2'-Azobis(isobutyronitrile) (AIBN) and 2,2'-azobis(2,4,4-trimethylpentane) (ATMP) were recrystallized from methanol and hexane, respectively. 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 containing water (or ethanol for the ODMA polymerization) and dried under vacuum. The polymer yield was determined gravimetrically.

Measurements

ESR spectra were recorded on a Bruker ESP 300 spectrometer with a 5-mm-diameter ESR tube at 30-120 °C. The intensity of the spectra was determined from double integration of the spectra which were recorded at a 5-G modulation amplitude. The radical concentration was calibrated using the spectrum of 1,3,5-triphenylverdazyl (TPV) under identical circumstances, i.e., dissolved in the monomer and benzene in the ESR tube. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-A400 spectrometer in deuteriochloroform at an ambient temperature. Number-average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) with a Tosoh 8000 series GPC system equipped with TSK-gel columns and calibrated with standard polystyrenes. The UV-visible spectrum of TPV was recorded on a Shimadzu UV-160 photometer with 1-cm quartz cell maintained at 60 °C to determine the initiation rate (R_i). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in a nitrogen stream at a heating rate of 10 °C/min by means of Shimadzu TG-50 and DSC-50, respectively.

RESULTS AND DISCUSSION

Polymerization Reactivity

Radical polymerization of RMA was carried out with AIBN in benzene at 60 °C. The results obtained are summarized in Table I. The polymerization rate (R_p) and $\bar{M}_n$ of the

Table I. Radical Polymerization of RMA in Benzene at 60 °C[a]

RMA	$R_p \times 10^5$ (mol/L•s)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$[P\bullet] \times 10^7$ (mol/L)	k_p	$R_i \times 10^7$ (mol/L•s)	f[b]	$k_t \times 10^{-6}$ (L/mol•s)
2BCHMA (100/0)[c]	4.4	1.0	1.8	6.0	73	4.37	0.45	1.2
(55/45)[c]	4.2	1.1	1.7	6.5	64	3.93	0.40	0.9
(25/75)[c]	4.3	1.1	1.7	-	-	-	-	-
MEMA	11.4	2.6	2.0	5.2	230	4.44	0.45	1.6
ODMA	21.2	15.5	1.8	4.8	530	3.09	0.32	1.4
DDMA	17.3	8.5	1.9	3.2	550	2.79	0.28	2.8
MNMA	15.7	8.2	1.8	2.9	540	2.39	0.24	2.8
BMA	8.9	4.2	1.6	-	-	-	-	-
4BCHMA (71/29)[d]	24.3	-	-	4.7	510	4.32	0.44	1.9
(0/100)[d]	26.7	7.5	2.1	4.9	550	4.53	0.46	1.9
CHMA[e]	14.6	3.3	2.1	2.9	510	4.51	0.46	5.4

a) [RMA] = 1.0 mol/L, [AIBN] = 5 x 10^{-2} mol/L. b) Calculated with $k_d = 9.8 \times 10^{-6}$ s^{-1} (Ref. 5). c) cis/trans %. d) Ref. 4. e) Ref. 3.

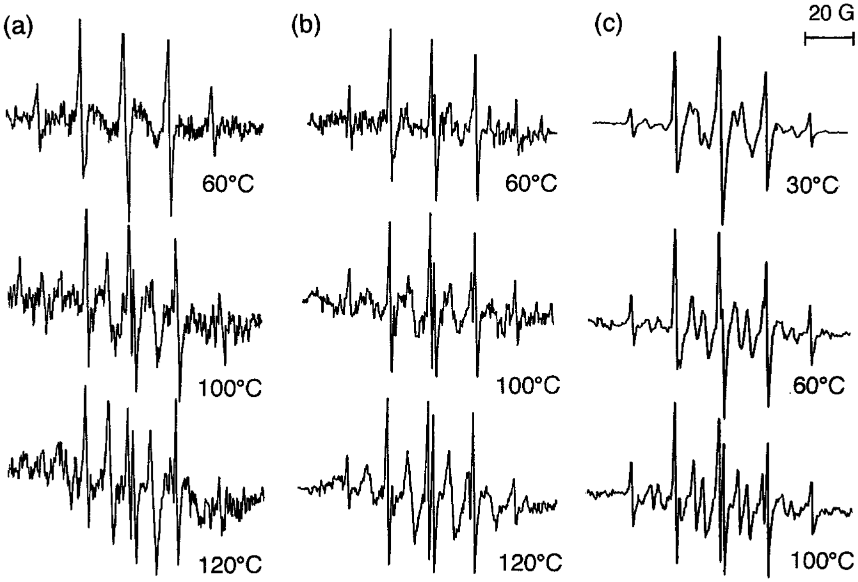

Figure 2. ESR spectra of poly(RMA) radicals observed under various conditions as follows: [RMA] = 1.0 mol/L, [Initiator] = 0.5 mol/L; AIBN/benzene/30 °C/UV, AIBN/benzene/60 °C, ATMP/toluene/100 °C, or ATMP/*p*-xylene/120 °C. (a) 2BCHMA, (b) MEMA, (c) 4BCHMA.

resulting polymers for the polymerization of 2BCHMA were revealed to be smaller than those for 4BCHMA, irrespective of the cis and trans composition in feed. The order of R_p and $\overline{M}_n$ for the other RMA was as follows: 4BCHMA > CHMA > MEMA > 2BCHMA for the cyclohexyl ester derivatives; ODMA > DDMA > BMA for the *n*-alkyl ester derivatives. MNMA as the *sec*-alkyl ester showed a reactivity similar to DDMA. These results mean that the bulky 2-substituents in the cyclohexyl ring decrease the polymerization reactivity, and an increase in the carbon number of the *n*-alkyl groups increases the reactivity.

In the polymerization of these RMA, the ESR spectra of the propagating radicals were observed. The ESR spectra observed during the polymerizations of 2BCHMA and MEMA were different from that of the poly(4BCHMA) radical, as depicted in Figure 2. In the spectra of the poly(2BCHMA) and poly(MEMA), the broad lines present as well as the lines with a narrow line-width suggest that the mobility of the segment around the propagating radical is not very high. Whereas well-split signals were observed for the poly(4BCHMA) radical at increased temperature, the spectra of poly(MEMA) and poly(2BCHMA) radicals consisted of sharp and broad components even at 100 °C. These distinct spectra may reflect the difference in the conformation and motion of the propagating radicals. Further detailed study of the conformation of the propagating radicals from RMA is now in progress.

The k_p and k_t were evaluated by the ESR method to clarify the polymerization reactivity depending on the structure of the ester alkyl groups. The concentrations of the propagating radical [P•] at a steady state were 2.9-6.5 x 10^{-7} mol/L. The [P•] for the polymerization of BMA was too low to determine precisely under these conditions. The k_p was calculated according to Eq. (1).

$$k_p = R_p/([\mathrm{P}\bullet][\mathrm{M}]) \tag{1}$$

The k_t was determined with Eq. (2), which was derived from a steady-state equation with respect to [P•].

$$k_t = R_i/[\mathrm{P}\bullet]^2 = (2k_d f\,[\mathrm{AIBN}])/[\mathrm{P}\bullet]^2 \tag{2}$$

where k_d and f are the dissociation rate constant and the initiator efficiency, respectively. R_i was determined by means of the primary radical trapping method with TPV.

The k_p for all the RMA are constant irrespective of the ester alkyl groups (510-550 L/mol•s), except for those of 2BCHMA and MEMA. The k_p of 2BCHMA is one order smaller than the values for the other RMA and that of MEMA is half of those values. This is due to the steric hindrance around the reactive center in the propagation, which is the reaction between the propagating radicals and the monomer bearing the bulky 2-substituent in the ester groups. It has also been revealed that the k_t for 2BCHMA is the smallest among the RMA examined, suggesting that the 2-*tert*-butyl group has a greater steric effect in termination than the 4-*tert*-butyl substituent. The k_t values determined in this work indicate that the termination is suppressed by the introduction of not only the bulky cyclohexyl derivative, but also a higher *n*-alkyl chain such as the octadecyl group. Because these *n*-alkyl substituents decrease k_t without any decreaese in k_p, the

Table II. Triad Tacticity of Poly(RMA)[a]

Polymer	cis/trans in Polymer(%)	*mm*	*mr*	*rr*
Poly(2BCHMA)	100/0	16	58	28
	58/42	14	61	25
Poly(4BCHMA)	76/24	4	25	71
	0/100	2	29	69
Poly(MEMA)	-	11	46	43

a) Prepared in benzene at 60 °C.

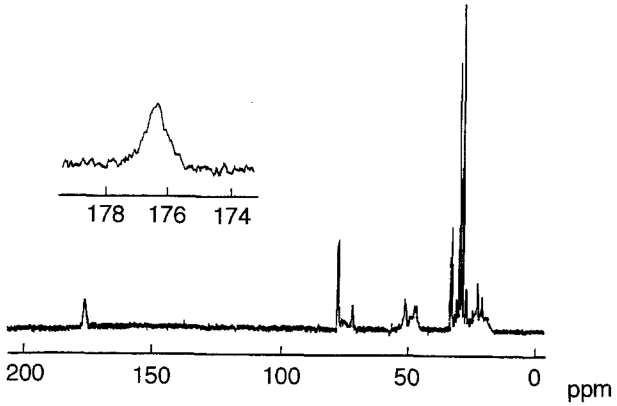

Figure 3. ^{13}C NMR spectrum of poly(2BCHMA) (cis/trans = 55/45) in $CDCl_3$.

polymerization reactivity increases efficiently according to the length of the alkyl chain.

Tacticity

The ^{13}C NMR spectrum of poly(2BCHMA) is depicted in Figure 3. The resonance of the carbonyl carbon of poly(2BCHMA) is so broad that it is difficult to make assignment and qualification; whereas, the splitting of the peaks at 176-178 ppm due to the carbonyl carbons was observed in the spectrum of poly(4BCHMA) which is an atactic polymer with a predominantly syndiotactic structure.[4] The broadening of the peak is considered to be due to lower mobility of the poly(2BCHMA) chain, but not due to cis-trans isomerism, because poly(2BCHMA) with 100% cis composition gave a similar spectrum. To determine the triad tacticity, hydrolysis and subsequent methylation of the polymers were carried out. The hydrolysis of the polymers was accomplished in concentrated H_2SO_4 at room temperature for 90 days. The resulting

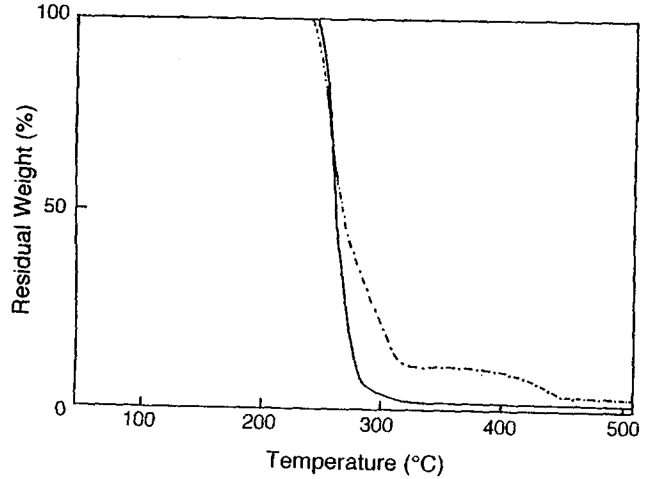

Figure 4. TGA curves of poly(2BCHMA) in a nitrogen stream at a heating rate of 10 °C/min. (—) cis 100% and (-·-) cis 25%.

poly(methacrylic acid) was reprecipitated from methanol and diethyl ether and subsequently methylated with diazomethane. The quantitative transformation of the poly(RMA) to poly(methyl methacrylate) (poly(MMA)) was confirmed by ^{1}H NMR. The triad tacticities determined are listed in Table II. It has been revealed that poly(2BCHMA) has a predominantly heterotactic structure, different from that of poly(MMA)[6] and poly(cycloalkyl methacrylate)s[1,3] including poly-(4BCHMA).[4] No effect of cis and trans configurations was observed for the tacticity of poly(2BCHMA). The tacticity of the poly(MEMA) agrees well with that reported in the literature;[7-9] for example, *mm* = 13, *mr* = 47, *rr* = 40%.[7] The preference of the meso propagation of 2BCHMA and MEMA compared with the other RMAs may be related to the conformation of the propagating radicals,[10] which are different from those for the other RMA as described above.

Thermal Properties of Poly(2BCHMA)

The thermal decomposition behavior of poly(2BCHMA) was investigated by TGA in a nitrogen stream at a heating rate of 10 °C/min (Figure 4). The initial decomposition temperature (T_{init}) and maximum decomposition temperature (T_{max}) determined are listed in Table III. T_{init} decreased slightly with an increase in the cis content from 245 °C for the 100%-cis poly(2BCHMA) to 235 °C for the 25%-cis polymer. While the decomposition of the 58 or 100%-cis polymer gave single T_{max} at ca. 260 °C, the decomposition of 25%-cis poly(2BCHMA) proceeded via three steps. These results mean that the main chain scission leading to depolymerization occurs predominantly in the decomposition for the high cis-content polymers, but the side chain scissions

Table III. Thermal Properties of Poly(2BCHMA) and Poly(4BCHMA)[a]

Polymer	cis/trans in Polymer (%)	$\overline{M}_n \times 10^{-4}$	T_{init} (°C)	T_{max} (°C)	T_g (°C)
Poly(2BCHMA)	100/0	5.1	245	261	214
	58/42	11.2	240	261	183
	25/75	10.4	235	261, 306, 443	163
Poly(4BCHMA)[b]	77/23	-	265	307, 346, 444	149
	46/54	5.1	254	302, 351, 441	156
	0/100	5.3	243	302, 357, 443	178

a) Prepared by radical polymerization in benzene at 60°C. b) Ref. 4.

additionally occur in the decomposition of the 25%-cis polymer. It was reported that the decomposition of poly(4BCHMA) proceeded via three steps irrespective of the cis-trans compositions; T_{max} values were ca. 300 °C, 350 °C, and 440 °C, due to the olefin elimination from the side chain, main chain scission (depolymerization), and the decomposition of the successive methacrylic anhydride sequences, respectively.[4] The high content of the *cis*-2-*tert*-butylcyclohexyl moiety in the polymer may accelerate the depolymerization because of the steric repulsion and probably the suppression of the olefin elimination from the ester alkyl moiety.[11] It has also been revealed that the glass transition temperature (T_g) of poly(2BCHMA) increases from 163 to 214 °C with an increase in the cis content. A similar dependence of T_g on the configuration of the side chain was also observed for poly(4BCHMA), as interpreted by the difference in the side chain mobility.[4]

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