Conformational Structure of Methacrylate Radicals as Studied by Electron Spin Resonance Spectroscopy: From Small Molecule Radicals to Polymer Radicals

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ABSTRACT: The structure of methacrylate radicals and other related enolate radicals with various molecular sizes from small molecules to polymers was investigated by ESR spectroscopy. The bromides as precursors for the radicals were prepared by the reaction of the corresponding alkenes with bromotrichloromethane. The radicals were formed by photoirradiation of a toluene solution of the precursor in the presence of hexabutylditin at 213−318 K. The polymer radicals were produced in the ESR tube by the radical polymerization of the corresponding methacrylate with an azo initiator in toluene at 373 K or in *p*-xylene at 393 K. The ESR spectra of the adduct radicals **1** was revealed to consist of binary components characterized by the following coupling constants and *g*-values: $a_1(3H) = 23.4-23.6$ G, $a_2(1H) = 21.6-22.3$ G, and $g = 2.0043-2.0044$ for conformation A and $a_1(3H) = 23.4-23.5$ G and $g = 2.0043-2.0044$ for conformation B. The α-nitrile radical **9**, the dimer or trimer radicals **5**−**7**, and the polymer radicals **8** also gave similar dual-conformation spectra. On the basis of the coupling constants determined for these spectra of the various enolate radicals, the conformation model of the radicals was discussed. It has been revealed that the pyramidalization of the radical center and the *A*-strain-controlled conformation due to the steric strain between the large substituents account for the coupling constants for the ESR spectra of the radicals. The propagation mechanism was also discussed in relation to the tacticity of the polymer.

Introduction

One of the most effective approaches for stereochemical control in radical reactions is the control of the conformation of radicals as demonstrated by recent success in radical asymmetric inductions with excellent efficiency under chiral auxiliary and substrate control.[1,2] A high diastereoselectivity in the reactions is interpreted with several ground state conformation models and transition state models based on calculation and ESR observations.[3] *A*-strain effect[4−6] and dipolar[3b,c] and steric[3g] repulsions account for the preferred conformations of enolate radicals in acyclic systems. In free-radical polymerization of methyl methacrylate (MMA) as well as other alkyl methacrylates, it is well-known that the reaction between a polymer radical and an attacking monomer prefers racemo propagation rather than meso propagation (1,3-stereoinduction), that is, ordinary radical polymerization of methacrylates yields predominantly syndiotactic polymers,[7,8] although its selectivity is not so high; for example, the probability of the racemo propagation is 0.79 for the polymerization of MMA at 60 °C.[8] The control of tacticity of polymers during polymerization is an important subject because the physical properties of polymers intensively depend on their tacticity. However, the synthesis of highly tactic polymers from the methacrylates through radical polymerization has still been one of the unsolved problems except for a few examples of isotactic polymers from triphenylmethyl methacrylate and its analog by helix formation;[9] whereas, recent progress in anionic and coordination polymerizations has enabled the synthesis of poly(MMA)s with a highly controlled structure, i.e., tacticity as well as molecular weight and its distribution.[8,10]

Electron spin resonance (ESR) spectroscopy has contributed to polymer research by revealing the structures and reactivity of the polymer radicals. A large number of ESR spectra have been reported for the propagating radicals of the methacrylate derivatives during solid state polymerization, solution polymerization by the flow method with redox initiators and the photolytic radical-generating technique, and bulk or solution polymerization using special cavities, as well as during the radiation and photo- and mechanochemical degradations of the polymers,[11−13] since the first observation of the ESR spectrum of the propagating radical of poly(MMA) in 1951 by X-ray irradiation of the polymer.[14] Historical surveys of the ESR studies can be seen in a book in 1977 by Rånby and Rabek[12] and a review in 1987 by Kamachi.[13] In some cases, however, different interpretations of the hyperfine splittings of the spectra have been made even for the same polymethacrylate radical, and simulation and speculation might lead to different conclusions because most of their discussions have been based on less-resolved and ambiguous spectra. The relationship between the spectra of the propagating radicals and the type of propagation, namely, the tacticity of the polymer, has also been discussed, but it has not been clarified yet.

We began this ESR work in order to examine the structure of the methacrylate radicals. Consequently, we obtained well-resolved ESR spectra for enolate radicals with well-defined structures over a wide range of the molecular sizes from small molecules to polymers, i.e., adduct radicals, dimer radicals, a trimer radical, and polymer radicals, as shown in Chart 1, by reduction of bromides as radical precursors with hexabutylditin and by direct ESR observation of the thermal polymerization of the methacrylate at high temperature. The

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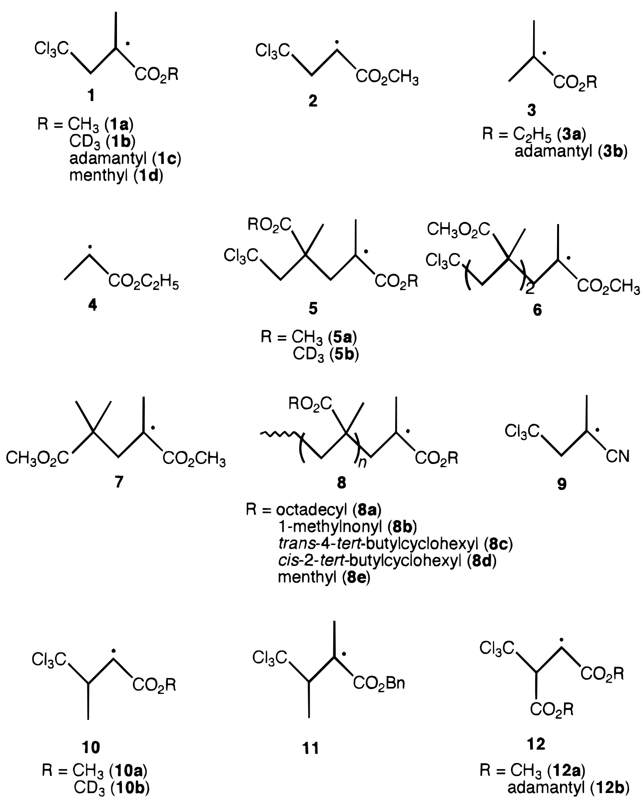
Chart 1



Scheme 1

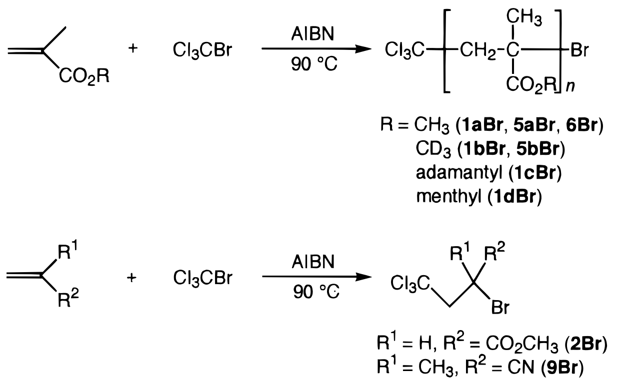
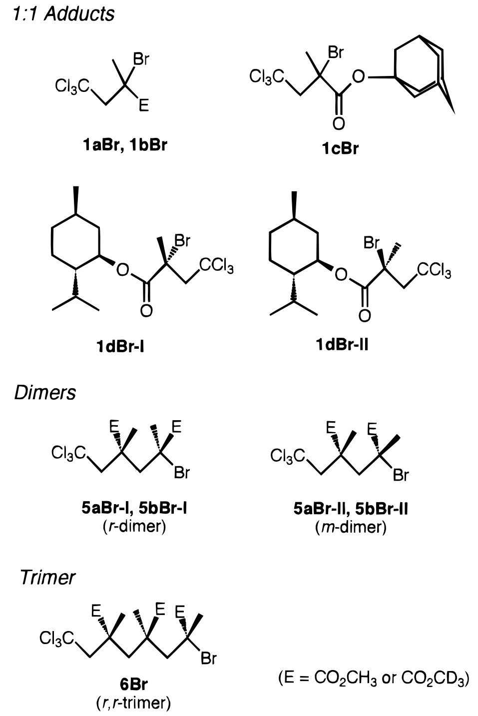


Chart 2



structure of the enolate radicals has been clarified based on the hyperfine splitting in the well-resolved ESR spectra. Eventually, we have reached the conclusion that the spectra observed for the methacrylate radicals are accounted for by hyperfine coupling constants different from those already reported in the literature. Thus, the conformation model of the radicals should be revised.

In this article, we describe the details of the preparation of the compounds as radical precursors, the observation of the ESR spectra, and the assignments of the hyperfine coupling constants in the spectra for various enolate radicals including methacrylate radicals as well as other radicals with related structures. The ground state conformations of the radicals and the mechanism of the propagation are discussed based on the results obtained in this ESR work.

Results and Discussion

1. Preparation of Precursors. The precursors for the radicals were prepared by the reaction of the corresponding alkenes with bromotrichloromethane in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) at 90 °C[15] (Scheme 1). The 1:1 adduct (unimer) (**1aBr** and **1bBr**), dimers (**5aBr-I**, **5aBr-II**, **5bBr-I**, and **5bBr-II**), and one of the trimers (**6Br**) in Chart 2 were isolated by flash chromatography from a mixture of the products in the reaction of MMA or MMA-d_3. Here only one kind of enantiomer of the dimers and the trimer is shown for simplicity, although the compounds were racemic mixtures (also for **10Br**−**12Br**). In the reactions of adamantyl and menthyl methacrylates, only the 1:1 adduct was isolated. The adduct **1dBr** was isolated as a mixture of two diastereomers (**1dBr-I** and **1dBr-II** in Chart 2).

The isolated yields of the products depended on the concentration of the methacrylates used (Table 1). When the ratio of the methacrylate to bromotrichloromethane decreased, the yield of the 1:1 adduct increased, as was expected. The rate of propagation also affected the yields, that is, a slow propagation would suppress formation of oligomers or polymers and increase the 1:1 adduct yield. The propagation rate constant has been reported to be 230 L/mol·s for menthyl methacrylate at 60 °C[16] but 510 L/mol·s for MMA[17] and 530 L/mol·s for adamantyl methacrylate.[18] The preferential formation of the *r*-dimer rather than the *m*-dimer and of the *r*,*r*-trimer rather than the other unisolated trimers is very consistent with the predominant syndiotactic propagation of the methacrylates, where *r* and *m* represent racemo and meso, respectively. These results agree with the results by Kimura et al.[15c] For **2Br** and **9Br**, only the 1:1 adducts were isolated in this work (Scheme 1).

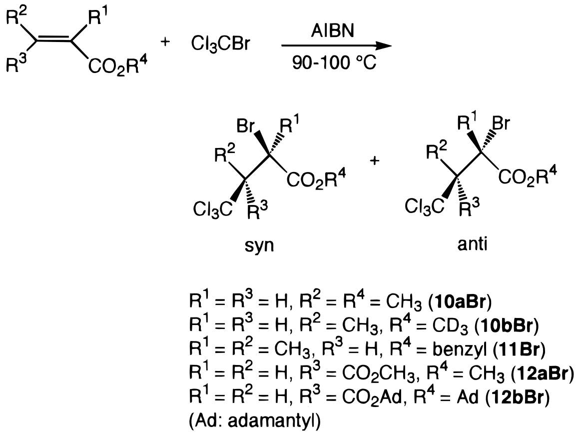
In the synthesis of **10Br**, the reaction provided two diastereomers, of which the ratio was 70:30 as the isolated yield for **10aBr** (Scheme 2). We used them as a mixture without further separation into the syn and anti products. In the reaction of the tiglate, only the syn compound of the two possible products (**11Br**) was isolated because of high stereoselectivity.[19] The reaction of the maleate gave both diastereomers (**12Br**), and the syn compound as a major isomer was isolated in this work.[20]

Table 1. Preparation of Precursors for Radicals 1[a]

R	methacrylate/Cl_3CBr (mol/mol)	isolated yield[b] (mol%)			
		1:1 adduct	*r*-dimer	*m*-dimer	*r,r*-trimer
methyl	1/8.2	15	7	2	6
methyl-d_3	1/11	26	8	3	*c*
adamantyl	1/24	36	*c*	*c*	*c*
menthyl	1/28	45	*c*	*c*	*c*

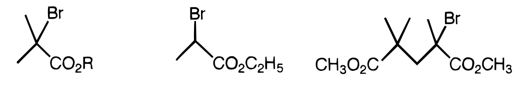
[a] With AIBN at 90 °C for 6 h. [b] Based on the methacrylate used. [c] Not determined.

Scheme 2



$R^1 = R^3 = H, R^2 = R^4 = CH_3$ (**10aBr**)
$R^1 = R^3 = H, R^2 = CH_3, R^4 = CD_3$ (**10bBr**)
$R^1 = R^2 = CH_3, R^3 = H, R^4 =$ benzyl (**11Br**)
$R^1 = R^2 = H, R^3 = CO_2CH_3, R^4 = CH_3$ (**12aBr**)
$R^1 = R^2 = H, R^3 = CO_2Ad, R^4 = Ad$ (**12bBr**)
(Ad: adamantyl)

Chart 3

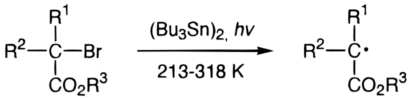


R = C_2H_5 (**3aBr**)
adamantyl (**3bBr**)

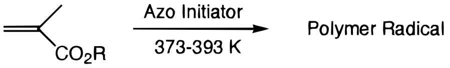
4Br

7Br

Scheme 3



Scheme 4



The precursor **7Br**[21] was prepared with methyl 2-lithioisobutyrate and MMA followed by the reaction with bromine. Adamantyl 2-bromoisobutyrate (**3bBr**) was prepared from 1-adamantanol and 2-bromoisobutyryl bromide. Ethyl 2-bromoisobutyrate (**3aBr**) and ethyl 2-bromopropionate (**4Br**) were commercially available.

2. Radical Formation. The bromides as precursors yielded the corresponding radicals by photoirradiation of the toluene solution in the ESR tube in the presence of hexabutylditin at 213–318 K (Scheme 3).

The polymer radicals **8** were produced in the ESR tube by the radical polymerization of the corresponding methacrylate with 2,2′-azobis(2,4,4-trimethylpentane) as an initiator in toluene at 373 K or in *p*-xylene at 393 K (Scheme 4).[16] The polymers produced during the ESR measurement were isolated by a precipitation method. The molecular weights of the polymers were more than 10^3 by gel permeation chromatography with a polystyrene standard.

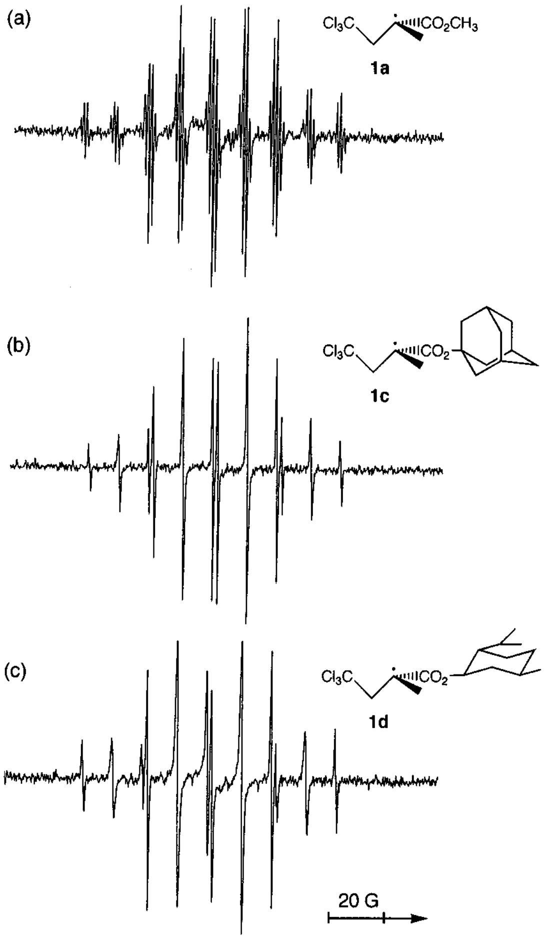


Figure 1. ESR spectra of adduct radicals observed in toluene at 243 K: (a) **1a**, (b) **1c**, and (c) **1d**.

Table 2. ESR Parameters for Dual-Conformation Adduct Radicals 1 and 9[a]

radical	conformation	coupling constant (G)			*g*-value
		$a_1(\beta, CH_3)$	$a_2(\beta, CH_2)$	$a_3(\delta$, ester)	
1a	A	23.48 (3H)	22.30 (1H)	1.14 (3H)	2.0044
	B	23.46 (3H)		1.25 (3H)	2.0044
1b	A	23.57 (3H)	22.02 (1H)		2.0043
	B	23.51 (3H)			2.0043
1c	A	23.43 (3H)	21.56 (1H)		2.0043
	B	23.40 (3H)			2.0043
1d	A	23.57 (3H)	21.75 (1H)	0.56 (1H)	2.0043
	B	23.54 (3H)			2.0043
9	A	21.99 (3H)	21.99 (1H)	3.20 (1N)[b]	2.0036
	B	22.07 (3H)		3.21 (1N)[b]	2.0036

[a] In toluene at 243 K. [b] Coupling to nitrogen.

3. ESR Spectra of Adduct Radicals. The radicals **1** gave well-resolved ESR spectra in toluene at 243 K, as shown in Figure 1, which are assigned as an overlap of binary components characterized by the coupling constants and *g*-values in Table 2. One is a doublet of quartets (a_1(3H) = 23.43–23.57 G and a_2(1H) = 21.56–22.30 G), and another is a quartet (a_1(3H) = 23.40–23.54 G), as illustrated in Figure 2. The *g*-values were 2.0043–2.0044. In the spectra of **1a**,**d**, further splittings due to the δ-protons of the ester alkyl groups were also observed (a_3(3H or 1H) = 0.56–1.25 G).[22] Both components in each spectrum have identical *g*-values and very close coupling constants due to the methyl protons, supporting the assumption that these species are radi-

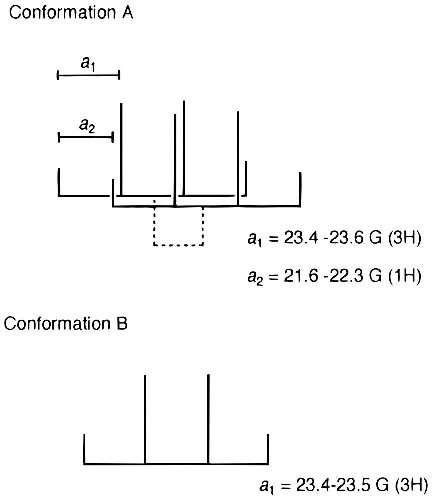


Figure 2. Stick plots for binary-component spectrum for radicals **1**.

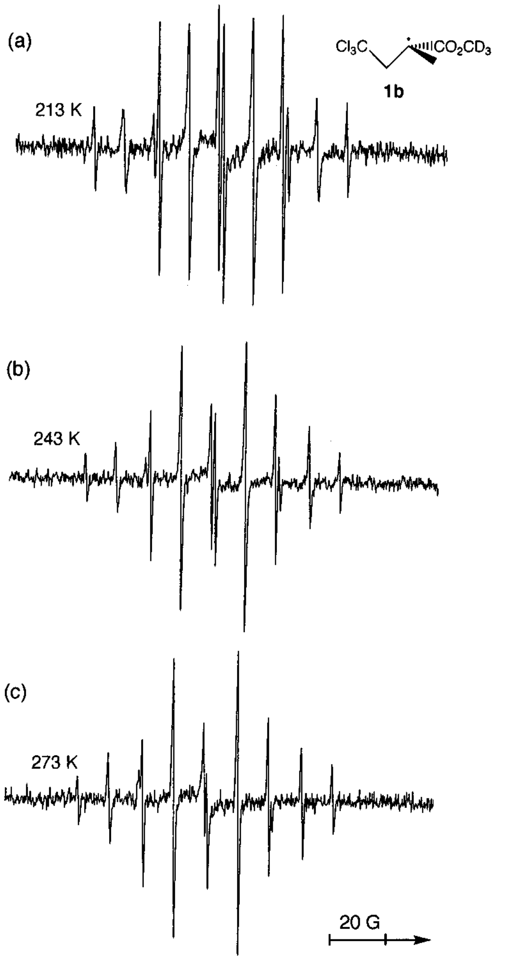


Figure 3. ESR spectra of **1b** observed in toluene at various temperatures: (a) 213, (b) 243, and (c) 273 K.

cals which have the same chemical structure but different conformations.

The temperature dependence of these spectra was examined to reveal the thermodynamic nature of the radicals. The relative peak height and the maximum slope line width (ΔH_{msl}) changed reversibly as a function of the temperature, as seen in the results for **1b** in Figure 3. The peaks due to conformation B were always broader than those of conformation A. In Table 3, the results are shown together with the temperature dependence of the coupling constants. The magnitude of the temperature dependence of the coupling constants due to the β-proton of CH_2 for conformation A, $\mathrm{d}a_2(\beta, CH_2)/\mathrm{d}T$, is large, 1.2×10^{-2} G/K, while the coupling constant due to the β-protons of CH_3 has a very small temperature dependency ($<1 \times 10^{-3}$ G/K) for both conformations. The other derivatives, **1a**,**c**,**d**, showed a similar temperature dependence of the β-CH_2 coupling irrespective of the ester alkyl groups (Table 4). Figure 4 illustrates the temperature dependence of the intensity ratio of the component due to conformations A and B in the spectrum. From the slope of the lines, the difference in the enthalpies for conformations A and B ($\Delta H_{\mathrm{B}} - \Delta H_{\mathrm{A}}$) was determined to be 7.9 and 11.2 kJ/mol for the radicals **1b**,**d**, respectively. The greater value for the latter might reflect more important steric hindrance due to the ester alkyl group in conformation B.

In the spectra of the radicals **1**, a coupling to only one proton of β-CH_2 was observed for conformation A and no coupling was detected in conformation B, despite the two methylene protons at the β-position. The hyperfine coupling constant of the β-protons depends on the angle between the p orbital of the radical and the plane defined by the $H-C_\beta-C_\alpha$ bonds.[23] The relationship is given in the following equation:[24]

$$a_{\beta\text{-H}} = A + B\cos^2\theta \qquad (6)$$

where A is approximately zero and B is estimated to be 47 G for the radicals **1** from the observed coupling constants to the freely rotating methyl group (23.4–23.6 G).

If an sp^2 radical with a planar structure prefers the conformation in which the allylic strain (A-strain) effect is minimized,[3c,5] the coupling constant to one of the β-protons would be zero. According to this model, however, the other proton would have a coupling constant of 35 G ($\theta = 30°$), much larger than the observed coupling constant in this work ($a = 21.6-22.3$ G). This conformation model cannot also account for the lack of any coupling to the β-protons of CH_2 in conformation B. The nitrile derivative **9** was also revealed to have dual conformations similar to those for **1**: $a_1(3H) = 21.99$ G, $a_2(1H) = 21.99$, and $a_3(1N) = 3.20$ G for conformation A and $a_1(3H) = 22.07$ G and $a_3(1N) = 3.21$ G for conformation B (Figure 5b and Table 2), although the A-strain effect is valid for enolate radicals but not for α-nitrile radicals.[2c,5]

Next, we examined the ESR spectra of several other radicals, i.e., **2** as a secondary carbon radical bearing a large β-substituent, **3** as a tertiary carbon radical without any β-substituent, and **4** as a secondary carbon radical with no β-substitution. In contrast to the dual conformations for **1** and **9**, the radicals **2**–**4** were confirmed to be of a single conformation. The observed spectrum of **2** is shown in Figure 5a as an example. The coupling constants are listed in Table 5, which were determined in the temperature region of 213–303 K. In every spectrum of the radicals **2-4**, the couplings to all the protons of β-CH_2 and β-CH_3 were observed as expected from their chemical structures, and the temperature dependence of the β-coupling for these radicals was found to be very small. In the spectra of **3**, a septet with a coupling of 21.5 G was observed. Namely, all methyl protons were observed as equivalent under our ESR conditions (Figure 6a), although it has recently been reported that *cis*- and *trans*-methyl protons relative to the carbonyl oxygen are distinguished unequiva-

Table 3. Temperature Dependence of ESR Parameters for Radical 1b

	conformation A			conformation B		
temp (K)	$a_1(\beta, CH_3)$ (G)	$a_2(\beta, CH_2)$ (G)	ΔH_{msl}[a] (G)	$a_1(\beta, CH_3)$ (G)	ΔH_{msl}[a] (G)	intensity ratio[b] (I_A/I_B)
213	23.57	21.63	0.80	23.54	0.95	1.42
228	23.57	21.83	0.75	23.54	0.90	1.01
243	23.57	22.02	0.75	23.51	0.85	0.84
258	23.56	22.17	0.70	23.53	0.85	0.69
273	23.55	22.34	0.60	23.51	0.75	0.50

[a] Maximum slope line width (peak-to-peak line width in a derivative spectrum). [b] The intensity was estimated from $(\Delta H_{msl})^2 \times$ peak height.

Table 4. Temperature Dependence of Coupling Constants of β-Methylene Protons

radical	conformation	$da_2(\beta, CH_2)/dT \times 10^2$ (G/K)
1a	A	1.17
1b	A	1.16
1c	A	1.18
1d	A	1.17
2		0.24
5a	A	0.20
	B	−2.00
5b	A	0.29
	B	−2.13
6	A	0.10
	B	−4.6
7	A	1.3

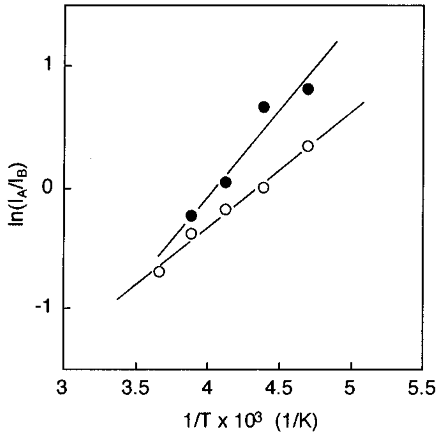


Figure 4. Temperature dependence of the intensity ratio of the spectrum due to conformation A to B (I_A/I_B) for radicals **1b** (○) and **1d** (●).

lently in the planar structure of the radicals **3**. For example, Lung-min and Fischer[25] reported the following values for **3a**: *a*(β, *trans*-CH_3) = 21.69 G and *a*(β, *cis*-CH_3) = 21.44 G (see also section 6).

The results obtained from the ESR parameters for the radicals **1**−**4** and **9** provide the following conclusion: The dual conformations and the lack of the coupling to the β-protons may be observed only for a tertiary carbon radical bearing large β-substituents but not for a secondary carbon radical such as **2**. Thus, the structure of the radicals **1** is different from those of a large number of enolate radicals having a planar structure with spin delocalization such as **3**.

It is also noted here that the peaks due to a persistent radical were additionally detected, as shown by the arrows in Figure 6b, during the continuous irradiation of the solution of **3** over 1 h. The persistent radical was probably produced according to the mechanism previously proposed by Tanaka et al.[26] (Scheme 5). In this mechanism, the olefin that is produced by disproportionation of the radical **3** or the dimer radical reacts with the radical **3**, whereas, no persistent radical was produced during the measurement for the other radicals in this work including **1**. This is consistent with the fact that the olefin produced by disproportionation of **1** is a sterically hindered 1,1- or 1,2-disubstituted ethylene, the reactivity of which is very low.[27]

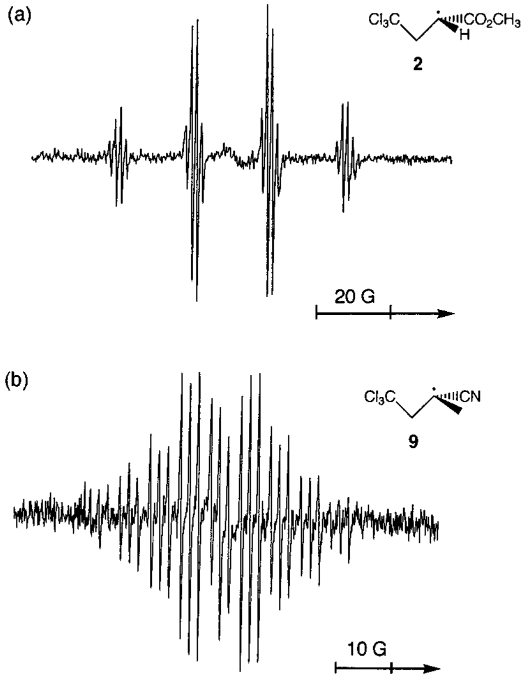


Figure 5. ESR spectra of radicals **2** and **9** observed in toluene at 243 K: (a) **2** and (b) **9**.

Table 5. ESR Parameters for Single-Conformation Adduct Radicals 2−4[a]

		coupling constant (G)			
radical	temp (K)	$a_1(\alpha, CH)$	$a_2(\beta, CH_2$ or $CH_3)$	$a_3(\delta$, ester)	*g*-value
2	213	20.64 (1H)	20.64 (2H)	1.48 (3H)	
	243	20.77 (1H)	20.77 (2H)	1.45 (3H)	2.0042
	288	20.82 (1H)	20.82 (2H)	1.41 (3H)	
3a	213		21.58 (6H)	1.40 (2H)	
	243		21.55 (6H)	1.33 (2H)	2.0034
	288		21.58 (6H)	1.24 (2H)	
3b	213		21.47 (6H)		
	243		21.48 (6H)		2.0034
	303		21.47 (6H)		
4	213	20.40 (1H)	24.66 (3H)	1.58 (2H)	
	243	20.45 (1H)	24.66 (3H)	1.50 (2H)	2.0035
	273	20.42 (1H)	24.65 (3H)	1.41 (2H)	

[a] In toluene.

4. ESR Spectra of Oligomer Radicals 5−7 and Polymer Radicals 8. Dual-conformation spectra were also observed for the larger size radicals **5**−**8**. Figure 7 and Table 6 show the results of the ESR observation for the oligomer radicals at 243 K. The radicals **5** and **6** are the dimer and trimer of the methacrylate, respectively. The diastereomers **5Br-I** and **5Br-II** (Chart 2) as precursors gave an identical ESR spectrum on

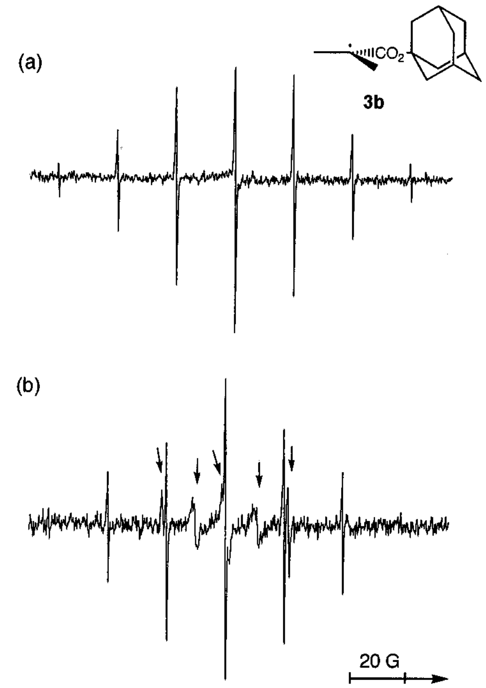
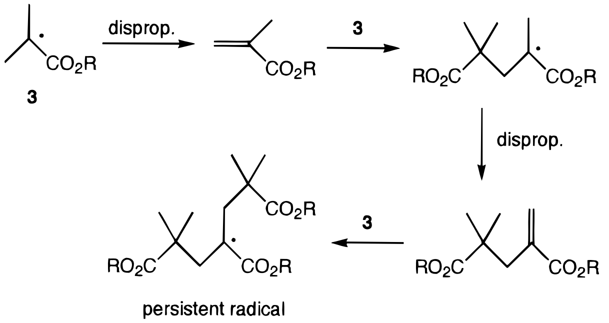


Figure 6. ESR spectra of **3b** observed in toluene at 243 K: (a) immediately and (b) after 1 h irradiation. The arrows indicate the resonances due to the persistent radicals (see text).

Scheme 5



photoirradiation as was expected. The spectrum of **6** was similar to that of **5**, indicating that the conformation of the propagating radical is less sensitive to the structure of the substituents on the carbons apart from the radical center, i.e., the structure of the pen-penultimate repeating unit. This may be closely related to the fact that the tacticity of poly(MMA) approximately obeys Bernoulli statistics during free-radical polymerization.[8]

For conformation A of the oligomer radicals **5** and **6**, the coupling constants to the β-protons of CH_3 and one of the β-protons of CH_2 were identical (22.4–22.6 G, Table 6). These values were intermediate in comparison with the β-CH_3 coupling ($a_1 = 23.4$–23.6 G, Table 2) and the β-CH_2 coupling ($a_2 = 21.6$–22.3 G, Table 2) for the adduct radicals **1**. Both couplings to the β-protons of CH_3 and CH_2 for the radicals **5** varied in identical fashion over the temperature range examined (Figure 8 and Table 7). The temperature dependence of these coupling constants was small, 2.0×10^{-3} and 2.9×10^{-3} G/K for **5a**,**b**, respectively (Table 4 and Figure 9). The difference in the enthalpies for both conformations for **5b** was determined to be 8.2 kJ/mol, which agrees very well with that for **1b** (7.9 kJ/mol).

For conformation B, a small β-CH_2 coupling was observed in the magnitude of 3–9 G. This is distinguished from the fact that no β-CH_2 coupling was observed for conformation B of the adduct radicals **1**. The temperature dependence of this β-CH_2 coupling was considerably large and negative (-2.0 to -4.6×10^{-2} G/K) (see Table 4).

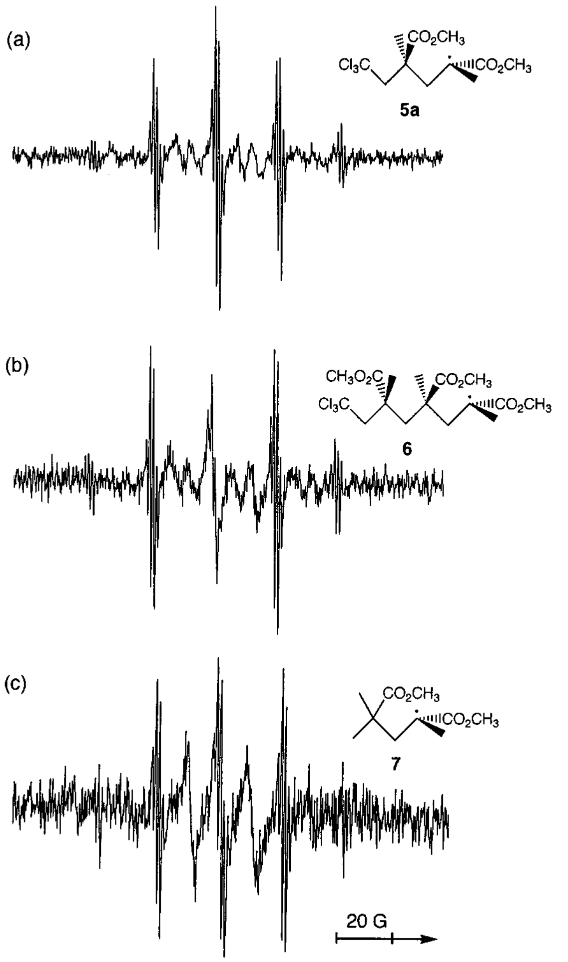


Figure 7. ESR spectra of oligomer radicals **5**–**7** observed in toluene at 243 K: (a) **5a**, (b) **6**, and (c) **7**.

Table 6. ESR Parameters for Dual-Conformation Oligomer Radicals 5–7[a]

radical	conformation	coupling constant (G) a_1(β, CH_3)	 a_2(β, CH_2)	 a_3(δ, ester)	g-value
5a	A	22.63 (3H)	22.63 (1H)	1.24 (3H)	2.0036
	B	22.6 (3H)	5.3 (1H)		
5b	A	22.60 (3H)	22.60 (1H)		2.0033
	B	22.42 (3H)	5.39 (1H)		
6	A	22.45 (3H)	22.45 (1H)	1.26 (3H)	2.0034
	B	22.4 (3H)	6.8 (1H)		
7	A	22.17 (3H)	24.14 (1H)	1.4 (3H)	2.0034
	B	22 (3H)			

[a] In toluene at 243 K.

The radical **7**, which is one of the dimer radicals, gave a spectrum slightly different from those of **5** and **6**, as depicted in Figure 7c. For conformation A, the couplings to the β-protons of CH_3 and CH_2 were not equivalent. The temperature dependence was similar to that of **1** rather than those of **5** and **6** (Table 4). This spectrum is the same as that reported in 1992 by Keah et al.[21] They determined the coupling constants (see Table 10) in a fashion similar to the assignments for several radicals ever reported in literature, as described in detail in section 6. This radical should be characterized by the parameters shown in Table 6 on the basis of the

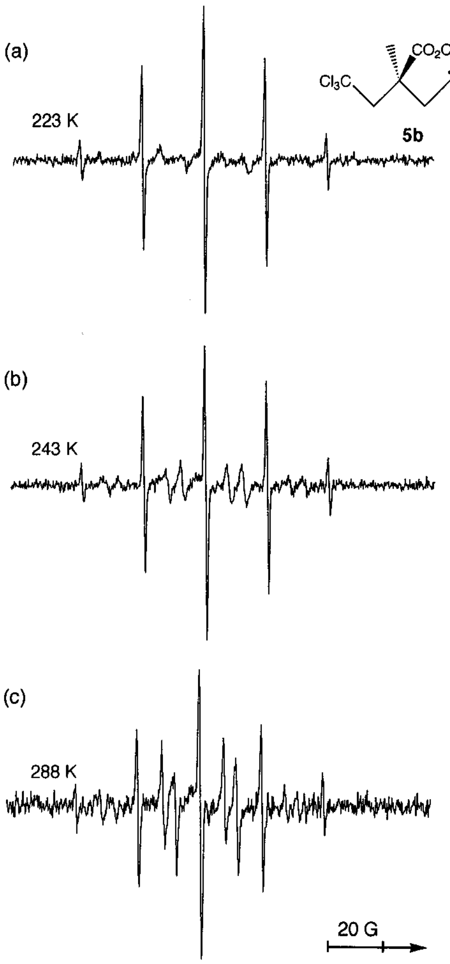


Figure 8. ESR spectra of **5b** observed in toluene at various temperatures: (a) 223, (b) 243, and (c) 288 K.

Table 7. Temperature Dependence of ESR Parameters for Radical 5b

	conformation A	conformation B		
temp (K)	a_1(β, CH_3, 3H) and a_2(β, CH_2, 1H) (G)	a_1(β, CH_3, 3H) (G)	a_2(β, CH_2, 1H) (G)	intensity ratio[a] (I_A/I_B)
213	22.57	22.8	9.2	4.15
223	22.58	22.6	7.8	2.48
233	22.60	22.7	6.3	2.44
243	22.60	22.42	5.39	1.72
258	22.64	22.53	4.80	1.68
273	22.68	22.53	4.69	1.27
288	22.75	22.58	4.54	1.10
303	22.83	22.50	4.18	0.92
318	22.86	22.55	3.55	0.75

[a] See Table 3.

consideration of the temperature dependence and the results for other related radicals.

The spectra for the polymer radicals, which are observed during the polymerization,[16,28] have been revealed to be essentially the same as the spectra of the adduct radicals and oligomer radicals. Figure 10 illustrates the ESR spectra of propagating radicals observed during the polymerization of several alkyl methacrylates at 373 or 393 K. At a lower temperature, broader and less-resolved spectra were obtained, as shown in the previous paper.[16] At a high temperature, the ESR measurement was difficult because of too rapid polymerization. Therefore, we could not quantify the temperature dependence of the coupling constants for **8**. Furthermore, we could never obtain the ESR spectrum of the poly(MMA) radical under similar conditions

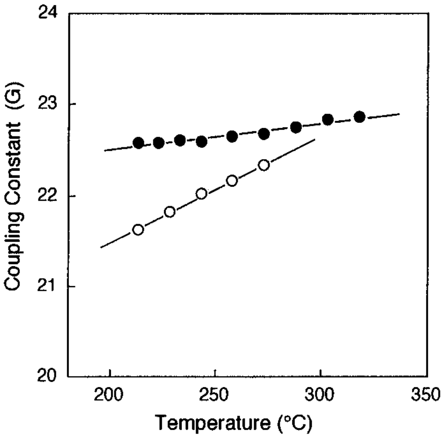


Figure 9. Temperature dependence of β-CH_2 coupling for radicals **1b** (○), and **5b** (conformation A) (●).

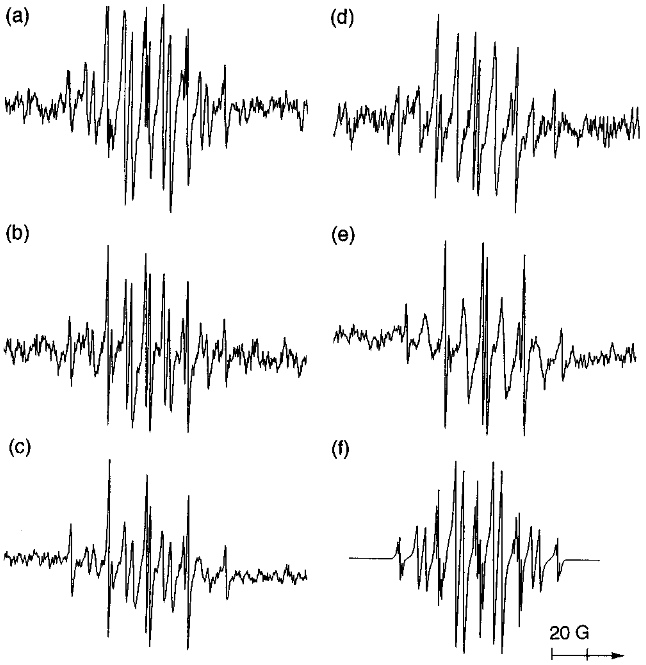


Figure 10. ESR spectra of polymer radicals **8** observed in *p*-xylene at 393 K: (a) **8a**, (b) **8b**, (c) **8c** (in toluene at 373 K), (d) **8d**, (e) **8e**, and (f) simulated spectrum for **8a**.

because the radical concentration was too low, that is, the termination occurred too frequently.[16] Because the bimolecular termination between mutual polymer radicals is a typical diffusion-controlled reaction for determining the termination rate, a steady state radical concentration depends on the chain length of the polymer chain,[29] in addition to many other factors including viscosity, temperature, and mobility of the chain segment.[7a]

The coupling constants determined are listed in Table 8. The coupling constants to β-CH_2 were obtained as larger values (24.6−25.3 G) than those for **5** and **6** observed at 243 K for conformation A, while the β-CH_3 couplings (a_1 = 22.2−22.6 G) were the same as those for the oligomer radicals (a_1 = 22.4−22.6 G). In conformation B, a smaller β-CH_2 coupling (3.4−4.8 G) than those of the dimer or trimer radicals (5.3−6.9 G, Table 6) was observed for **8a**−**c**. These small couplings are quite consistent with the negative temperature dependence of the oligomer radicals because we can assume that **8** shows a temperature dependence similar to those of **5** and **6** as described in Table 4. In the

Table 8. ESR Parameters for Dual-Conformation Polymer Radicals 8[a]

		coupling constant (G)		
radical	conformation	a_1(β, CH$_3$)	a_2(β, CH$_2$)	a_3(δ, ester)
8a	A	22.3 (3H)	24.6 (1H)	1.1 (2H)
	B	22.2 (3H)	4.7 (1H)	
8b	A	22.3 (3H)	24.9 (1H)	
	B	22.3 (3H)	3.4	
8c[b]	A	22.2 (3H)	24.6 (1H)	
	B	22.3 (3H)	4.8	
8d	A	22.3 (3H)	25.3 (1H)	
	B	22.6 (3H)		
8e	A	22.3 (3H)	25.2 (1H)	
	B	22.6 (3H)		

[a] In *p*-xylene at 393 K. [b] In toluene at 373 K.

spectra of **8d**,**e**, no coupling was observed for β-CH$_2$ in conformation B. In the case of the polymer radicals, the values of the couplings to β-CH$_3$ and β-CH$_2$ were independent, being different from the results for the dimer and trimer radicals and similar to those for the adduct radicals **1** and one of the dimer radicals **7**.

A large number of spectra of polymethacrylate radicals have been reported in the literature,[12,13] but most of them were broad and less resolved so that simulation and in some cases speculation often led to a wrong conclusion. In this work, well-resolved spectra of the polymer radicals were obtained in solution at a high temperature such as 373 or 393 K. These spectra enable us to discuss the conformations of the polymer radicals similarly to those of the small radicals.

5. ESR Spectra of β,β-Disubstituted Enolate Radicals 10−12. Subsequently, three kinds of β,β-disubstituted enolate radicals (**10**−**12**) were examined to discuss the effect of the α- and β-substitution of the enolate radicals. **10a** gave a complicated spectrum as shown in Figure 11a. The coupling constants were determined with the aid of the spectrum of the deuterio compound (Figure 11c) and by computer simulation (Figure 11b). All the couplings due to the protons included were observed as follows: a_1(α, CH) = 20.7−20.8 G, a_2(β, CH) = 7.4−9.4 G, a_3(γ, CH$_3$) = 2.0 G, and a_4(δ, CH$_3$) = 1.5 G. Figure 12 shows the spectra of **11** and **12b**. In contrast to **10**, **11** gave only a broad spectrum because of a very small coupling due to γ- and δ-protons. The radicals **12** provided spectra which are interpreted by the coupling constants listed in Table 9. The coupling constants for **11** and **12** are consistent with those for the radicals **13** and **14** (Chart 4) previously reported by Giese et al.,[3b] i.e., a_1(β, CH) = 4.8 G and a_2(β, CH$_3$) = 21.9 G for **13** and a_1(α, CH) = 20.4 G, a_2(β, CH) = 7.6 G, a_3(δ, CH$_2$) = 1.54 G, and a_4(δ, CH$_3$) = 0.36 G for **14**. For these radicals, the *A*-strain effect accounts for the small coupling due to the β-proton.[3b] The radicals **11** and **13** are likely to have a single stable conformation, although they were expected to show some characteristics similar to those of the methacrylate radicals **1**.

6. Conformational Structure of Methacrylate Radicals Reported in the Literature. A large number of ESR spectra of the enolate radicals with a small molecular size have been reported in the literature, and the coupling constants are collected in the Landolt−Börnstein series.[30] Especially, the radical **3**, which consists of the simplest structure as a tertiary enolate radical, has been most often investigated. It has been verified that this radical has a planar structure with spin delocalization by the fact that the *cis* and *trans*-methyl groups to the carbonyl oxygen atom are observed unequivalently in the high-resolution ESR[25] and the μSR[31] experiments. Recently, Giese et al.[5,32] determined the coupling constant to the tertiary carbon to be 29.5 G in an experiment with a ^{13}C-enriched

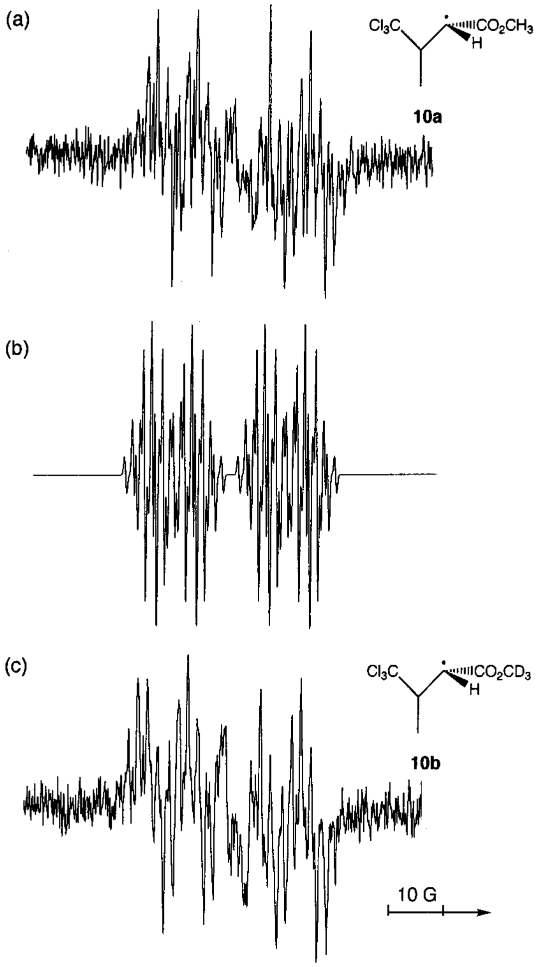


Figure 11. ESR spectra of radicals **10** in toluene at 243 K: (a) **10a**, (b) simulated spectrum for **10a**, and (c) **10b**.

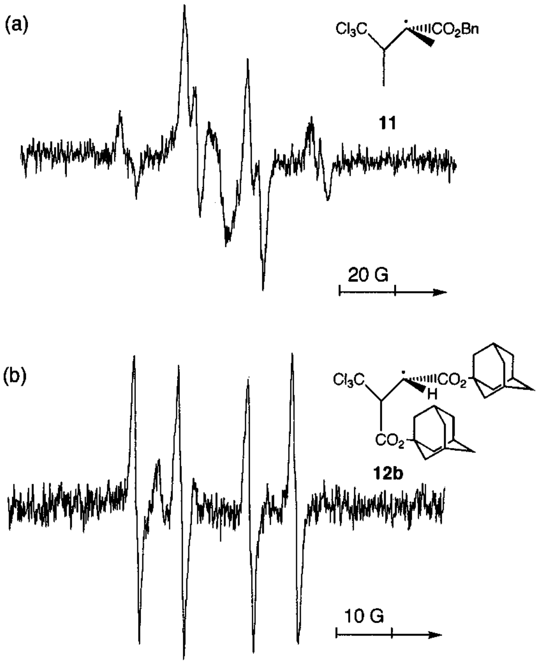


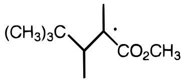
Figure 12. ESR spectra of radicals (a) **11** and (b) **12b** in toluene at 243 K.

Table 9. ESR Parameters for β,β-Disubstituted Radicals 10−12[a]

radical	temp (K)	coupling constant (G)				*g*-value
		a_1(α, CH)	a_2(β, CH)	a_3(γ, CH_3)	a_4(δ, ester)	
10a	243	20.73 (1H)	7.39 (1H)	2.00 (3H)	1.45 (3H)	
10b	213	20.71 (1H)	8.95 (1H)	2.00 (3H)		
	243	20.75 (1H)	9.35 (1H)	2.03 (3H)		2.0044
11	243	23.36 (3H)[b]	3.90 (1H)			2.0040
12a	243	20.94 (1H)	6.6 (1H)			
12b	243	20.86 (1H)	8.0 (1H)			2.0043
13[c]	243	21.9 (3H)[b]	4.8 (1H)			2.0035
14[c]	243	20.4 (1H)	7.6 (1H)	0.39 (9H)[d]	1.54 (2H)	2.0034

[a] In toluene. [b] Coupling to β-protons of CH_3. [c] Reference 3b. [d] Coupling to δ-protons of CH_3 (*tert*-butyl).

Chart 4



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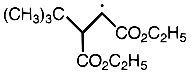

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Table 10. Typical Coupling Constants for β-Protons of Substituted Isobutyrate Radicals $XCH_2C(CH_3)CO_2R$ in the Literature

X	coupling constant (G)	authors	ref
$-H$	21.3 (6H, CH_3)	Smith et al. (1965)	33
	21.69 (3H, *trans*-CH_3) 21.44 (3H, *cis*-CH_3)	Lung-min et al. (1983)	25
$-OH$	23.03 (3H, CH_3) 19.98 (2H, CH_2)	Fischer (1964)	34a
	23.0 (3H, CH_3) 19.9 (2H, CH_2)	Takakura et al. (1968)	35
	23.0 (3H, CH_3) 19.9 (2H, CH_2)	Davies et al. (1984)	36
$-CH_3$	21.83 (3H, CH_3) 15.37 (2H, CH_2)	Fischer et al. (1967)	34b
$-CH_2OH$	22.27 (3H, CH_3) 14.45 (2H, CH_2)	Corvaja et al. (1965)	34c
$-CO_2CH_3$	22.55 (3H, CH_3) 14.05 (2H, CH_2)	Brumby (1973)	37
$-CH_2CH_3$	21.5 (3H, CH_3) 13.5 (2H, CH_2)	Hewgill et al. (1981)	38
$-\underset{\mathrm{OCOCH_3}}{\mathrm{CH}}\mathrm{CH_2OH}$	22.4 (3H, CH_3) 15.5 (1H, CH_2) 9.5 (1H, CH_2)	Takakura et al. (1968)	35
$-\overset{\mathrm{CH_3}}{\underset{\mathrm{CO_2CH_3}}{\mathrm{C}}}\mathrm{-CH_3}$	22.3 (3H, CH_3) 12.6 (1H, CH_3) 10.1 (1H, CH_2)	Keah et al. (1992)	21
$-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-CH_3}$	21.8 (3H, CH_3) 25.1 (1H, CH_2)	Yamada et al. (1983)	39

compound. This small coupling constant supports the planar structure of the radical **3**. For the enolate radicals with more complicated structure, the magnitude of the equivalent or unequivalent β-CH_2 couplings has been reported to depend on the structure of the substituents. Typical examples are summarized in Table 10.[21,25,33−39]

In the period of the 1950−1970s, many workers reported independently the ESR spectra of polymethacrylate radicals, which were obtained by decomposition of the polymers or by polymerizations in the solid (glassy or crystalline) state and in solution.[12,13] The conformation of the methacrylate radicals has been discussed based on the splittings in the spectra, which were observed as a 5- or 9-line spectrum in many systems. In earlier days, several workers considered that the 9-line spectrum consisted of the 5- and 4-line components.[40] Later, Harris et al.[41] reported the 9-line spectrum due to the two conformations observed for the photoinduced polymerization of methacrylates. Bresler et al.[42] observed in situ the ESR spectrum of the radical produced during bulk polymerization of MMA as a well-resolved 9-line spectrum by using a specially designed highly sensitive cavity, and they interpreted the spectra as an overlap of five lines with an intensity of 1:4:6:4:1 and four lines of 1:3:3:1.

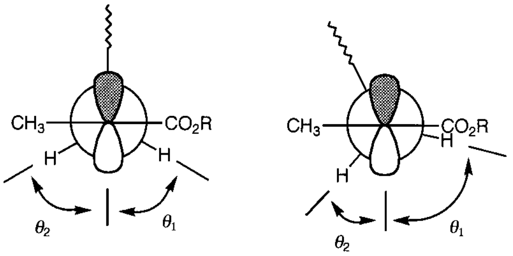

Figure 13. Stable conformations proposed for polymethacrylate radicals in the literature.

On the other hand, Symons[43] proposed another interpretation for the 9-line spectrum. He considered that two unequivalent protons of β-CH_2 resulted in the hyperfine coupling constants of 8.1 and 15.1 G giving a 13-line spectrum theoretically, and the 13 lines reduced to nine lines in the observed spectrum because of broadening. In 1964, Fischer[44] observed a well-split 16-line spectrum of the polymer radicals of methacrylic acid at 320 K in aqueous solution by the flow method. He determined the coupling constants to the β-protons as follows: $a_1(\beta, CH_3, 3H) = 22.46$ G, $a_2(\beta, CH_2, 1H) = 13.75$ G, and $a_3(\beta, CH_2, 1H) = 11.04$ G. Similar coupling constants have independently been reported by other investigators, for example, $a_1 = 23$ G, $a_2 = 12.5$ G, and $a_3 = 10.6$ G by O'Donnell et al.,[45] $a_1 = 22.2$ G, $a_2 = 14.7$ G, and $a_3 = 7.5$ G by Sakai and Iwasaki,[46] and $a_1 = 22.19$ G, $a_2 = 14.18$ G, and $a_3 = 9.27$ G by Smith et al.[47] The extraordinary intensity distribution of the observed 9-line spectrum was accounted for by superposition of the spectra for two conformations of the radical, $\theta_1 = 75°$ and $\theta_2 = 45°$ and $\theta_1 = \theta_2 = 60°$ in Figure 13.[43,48] Kamachi et al.[49] explained the temperature dependence of the spectra of poly(triphenylmethyl methacrylate) and other esters on the basis of two conformations: $\theta_1 = 75°$ and $\theta_2 = 45°$ for one conformation and $\theta_1 = 65°$ and $\theta_2 = 55°$ or $\theta_1 = \theta_2 = 60°$ for another conformation. Thereafter, the interpretations that the ESR spectrum of polymethacrylate radicals consists of overlapping of a 5-line spectrum and a 9- or 13-line spectrum have been accepted by many investigators.[13,28] However, this idea does not account for the spectra obtained in this work.

7. Revised Conformation Models of Methacrylate Radicals. The results obtained in this work require a conformation model different from any other models reported for the enolate radicals.

When an enolate radical contains steric strain between the large β-substituent L and the groups R and/

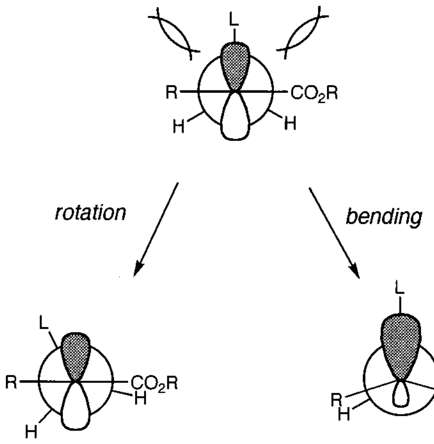

Figure 14. Two possible ways for relief of steric strain of enolate radicals.

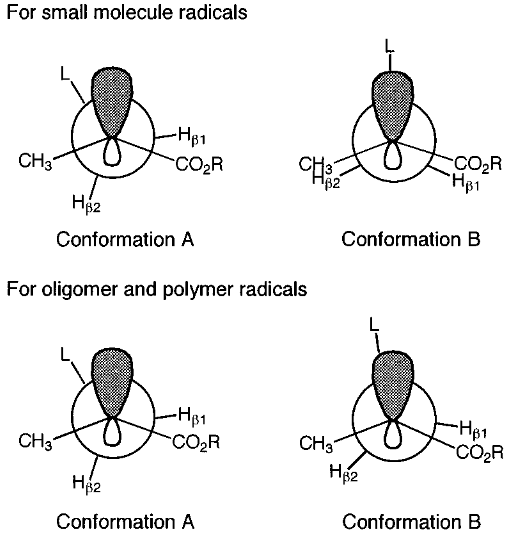

Figure 15. Schematic conformation models for pyramidal radicals in ground state.

or CO_2R, the strain could be relieved by rotation around the C_α–C_β axis or by bending, i.e., a change in the C_β–C_α–C_β angles (Figure 14). This leads to the *A*-strain-controlled conformation, or to pyramidalization of the radical center. When the interaction between L and R is not very significant, the radical exists in the *A*-strain conformation; when both the repulsions between L and R and L and CO_2R are large, the radical could also be pyramidalized.

In the pyramidal (sp^3) radicals, the β-protons would have smaller coupling constants than in planar (sp^2) radicals. This can be assumed from the experimental and calculated values for β-H coupling of cyclopropyl radicals as typical σ-radicals. For example, Fessenden et al.,[50] Kochi et al.,[51] and Ingold et al.[52] reported the coupling constants to the β-protons of a cyclopropyl radical to be 23.42, 23.54, and 23.5 G, respectively, which agree well with the results of INDO and ab initio calculations.[50–53] In this work, the coupling constant due to one β-CH_2 proton is 21–25 G and that of the other is zero in conformation A; both protons may have small or no coupling constants in conformation B. On the basis of these results, the proposed schematic models are illustrated in Figure 15 for the pyramidalized radicals for small molecule radicals and oligomer or polymer radicals. In conformation A, both the bending and the rotation contribute to the deformation of the radical, while the bending is predominant in conformation B. The small coupling observed in the spectra of the oligomer and polymer radicals might be due to the β-proton in the slightly inclined conformation of B, in which the steric repulsion between the L and CO_2R groups is larger than in the small molecules.

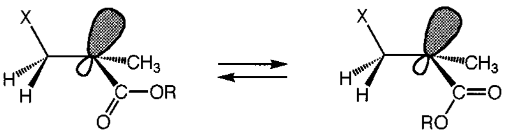

Figure 16. Cis–trans isomerism of the enolate radicals.

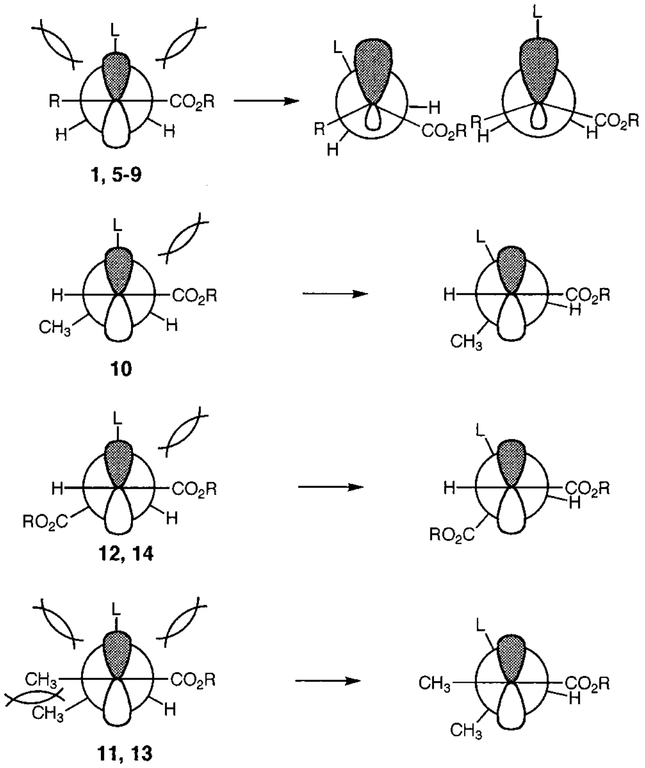

Figure 17. Conformational changes for the relief of steric hindrance in enolate radicals.

The fact that the ESR signals for both conformations are distinct without broadening even at a high temperature, for example, as seen in the polymer radicals at 393 K, requires a large energy barrier between those two stable conformations, A and B. The magnitude of the barrier, which would reach at least 40 kJ/mol, is too large as a barrier between similar structure of the two conformations without considering any other additional interaction. The substantial barrier to internal rotation around the C_α–CO_2R bond as a partial double bond accounts for this large value. The pyramidalized radical would be in two states as shown in Figure 16, i.e., cis- and trans-isomeric structures. Such an isomerism has been demonstrated in sp^2 enolate radicals, and the activation energies have been estimated to be 30–50 kJ/mol.[25,31a,51b] The transformation between conformations A and B possibly includes the cis–trans isomerization in the C_α–CO_2R bond, resulting in the observation of the two conformations without any exchange broadening of the ESR spectra.

The pyramidalized radicals consisting of the dual conformations are uniquely observed for the α-alkyl-substituted radicals, the structure of which is represented at the top in Figure 17. Here, L represents CCl_3 or $C(CH_3)_3$ as a large substituent. In the secondary radicals such as **10**, **12**, and **14**, the steric strain can be

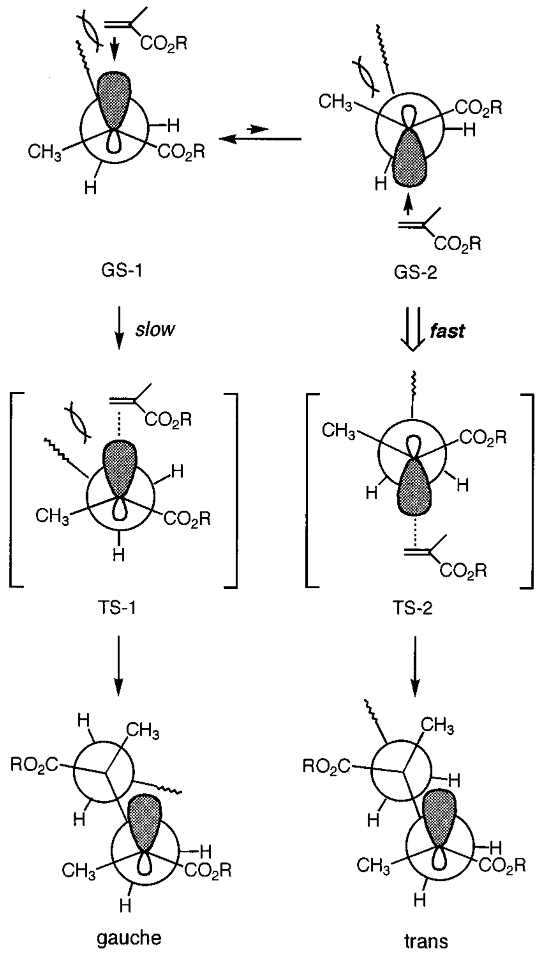

Figure 18. Proposed mechanism of chain propagation in radical polymerization of alkyl methacrylates.

relieved only by rotation because of a lack of steric repulsion between L and α-hydrogen, giving an *A*-strain-controlled conformation. The β-methyl substitution in the radicals **11** and **13** might prevent the pyramidalization because of the increased steric repulsion between the two methyl groups.

The pyramidalized conformations are likely to be disadvantageous for the subsequent reaction such as H or atom abstraction or addition to olefins because of the steric hindrance of the bulky L group. Figure 18 represents two possible paths for chain propagation in polymerization, that is, the addition to a double bond. The ground state model GS-1 is stable thermodynamically but can be in equilibrium with an inverted conformation (model GS-2) with a higher energy. The inverted one readily reacts with the monomer, and the steric repulsion would be relieved in the transition state model TS-2. This transition state model results in a trans-chain conformation. The preferred trans conformation of polymethacrylate chains rather than the gauche one has been confirmed by calculation and X-ray and NMR analyses.[54,55] The reaction of the less stable conformer of substrate at a greater rate via a preferred transition state with a lower energy is interpreted by Curtin–Hammett principle, and an example of radical addition has been demonstrated.[56]

In the literature, the conformation of the polymethacrylate radicals as an active site at the chain end has been discussed in view of the tacticity.[13] In radical polymerization, the stereochemistry at the propagating chain end is not determined until the addition of the attacking monomer to the propagating radical because the end group rotates rapidly around the $C_\alpha-C_\beta$ axis, which is different from the propagation in coordination polymerizations. Figure 19 illustrates meso and racemo propagations in radical polymerization. Here it is assumed that the monomer attacks only from the side opposite to the polymer chain. The tacticity is determined by the competition of meso and racemo propagations, the transition states of which are represented in Figure 20.

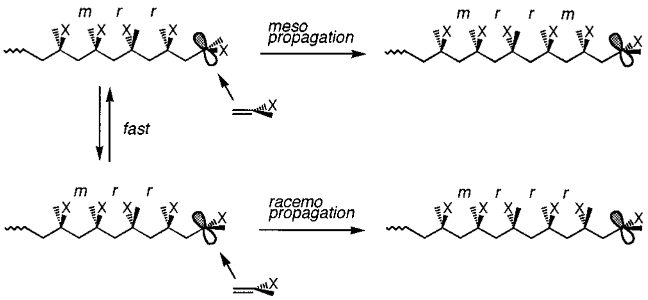

Figure 19. Meso and racemo propagation in radical polymerization.

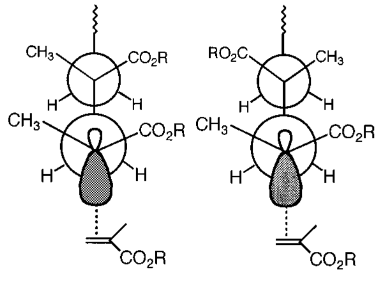

Figure 20. Transition state models for meso and racemo propagation.

In this work, we revealed dual conformations of the methacrylate radicals characterized by the pyramidalization and the *A*-strain effect, but it is concluded that these two stable conformations in the ground state do not directly correspond to the two active sites for the meso and racemo propagations in Figure 19 for the following reason: The dual-conformation radicals were observed not only for the oligomer or polymer radicals but also for the adduct radicals or one of the dimer radicals that has no asymmetric center at the γ-position, i.e., the radicals **1** and **7**.

This work also revealed other several characteristics of the methacrylate radicals. The coupling constants in the spectra due to the adduct, dimer, trimer, and polymer radicals are very similar but not identical. The temperature dependence of the constants varies with respect to the structure (or size) of the radicals, although we have no data for the polymer radicals at the present time. These results may suggest the non-negligible effects of the penultimate or more distant group on the conformation of the radicals. In the radical polymerization of MMA and menthyl methacrylate, the probability of the meso propagation is 0.21 and 0.34, respectively.[16] **1b**,**d** provided similar coupling constants and temperature dependence, but the difference in the enthalpies of conformation A to B for **1d** was larger than that for **1b**, as described in section 3. The β-CH_2 coupling in conformation B of the polymer radicals **8d**,**e** also differs from those of **8a**–**c**. These might be related to the variation in the tacticity in the polymerization of the methacrylates bearing a 2-alkylcyclohexyl ester.[16] However, further experiments and calculations are required for more detailed discussion of the relationship between the tacticity and the conformation of the radicals in the ground or transition state.

Conclusions

We examined the structure of methacrylate radicals with various molecular sizes from small molecules to polymers by reduction of bromides as radical precursors with hexabutylditin and by direct observation of the thermal polymerization of the methacrylates at high temperature using ESR spectroscopy. The structure of the methacrylate radicals was clarified based on the hyperfine splitting in the well-resolved ESR spectra. The adduct radicals (unimer radicals) provided binary-component spectra which are characterized by a_1(3H) = 23.4−23.6 G and a_2(1H) = 21.6−22.3 G, g = 2.0043−2.0044 for conformation A and a_1(3H) = 23.4−23.5 G and g = 2.0043−2.0044 for conformation B. In these spectra, a coupling to only one proton of β-CH$_2$ was observed for conformation A and no coupling was detected in conformation B despite the two methylene protons at the β-position. The α-nitrile radical and the dimer or trimer radicals as well as the polymer radicals also consisted of dual conformations similar to those of the adduct radicals. It has been clarified that such dual conformations and small or no coupling to the β-protons are observed only for a tertiary-carbon radical bearing large β-substituents but not for the secondary-carbon radicals and the unsubstituted tertiary radicals. The spectra are accounted for by the pyramidalization of the radical center and the *A*-strain-controlled conformation, which relieve the steric strain between the large β-substituent and CH$_3$ and/or CO$_2$R. These revised conformation models are different from any other models reported for the enolate radicals. The determination of the conformation of the propagating radicals would be significant for control of the stereoregularity of the polymers during radical polymerization. In this work, we have established the interpretation of the ESR spectra of methacrylate radicals and proposed a revised conformation model. Our findings may open a new route to a controlled propagation in methacrylate polymerization through radical mechanism, i.e., to full understanding of the transition state of propagation depicted in Figure 20.

Experimental Section

Synthetic Procedures of Precursors. Reaction with MMA. A mixture of MMA (4 mL, 37 mmol), bromotrichloromethane (30 mL, 300 mmol), and AIBN (1.5 g, 9.1 mmol) was flushed with argon and heated at 90 °C for 6 h.[15] The reaction mixture was concentrated *in vacuo*. Flash chromatography (pentane/CH$_2$Cl$_2$/*tert*-butyl methyl ether = 40/4/1−20/4/1) gave the following products.

Methyl 2-bromo-2-methyl-4,4,4-trichlorobutanoate (1aBr): colorless oil; yield 1.72 g (15% based on MMA); R_f 0.90 (pentane/CH$_2$Cl$_2$/ether = 20/4/1); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.23 (d, J = 15.3 Hz, 1H, CH$_2$), 3.83 (s, 3H, OCH$_3$), 3.57 (d, J = 15.3 Hz, 1H, CH$_2$), 2.21 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 170.48 (C=O), 95.04 (CCl$_3$), 62.69 (CH$_2$), 55.29 (CBr), 53.44 (OCH$_3$), 26.53 (CH$_3$); MS (EI, 70 eV) m/z 263 (30), 239 (8), 181 (62), 153 (100), 141 (40), 123 (71), 97 (42), 87 (40), 69 (24), 59 (86), 51 (46), 41 (50); MS (CI, NH$_3$) m/z 316 (M$^+$ + 17, 46), 263 (13), 181 (26), 153 (36), 134 (6), 118 (9), 102 (5), 52 (100), 44 (9). Anal. Calcd for C$_6$H$_8$O$_2$BrCl$_3$: C, 24.15; H, 2.70. Found: C, 24.25; H, 2.69.

Methyl *(2SR,4RS)*-2-bromo-4-carbomethoxy-2,4-dimethyl-6,6,6-trichlorohexanoate (5aBr-I): prism, mp 59.6−60.3 °C (pentane) (lit. mp 58−59.5 °C);[15c] yield 1.06 g (7%); R_f 0.65 (pentane/CH$_2$Cl$_2$/ether = 20/4/1); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.80 (s, 3H, OCH$_3$), 3.71 (s, 3H, OCH$_3$), 3.54 (d, J = 15.3 Hz, 1H, CH$_2$), 2.897 (d, J = 15.3 Hz, 1H, CH$_2$), 2.890 (d, J = 14.3 Hz, 1H, CH$_2$), 2.79 (d, J = 14.3 Hz, 1H, CH$_2$), 1.88 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 175.18 (C=O), 171.56 (C=O), 96.13 (CCl$_3$), 62.92 (CH$_2$), 57.89 (CBr), 53.20 (OCH$_3$), 52.51 (OCH$_3$), 51.71 (CH$_2$), 47.40 (C$_q$), 26.20 (CH$_3$), 18.02 (CH$_3$); MS (EI, 70 eV) m/z 317 (11), 285 (13), 257 (7), 221 (20), 181 (10), 153 (12), 127 (9), 115 (7), 101 (46), 87 (6), 69 (47), 59 (48), 51 (9), 41 (100); MS (CI, NH$_3$) m/z 416 (M$^+$ + 17, 100), 336 (5), 319 (17), 204 (5). Anal. Calcd for C$_{11}$H$_{16}$O$_4$BrCl$_3$: C, 33.15; H, 4.05. Found: C, 33.18; H, 4.02.

Methyl *(2SR,4SR)*-2-bromo-4-carbomethoxy-2,4-dimethyl-6,6,6-trichlorohexanoate (5aBr-II): needles, mp 79.1−79.8 °C (pentane) (lit. mp 79−80 °C);[15c] yield 0.33 g (2%); R_f 0.50 (pentane/CH$_2$Cl$_2$/ether = 20/4/1); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.80 (s, 3H, OCH$_3$), 3.69 (s, 3H, OCH$_3$), 3.57 (d, J = 15.3 Hz, 1H, CH$_2$), 2.95 (d, J = 15.3 Hz, 1H, CH$_2$), 2.85 (d, J = 14.9 Hz, 1H, CH$_2$), 2.50 (d, J = 14.9 Hz, 1H, CH$_2$), 1.99 (s, 3H, CH$_3$), 1.57 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 174.72 (C=O), 171.38 (C=O), 96.34 (CCl$_3$), 61.95 (CH$_2$), 58.43 (CBr), 53.39 (OCH$_3$), 52.49 (OCH$_3$), 51.43 (CH$_2$), 47.28 (C$_q$), 29.96 (CH$_3$), 19.44 (CH$_3$); MS (EI, 70 eV) m/z 339 (5), 317 (20), 285 (19), 257 (13), 221 (30), 181 (13), 153 (16), 141 (6), 127 (13), 115 (15), 101 (47), 87 (8), 69 (56), 59 (57), 51 (11), 41 (100); MS (CI, NH$_3$) m/z 416 (M$^+$ + 17, 100), 336 (5), 317 (42), 204 (6). Anal. Calcd for C$_{11}$H$_{16}$O$_4$BrCl$_3$: C, 33.15; H, 4.05. Found: C, 33.11; H, 3.94.

Methyl *(2SR,4SR,6SR)*-2-bromo-4,6-dicarbomethoxy-8,8,8-trichloro-2,4,6-trimethyloctanoate (6Br): prism, mp 111.0−112.2 °C (methanol) (lit. mp 111−112 °C);[15c] yield 1.14 g (6%); R_f 0.30 (pentane/CH$_2$Cl$_2$/ether = 20/4/1); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.77 (s, 3H, OCH$_3$), 3.694 (s, 3H, OCH$_3$), 3.686 (s, 3H, OCH$_3$), 3.44 (d, J = 15.3 Hz, 1H, CH$_2$), 2.795 (d, J = 15.3 Hz, 1H, CH$_2$), 2.793 (d, J = 14.2 Hz, 1H, CH$_2$), 2.70 (d, J = 14.2 Hz, 1H, CH$_2$), 2.12 (d, J = 14.2 Hz, 1H, CH$_2$), 2.04 (d, J = 14.2 Hz, 1H, CH$_2$), 1.83 (s, 3H, CH$_3$), 1.35 (s, 3H, CH$_3$), 0.94 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 176.89 (C=O), 175.82 (C=O), 171.73 (C=O), 96.30 (CCl$_3$), 63.66 (CH$_2$), 58.32 (CBr), 53.28 (OCH$_3$), 53.12 (OCH$_3$), 52.38 (OCH$_3$), 52.20 (CH$_2$), 51.87 (CH$_2$), 46.36 (C$_q$), 45.75 (C$_q$), 26.03 (CH$_3$), 17.58 (CH$_3$), 16.88 (CH$_3$); MS (EI, 70 eV) m/z 439 (11), 417 (5), 385 (11), 317 (6), 297 (11), 279 (8), 265 (5), 247 (10), 218 (12), 201 (6), 181 (12), 153 (13), 141 (15), 127 (20), 101 (84), 94 (10), 81 (11), 69 (75), 59 (56), 51 (6), 41 (100); MS (CI, NH$_3$) m/z 516 (M$^+$ + 17, 64), 467 (8), 420 (100). Anal. Calcd for C$_{16}$H$_{24}$O$_6$BrCl$_3$: C, 38.54; H, 4.85. Found: C, 38.43; H, 4.78.

Reaction with MMA-*d*$_3$. Methyl-*d*$_3$ methacrylate (1.19 g, 11.5 mmol), bromotrichloromethane (15 mL, 150 mmol), and AIBN (0.40 g, 2.4 mmol) provided the following products in a procedure similar to reaction with MMA.

Methyl-*d*$_3$ 2-bromo-2-methyl-4,4,4-trichlorobutanoate (1bBr): colorless oil; yield 0.91 g (26%); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.24 (d, J = 15.3 Hz, 1H, CH$_2$), 3.57 (d, J = 15.3 Hz, 1H, CH$_2$), 2.22 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 170.31 (C=O), 94.98 (CCl$_3$), 62.57 (CH$_2$), 55.21 (CBr), 52.62 (CD$_3$), 26.47 (CH$_3$); MS (EI, 70 eV) m/z 266 (16), 184 (47), 156 (99), 143 (38), 123 (64), 97 (31), 87 (38), 69 (26), 62 (100), 51 (49), 41 (58); MS (CI, NH$_3$), m/z 319 (M$^+$ + 17, 57), 266 (22), 184 (64), 156 (100), 137 (11), 121 (9), 69 (9), 52 (38). Anal. Calcd for C$_6$H$_5$D$_3$O$_2$BrCl$_3$: C, 23.91; O, 10.62. Found: C, 23.95; O, 10.73.

Methyl-*d*$_3$ *(2SR,4RS)*-2-bromo-4-carbomethoxy-*d*$_3$-2,4-dimethyl-6,6,6-trichlorohexanoate (5bBr-I): mp 59.1−60.5 °C (pentane); yield 0.38 g (8%); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.54 (d, J = 15.3 Hz, 1H, CH$_2$), 2.896 (d, J = 15.3 Hz, 1H, CH$_2$), 2.889 (d, J = 14.2 Hz, 1H, CH$_2$), 2.79 (d, J = 14.2 Hz, 1H, CH$_2$), 1.88 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 175.17 (C=O), 171.54 (C=O), 96.13 (CCl$_3$), 62.91 (CH$_2$), 57.91 (CBr), 52.45 (CD$_3$), 51.7 (CD$_3$), 51.70 (CH$_2$), 47.38 (C$_q$), 26.21 (CH$_3$), 18.04 (CH$_3$); MS (EI, 70 eV) m/z 323 (9), 288 (11), 260 (7), 224 (19), 184 (8), 156 (13), 121 (9), 104 (40), 87 (7), 62 (53), 51 (11), 41 (100); MS (CI, NH$_3$) m/z 422 (M$^+$ + 17, 100), 405 (35), 387 (6), 370 (41), 323 (65), 290 (7), 224 (8), 121 (6), 69 (20). Anal. Calcd for C$_{11}$H$_{10}$D$_6$O$_4$BrCl$_3$: C, 32.66; O, 15.82. Found: C, 33.00; O, 15.82.

Methyl-d_3 *(2SR,4SR)*-2-bromo-4-carbomethoxy-d_3-2,4-dimethyl-6,6,6-trichlorohexanoate (5bBr-II): mp 77.9−79.7 °C (pentane); yield 0.14 g (3%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.57 (d, J = 15.3 Hz, 1H, CH_2), 2.95 (d, J = 15.3 Hz, 1H, CH_2), 2.84 (d, J = 14.9 Hz, 1H, CH_2), 2.50 (d, J = 14.9 Hz, 1H, CH_2), 1.99 (s, 3H, CH_3), 1.57 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 174.74 (C═O), 171.41 (C═O), 96.36 (CCl_3), 61.95 (CH_2), 58.44 (CBr), 52.64 (CD_3), 51.74 (CD_3), 51.44 (CH_2), 47.29 (C_q), 29.95 (CH_3), 19.46 (CH_3); MS (EI, 70 eV) m/z 323 (10), 288 (10), 260 (8), 224 (20), 189 (8), 156 (13), 121 (11), 104 (27), 96 (6), 87 (7), 62 (56), 51 (12), 41 (100); MS (CI, NH_3) m/z 422 ($M^+ + 17$, 77), 405 (18), 387 (10), 370 (30), 323 (100), 307 (6), 290 (6), 224 (5), 193 (9), 121 (12), 69 (27). Anal. Calcd for $C_{11}H_{10}D_6O_4BrCl_3$: C, 32.66; O, 15.82. Found: C, 33.16; O, 15.62.

Synthesis of Other Precursors. Adamantyl 2-Bromo-2-methyl-4,4,4-trichlorobutanoate (1cBr). Adamantyl methacrylate (2.75 g, 12.5 mmol) and bromotrichloromethane (30 mL, 300 mmol) were heated at 90 °C for 6 h in the presence of AIBN (1.0 g, 6.1 mmol). Flash chromatography (pentane/ether = 40/1) provided the adduct: plate, mp 69.9−71.8 °C (methanol); yield 1.90 g (36%); R_f 0.65; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.22 (d, J = 15.2 Hz, 1H, CH_2CCl_3), 3.53 (d, J = 15.2 Hz, 1H, CH_2CCl_3), 2.20 (br, 3H, CH), 2.16 (br, 9H, CH_3, CH_2 (adamantyl)), 1.68 (br, 6H, CH_2 (adamantyl)); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 168.16 (C═O), 95.34 (CCl_3), 82.91 (OC_q), 62.54 (CH_2), 57.49 (CBr), 40.58 (CH_2), 36.03 (CH_2 (adamantyl)), 30.78 (CH (adamantyl)), 26.18 (CH_3). Anal. Calcd for $C_{15}H_{20}O_2BrCl_3$: C, 43.04; H, 4.82. Found: C, 43.08; H, 4.79.

***(1R,2S,5R)*-(−)-Menthyl *(2SR)*-2-Bromo-2-methyl-4,4,4-trichlorobutanoate (1dBr).** The reaction of menthyl methacrylate (2.20 g, 10 mmol) with bromotrichloromethane (30 mL, 300 mmol) in the presence of AIBN (1.0 g, 6.1 mmol) followed by flash chromatography (pentane/ether = 40/1) provided the adduct as a mixture of diastereomers: colorless oil; yield 1.88 g (45%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.75 and 4.71 (dt, J = 12.3, 4.3 Hz, 1H, OCH), 4.30 and 4.28 (d, J = 15.3 Hz, 1H, CH_2CCl_3), 3.57 (d, J = 15.3 Hz, 1H, CH_2CCl_3), 2.215 and 2.209 (s, 3H, $CBrCH_3$), 2.01−2.14 (m, 2H), 1.69−1.73 (m, 2H), 1.44−1.56 (m, 2H), 0.83−1.99 (m, 10H), 0.751 and 0.740 (d, J = 7.0 Hz, 3H, $CHCH_3$); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 169.28 and 169.12 (C═O), 95.14 (CCl_3), 76.81 (OCH), 62.37 and 62.30 (CH_2CCl_3), 56.27 and 56.18 (CBr), 46.99 and 46.87, 39.64 and 39.34, 34.04, 31.28 and 31.19, 26.17 and 26.02 ($CBrCH_3$), 25.67 and 25.67, 22.98 and 22.94, 21.95 and 20.75, 15.88 and 15.74. Anal. Calcd for $C_{15}H_{24}O_2BrCl_3$: C, 42.63; H, 5.72. Found: C, 42.65; H, 5.55.

2-Bromo-2-methyl-4,4,4-trichlorobutanenitrile (9Br). Methacrylonitrile (4.0 mL, 48 mmol), bromotrichloromethane (20 mL, 200 mmol), and AIBN (1.0 g, 6.1 mmol) provided the adduct at 90 °C for 4 h followed by flash chromatography (pentane/CH_2Cl_2/ether = 40/5/1): pale yellow solid; yield 0.37 g (3%); R_f 0.70 (pentane/CH_2Cl_2/ether = 20/10/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.79 (d, J = 15.6 Hz, 1H, CH_2), 3.55 (d, J = 15.6 Hz, 1H, CH_2), 2.37 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 118.95 (CN), 93.71 (CCl_3), 63.62 (CH_2), 38.15 (CBr), 31.14 (CH_3). Anal. Calcd for $C_5H_5NBrCl_3$: C, 22.63; H, 1.90; N, 5.28. Found: C, 22.59; H, 1.95; N, 5.25.

Methyl 2-Bromo-4,4,4-trichlorobutanoate (2Br). Methyl acrylate (2.0 mL, 22 mmol) was reacted with bromotrichloromethane (30 mL, 300 mmol) in the presence of AIBN (1.0 g, 6.1 mmol) at 90 °C for 2 h. Distillation (oven temperature 150 °C/0.2 mbar) followed by flash chromatography (pentane/ether = 20/1) provided the product: colorless oil; yield 2.38 g (38%); R_f 0.60; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.58 (dd, J = 9.5, 2.7 Hz, 1H, CH), 3.88 (dd, J = 15.1, 9.5 Hz, 1H, CH_2), 3.83 (s, 3H, CH_3), 3.31 (dd, J = 15.1, 2.7 Hz, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 169.09 (C═O), 95.95 (CCl_3), 58.37 (CH_3), 53.42 (CH), 37.59 (CH_2). Anal. Calcd for $C_5H_6O_2BrCl_3$: C, 21.12; H, 2.13. Found: C, 21.17; H, 2.10.

Adamantyl 2-Bromo-2-methylpropionate (3bBr). 1-Adamantanol (1.52 g, 10 mmol) was reacted with nBuLi (2 M in pentane, 5 mL), in THF at 0 °C. The reaction mixture was further stirred at room temperature for 15 min, and then it was cooled to 0 °C. α-Bromoisobutyryl bromide (1.24 mL, 20 mmol) in 40 mL of THF was added dropwise at 0 °C and stirred overnight. THF was replaced with ether, and the mixture was washed with brine and then dried on Na_2SO_4. The residual solid was purified by flash chromatography (pentane/ether = 40/1) followed by recrystallization: plate, mp 50.8−51.3 °C (methanol); yield 2.21 g (73%); R_f 0.50; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.19 (br, 3H, CH), 2.15 (br, 6H, CH_2), 1.88 (s, 6H, CH_3), 1.68 (br, 6H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 170.17 (C═O), 81.83 (OC_q), 57.62 (CBr), 40.77 (CH_2), 36.08 (CH_2), 30.79 (CH), 26.18 (CH_3). Anal. Calcd for $C_{15}H_{20}O_2BrCl_3$: C, 43.04; H, 4.82. Found: C, 43.08; H, 4.79.

Dimethyl 2-Bromo-2,4,4-trimethylpentanedioate (7Br). To LDA (50 mmol) in dry THF (50 mL) was added methyl isobutyrate (5.7 mL, 50 mmol) at −78 °C. The reaction mixture was stirred for 10 min, and then MMA (5.3 mL, 50 mmol) in THF (20 mL) was added dropwise at −78 °C over 40 min. After further stirring for 20 min, Br_2 (5.2 mL, 100 mmol) in THF (20 mL) was added at −78 °C, and the mixture was allowed to warm to room temperature. After the solvent was removed *in vacuo* and replaced with CH_2Cl_2, the mixture was washed with $Na_2S_2O_3$ and brine, dried on Na_2SO_4, and concentrated. Flash chromatography (pentane/ether = 10/1) followed by recrystallization gave colorless prisms: mp 54.0−55.0 °C (pentane) (lit. mp 53.1−54.8 °C);[21] yield 0.24 g (2%); R_f 0.45. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.78 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.80 (d, J = 14.6 Hz, 1H, CH_2), 2.74 (d, J = 14.6 Hz, 1H, CH_2), 1.85 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.08 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 177.36 (C═O), 171.81 (C═O), 58.86 (CBr), 52.98 (OCH_3), 51.94 (OCH_3), 50.80 (CH_2), 42.55 (C_q), 28.20 (CH_3), 27.03 (CH_3), 22.99 (CH_3). Anal. Calcd for $C_{10}H_{17}O_4Br$: C, 42.72; H, 6.09. Found: C, 42.83; H, 6.06.

Methyl *(2SR,3RS)*-2-Bromo-3-methyl-4,4,4-trichlorobutanoate and Methyl *(2SR,3SR)*-2-Bromo-3-methyl-4,4,4-trichlorobutanoate (10aBr). A mixture of methyl crotonate (2.0 g, 20 mmol), bromotrichloromethane (5 mL, 50 mmol), and AIBN (0.82 g, 5 mmol) was heated at 90 °C for 4 h. The reaction mixture was concentrated *in vacuo*. Flash chromatography (pentane/ether = 20/1) provided a colorless oil as a mixture of diastereomers: bp 88 °C (0.15 mbar); yield 3.06 g (51%); R_f 0.80−0.85; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.97 (d, J = 4.0 Hz, 1H, CHBr), 3.82 (s, 3H, OCH_3), 3.30 (qd, J = 6.6, 4.6 Hz, 1H, $CHCH_3$), 1.61 (d, J = 6.6 Hz, 3H, CH_3) for the major diastereomer (70%); ^{1}H NMR δ 5.06 (d, J = 3.1 Hz, 1H, CHBr), 3.75 (s, 3H, OCH_3), 3.16 (qd, J = 6.9, 3.1 Hz, 1H, $CHCH_3$), 1.75 (d, J = 6.9 Hz, 3H, CH_3) for the minor diastereomer (30%); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 169.18 (C═O), 102.29 (CCl_3), 54.24 (CHBr), 53.45 (OCH_3), 46.49 ($CHCH_3$), 16.43 ($CHCH_3$) for the major diastereomer; ^{13}C NMR δ 167.94 (C═O), 101.28 (CCl_3), 59.92 (CHBr), 52.94 (OCH_3), 43.21 ($CHCH_3$), 12.58 ($CHCH_3$) for the minor diastereomer. Anal. Calcd for $C_6H_8O_2BrCl_3$: C, 24.15; H, 2.70. Found: C, 24.20; H, 2.63.

Methyl-d_3 *(2SR,3RS)*-2-Bromo-3-methyl-4,4,4-trichlorobutanoate and Methyl *(2SR,3SR)*-2-Bromo-3-methyl-4,4,4-trichlorobutanoate (10bBr). A toluene solution of AIBN (0.82 g, 5 mmol in 10 mL) was injected into a mixture of methyl-d_3 crotonate (2.07 g, 20 mmol) and bromotrichloromethane (10 mL, 100 mmol) at 100 °C over 20 h by a syringe pump. The yellow oil obtained by distillation was flash chromatographed (pentane/ether = 40/1): colorless oil; yield 0.65 g (11%); R_f 0.55−0.60; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.97 (d, J = 3.9 Hz, 1H, CHBr), 3.30 (qd, J = 6.6, 3.9 Hz, 1H, $CHCH_3$), 1.61 (d, J = 6.6 Hz, 3H, CH_3) for the major diastereomer (65%); ^{1}H NMR δ 5.06 (d, J = 3.0 Hz, 1H, CHBr), 3.16 (qd, J = 6.8, 3.0 Hz, 1H, $CHCH_3$), 1.75 (d, J = 6.8 Hz, 3H, CH_3) for the minor diastereomer (35%); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 169.20 (C═O), 102.27 (CCl_3), 54.20 (CHBr), 52.69 (CD_3), 46.47 ($CHCH_3$), 16.40 (CH_3) for the major diastereomer. Anal. Calcd for $C_6H_5D_3O_2BrCl_3$: C, 23.91; O, 10.62. Found: C, 23.96; O, 10.70.

Benzyl (2*SR*,3*SR*)-2-Bromo-2,3-dimethyl-4,4,4-trichlorobutanoate (11Br). To a mixture of benzyl tiglate (1.90 g, 10 mmol) and bromotrichloromethane (10 mL, 100 mmol) was injected a toluene solution (15 mL) of AIBN (0.82 g, 5 mmol) at 100 °C over 24 h by a syringe pump. Flash chromatography (pentane/CH_2Cl_2 = 1/1) provided a major diastereomer: colorless oil; yield 1.92 g (49%); R_f 0.85; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31−7.41 (m, 5H, Ph), 5.29 (d, J = 12.3 Hz, 1H, CH_2), 5.17 (d, J = 12.3 Hz, 1H, CH_2), 4.03 (q, J = 6.7 Hz, 1H, CH), 2.08 (s, 3H, $CBrCH_3$), 1.78 (d, J = 6.7 Hz, 3H, $CHCH_3$); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 170.63 (C═O), 134.72, 128.47, 128.39, 128.33 (Ph), 100.19 (CCl_3), 68.03 (CH_2), 62.94 (CBr), 57.92 (CCH_3), 22.39 ($CBrCH_3$), 17.27 ($CHCH_3$). Anal. Calcd for $C_{13}H_{14}O_2BrCl_3$: C, 40.19; H, 3.63. Found: C, 39.84; H, 3.57.

Methyl (2*SR*,3*RS*)-2-Bromo-3-(methoxycarbonyl)-4,4,4-trichlorobutanoate (12aBr).[20] Dimethyl maleate (2.88 g, 20 mmol), bromotrichloromethane (5 mL, 50 mmol), and AIBN (0.82 g, 5 mmol) were heated at 90 °C for 4 h. Flash chromatography (pentane/ether = 20/1) followed by recrystallization provided the erythro compound as a major diastereomer: needles, mp 52.5−54.0 °C (pentane) (lit. mp 55−56 °C);[20] yield 1.87 g (27%); R_f 0.80 for major diastereomer and 0.65 for the minor diastereomer; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.83 (d, J = 9.5 Hz, 1H, CH), 4.50 (d, J = 9.5 Hz, 1H, CH), 3.851 (s, 3H, CH_3), 3.833 (s, 3H, CH_3) for the major diastereomer; ^{1}H NMR δ 4.92 (d, J = 6.7 Hz, 1H, CH), 4.20 (d, J = 6.7 Hz, 1H, CH), 3.82 (s, 3H, CH_3), 3.79 (s, 3H, CH_3) for the minor diastereomer. Anal. Calcd for $C_7H_8O_4BrCl_3$: C, 24.55; H, 2.36. Found: C, 24.61; H, 2.36 for the major diastereomer.

Adamantyl (2*SR*,3*RS*)-3-[(Adamantyloxy)carbonyl]-2-bromo-4,4,4-trichlorobutanoate (12bBr). Diadamantyl maleate (5.05 g, 13.1 mmol), bromotrichloromethane (6.4 mL, 65 mmol), and AIBN (1.09 g, 6.6 mmol) were heated at 90 °C for 6 h. The erythro compound was isolated as a major diastereomer by flash chromatography (hexane/$CHCl_3$ = 2/1): needles, mp 162.5−163.0 °C (haxane); yield 3.58 g (47%); R_f 0.30; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.65 (d, J = 9.8 Hz, 1H, CH), 4.25 (d, J = 9.8 Hz, 1H, CH), 2.19 (br, 6H, CH), 2.14 (br, 12H, CH_2), 1.67 (br, 12H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.10 (C═O), 163.66 (C═O), 95.23 (CCl_3), 84.32 (OC_q), 83.65 (OC_q), 67.26 (CBr), 43.61 (Cl_3CC), 41.06 (CH_2), 40.75 (CH_2), 36.05 (CH_2), 36.00 (CH_2), 30.86 (CH).

Other Materials. Commercial ethyl 2-bromoisobutyrate (**3aBr**) and ethyl 2-bromopropionate (**4Br**) were used after distillation. Hexabutylditin, di-*tert*-butyl peroxide, and 2,2′-azobis(2,4,4-trimethylpentane) were used as received without further purification. Solvents and bromotrichloromethane were distilled before use.

ESR Measurements. ESR spectra were recorded on a Bruker ESP-300 spectrometer equipped with an X-band microwave unit and 100-kHz field modulation.

(a) Reduction of the Bromides. Radicals were generated in Suprasil quartz tubes (o.d. 4.0 or 5.0 mm) by UV irradiation of the filtered light on the solutions, which were prepared by dissolving the bromide (70−120 mg), hexabutylditin (0.1 mL), and di-*tert*-butyl peroxide (0.03 mL) in toluene (0.7 mL) followed by purging with dry argon for ca. 20 min. The filtered UV light (water-cooled Schott Filter UG-5) was generated using a Hanovia 977-B1 1-kW He−Xe high-pressure lamp.[57]

(b) Thermal Polymerization. Alkyl methacrylates (1 M), and 2,2′-azobis(2,4,4-trimethylpentane) (0.5 M) in toluene or *p*-xylene were charged in an ESR tube and sealed *in vacuo* after removing oxygen by the freeze−thaw method.

The *g*-value was determined using an NMR field meter (Echo Electronics, Co., Ltd.) and a microwave counter (Advantest, R5372) with an accuracy of ±0.0001. The values of $6.626\,075\,5 \times 10^{-27}$ erg/s and $-9.274\,015\,4 \times 10^{-21}$ erg/G as the Plank's constant and the Bohr magniton were used for the calculation, respectively. The coupling constants were determined with an accuracy of ±0.05 G, at least for the spectra with a narrow line width.

Typical measurement parameters are as follows: (a) microwave power, 2.0 mW; sweep width, 80−160 G; modulation amplitude, 0.5 G; conversion time, 82 ms; time constant, 41 ms; 2−10 scans for small molecule and oligomer radicals; and (b) microwave power, 6.3 mW; sweep width, 180 G; modulation amplitude, 1.0 G; conversion time, 41 ms; time constant, 164 ms; 20−50 scans for polymer radicals.

Other Measurements. NMR spectra were recorded on a Varian Gemini 300 or a JEOL JMN-A400 spectrometer. Mass spectra were taken in the Mass Spectroscopy Laboratory of the University of Basel using a VG 70-250 spectrometer. Elemental analyses were performed in the Microanalysis Laboratory of the University of Basel. Gel permeation chromatography was performed with a Tosoh 8000 series system equipped with TSK-gel columns.

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