

Study on Telomerization of Methyl Methacrylate with Carbon Tetrabromide and Characteristics of the Resulting Adducts

Takao KIMURA,* Hiroshi EZURA,[†] and Motome HAMASHIMA^{††}

*Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University,
Ishii-machi, Utsunomiya 321, Japan*

(Received July 4, 1991)

ABSTRACT: Using carbon tetrabromide (CTB) as a telogen, the radical telomerization of methyl methacrylate (MMA) was carried out with varying temperature, molar ratio of CTB to MMA, and with or without benzene as solvent. The telomerization behavior of MMA, and structure and properties of the resulting adducts were compared with those in MMA–bromotrichloromethane (BTCM) system. The telomerization using CTB gave preferentially adducts with a lower average degree of telomerization (\bar{n}) than that using BTCM. A kind of linear monoadduct ($n=1$), two kinds of linear diadducts ($n=2$), two kinds of cyclic diadducts ($n=2$), and two kinds of linear triadducts ($n=3$) were isolated, and the structures of all adducts were determined by ¹H, ¹³C, and 2D NMR techniques. It was found that the linear diadducts from CTB show a lowering of the priority of syndiotacticity and higher extent of cyclization in comparison with the ones from BTCM.

KEY WORDS Telomerization / Methyl Methacrylate / Carbon Tetrabromide / Bromotrichloromethane / Linear Adduct / Cyclic Adduct / Nuclear Magnetic Resonance / Diastereoisomer / Tacticity / Lactonization /

The concept of telomerization has been known for a long time.^{1,2} In particular, halo- and sulfur-compounds as telogens play an important part in the radical telomerization of methyl methacrylate (MMA). Since the resulting adducts are considered to be good model compounds of poly(methyl methacrylate) (PMMA) and precursors of reactive oligomers, the separation and NMR structural analysis of adducts have become of interest in recent years. For example, Bessiere *et al.*^{3,4} studied the ¹H and ¹³C NMR spectra of telomers from monoadduct to tetraadducts prepared by radical telomerization of MMA with thiophenol (PhSH), and determined the structure and amount of each isomer. On the other hand, Ute *et al.*⁵ isolated the pure-isotactic and pure-syndiotactic MMA oligomers

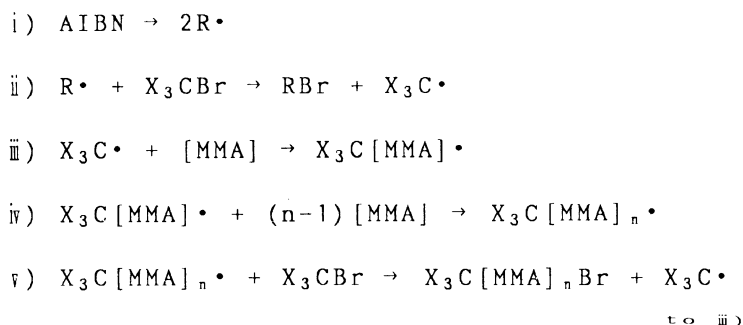
from dimers to octamers from stereoregular living polymerization systems of MMA, and investigated the ¹H and ¹³C NMR spectra of the pure diastereoisomers in detail.

Barson *et al.*^{6,7} investigated kinetically the telomerization of MMA with bromotrichloromethane (BTCM), and determined the transfer constants of individual telomeric radicals to BTCM from the analysis of products by gel permeation chromatography. However, the separation and properties of MMA telomers synthesized using BTCM as a telogen have been not reported. In a previous paper,⁸ we reported the separation and ¹H NMR structural analysis of mono- ($n=1$), di- ($n=2$), and triadducts ($n=3$), produced by a series of radical chain reactions as shown in Scheme 1. In particular, it was found that the

* To whom all correspondence should be addressed.

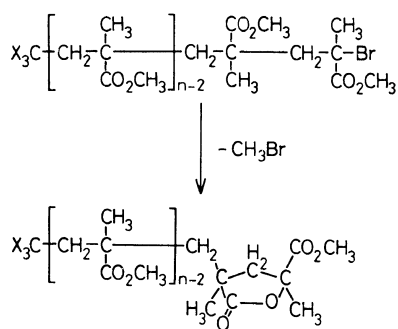
[†] Present address: *Tada Elementary School, Tamuma-machi, Aso-gun 327-03, Japan.*

^{††} Retired under an age clause.



(v) iii)

Scheme 1.



Scheme 2.

linear adducts ($n \geq 2$) are easily converted into cyclic ones ($n \geq 2$) by a S_N1 intramolecular cyclization as shown in Scheme 2.⁹ In the preceding paper,¹⁰ we reported the preparation of bifunctional lactone monomer, namely (2*R**,4*S**)-4-chloroformyl-2-chloroformylmethyl-2,4-dimethyl-4-butanolide by the chemical transformation of *t*-butyl methacrylate dimer telomerized using BTCM. The interfacial polycondensation of this acid dichloride with hexamethylenediamine was accompanied by a partial hydrolytic cleavage of the lactone ring, and gave an unique 6,6-type polyamide containing both lactone rings and hydrophilic groups such as carboxyl- and hydroxyl-groups.

The present paper deals with the telomerization of MMA with carbon tetrabromide (CTB) in the place of BTCM. The separation and properties of MMA telomers prepared using CTB as the telogen have not

been reported yet. The telomerization behavior of MMA in both systems is discussed, and ^1H and ^{13}C NMR data, and characteristics of the resulting adducts ($n=1-3$) are compared in detail.

EXPERIMENTAL

General Methods

All melting points were determined on Yamato MP-21 melting point apparatus and uncorrected. IR spectra were measured with a JASCO REPORT-100 spectrophotometer. ^1H NMR spectra were recorded on a Varian VXR-300 (300 MHz) spectrometer with chloroform-*d* as solvent and tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded on the same instrument (75 MHz) with chloroform-*d* as the solvent and internal standard ($\delta=76.9$). Mass spectra were taken on a Hitachi M-80 spectrometer by a chemical ionization method at 20 eV. All isotope peaks resulting from bromine and chlorine atoms were satisfactorily detected in the mass spectra. The isotope peaks corresponding only to ^{79}Br and ^{35}Cl are described in this paper. The carbon content values found by elemental analysis agreed with the calculated values with an error of $\pm 0.3\%$.

Materials

Commercial MMA and 2,2'-azobisisobutyronitrile (AIBN) were purified by ordinary

methods. Commercial benzene was dried over calcium hydride and distilled before use. Other reagents and solvents were commercially obtained and used without further purification.

Typical Procedure of Telomerization

A solution of CTB in benzene (100 ml) was placed in a three-necked round bottom flask equipped with a magnetic stirrer. MMA was added to the solution, and the mixture was heated at a desired temperature with stirring under a nitrogen atmosphere. AIBN was then added to the solution to initiate the reaction. After the reaction, the solvent and unconsumed monomer were distilled off *in vacuo* to afford a telomeric product containing unconsumed CTB.

Separation of Adducts

The resulting adducts ($n=1-3$) were separated by silica gel column chromatography (packing material, Wakogel C-300; first eluent, carbon tetrachloride; second one, benzene), and eluted in the following order: (unconsumed CTB), linear monoadduct (**1**), linear diadduct (**2a**), linear diadduct (**2b**), linear triadducts (**3a**) and (**3c**), cyclic diadducts (**2c**) and (**2d**), and higher adducts.

Cyclization of Linear Diadducts

The cyclization of linear diadducts was carried out according to the two methods described in the previous paper.⁹ The lactone yield was calculated from ¹H NMR data.

RESULTS AND DISCUSSION

Telomerization Behavior of Methyl Methacrylate with CTB

Though at first this telomerization was carried out at 90°C, with a molar ratio of [CTB]₀/[MMA]₀ equal to 1, conditions were not adequate to afford lower molecular weight adducts ($n < 3$) as shown in Table I. The corresponding adducts were preferentially formed at a molar ratio of 8.

Table I. Effects of CBr₄ concentration on the telomerization behavior of methyl methacrylate^a

[CBr ₄] ₀	$R_p' \times 10^4$	Adduct/wt%		
		$n=1$	$n=2^b$	$n \geq 3$
[MMA] ₀	mol l ⁻¹ s ⁻¹			
1	3.72	10	17 [88]	73
8	2.08	73	21 [95]	6

^a [MMA]₀, 1.13 × 10⁻¹ mol; [AIBN]₀, 3.21 × 10⁻³ mol; temp, 90°C; time, 4 h.

^b [], production ratio of cyclic diadducts in %.

Table II. Effects of temperature on the telomerization behavior of methyl methacrylate^a

Telogen	Temp ^b	$R_p' \times 10^4$	Adduct/wt%		
	°C		mol l ⁻¹ s ⁻¹	$n=1$	$n=2^c$
CBr ₄	50 ^d	0.17	38	36 [22]	26
	70 ^d	0.67	51	31 [36]	18
	90 ^d	1.26	65	25 [64]	10
	90	2.08	73	21 [95]	6
Cl ₃ CBr	50	0.08	6	13 [0]	81
	70	0.79	22	26 [8]	52
	90	1.47	29	30 [10]	41

^a [Telogen]₀/[MMA]₀ = 8; [AIBN]₀^{0.5}/[MMA]₀ = 0.5; total volume of telogen and MMA, 100 ml.

^b Time, 24 h (50°C); 8 h (70°C); 4 h (90°C).

^c [], production ratio of cyclic diadducts in %.

^d Carried out in the presence of benzene (100 ml).

Table II shows the results of the telomerization of MMA with CTB at temperatures from 50 to 90°C, at which the results were compared with those of the MMA-BTCM system discussed in the previous paper.⁹ The reactions at 50 and 70°C required a solvent for dissolving CTB, benzene, used in this study, to keep a homogeneous reaction solution, since CTB has a melting point of 93°C. From the results of the telomerization at 90°C with and without benzene, it was found that dilution with benzene caused a decrease in the apparent rate of telomerization (R_p') and a slight shift in the product distribution of adducts to a higher molecular weight region. However, lower molecular weight adducts ($n < 3$) were

obtained in about 90 wt% of the overall one regardless of the presence of benzene.

As shown in Table II, the temperature dependence of the telomerization of MMA with CTB on R_p' and the product distribution of adducts was analogous to that of MMA with BTCM. However, the MMA-CTB system resulted in further lowering of \bar{n} and the preferential formation of cyclic diadducts than linear ones with increasing temperature.

The apparent activation energy of the overall telomerization (E_a) was determined from the relationship between temperature and R_p' . E_a for this system was calculated as 49 kJ mol^{-1} , which is apparently low relative to $E_a = 72 \text{ kJ mol}^{-1}$ for MMA-BTCM system. This difference is associated with the degree of radical fission of telogen, and suggests that the tribromomethyl radical from CTB is formed with greater ease than the trichloromethyl radical from BTCM at the stage of elementary reactions ii) and v) shown in Scheme 1. Furthermore, the chain transfer constant of PMMA radical to CTB has been indicated as 2.7×10^{-1} at 60°C in benzene,¹¹ whereas that to BTCM was determined as 7.9×10^{-2} according to Mayo's plot.¹² These observations indicate that the chain transfer of the growing end radical is very feasible for CTB in comparison with BTCM, and are consistent with the results shown in Table II.

Characterization and Structural Analysis of Adducts

The characterization of the homologous adducts in both systems is summarized in Table III. The structures of the resulting adducts were confirmed by IR, MS, FT-NMR spectra, and elemental analysis data. The homologous adducts from CTB had higher boiling or melting points than the homologous ones from BTCM, except for **2b**.

An adduct having asymmetric carbon atoms equal to n is composed of $2^n/2$ diastereoisomers. Actually, two diastereoisomers, syndiotactic **2a** (r diad) and isotactic **2b** (m diad), were isolated

Table III. Characterization of adducts

Adduct	X	mp [bp]	ν (C=O)	m/z (M+H) ⁺
		$^\circ\text{C}$	cm^{-1}	
1	Br	[143— 144/2 mmHg] ^a	1750	429
	Cl	[111— 113/8 mmHg]	1750	297
2a	Br	80.5—82	1730	529
	Cl	58—59.5	1735	397
2b	Br	62.5—63.5	1730	529
	Cl	79—80	1730	397
2c	Br	124—125.5	1780, 1755	435
	Cl	73.5—75	1770, 1740	303
2d	Br	125.5—126.5	1775, 1760	435
	Cl	94—95.5	1765, 1735	303
3a	Br	121—122.5	1730	629
	Cl	111—112	1735	497
3c	Br	136—137.5	1730	629

^a mp, 38—39.5°C.

as linear diadducts and two diastereoisomers, *cis* **2c** and *trans* **2d**, as cyclic ones. ¹H NMR spectroscopy is an effective method for the identification of diastereoisomers. For example, the magnetic environment about the geminal methylene protons (d) is obviously different for **2a** and **2b**. Therefore, the corresponding signals should show significant differences with each other. That is, the chemical shift ($\Delta\delta$) between the geminal methylene protons (d) will be larger for isotactic **2b** than for syndiotactic **2a** owing to increasing nonequivalency.

On the other hand, four possible diastereoisomers, syndiotactic **3a** (*rr* triad), heterotactic **3b** (*rm* triad), heterotactic **3c** (*mr* triad), and isotactic **3d** (*mm* triad), can be formed as linear triadducts. The magnetic environment about the methyl protons (a) of **3a** and **3b** is analogous to that about the methyl protons (a) of **2a**, whereas the magnetic

Table IV. ¹H NMR parameters of linear adducts^a

Adduct	Proton	Symbol	Chemical shift in CDCl ₃ δ/ppm	
			X = Br	X = Cl
1	-CH ₃	<i>a</i>	2.29 (s)	2.22 (s)
	-CH ₂ -	<i>b</i>	3.94 (d) 4.70 (d) {15.5} [0.76]	3.58 (d) 4.24 (d) {15.2} [0.66]
	-OCH ₃	<i>c</i>	3.85 (s)	3.83 (s)
2a	-CH ₃	<i>a, b</i>	1.42 (s), 1.90 (s)	1.35 (s), 1.89 (s)
	-CH ₂ -	<i>c</i>	3.28 (d) 4.04 (d) {15.5} [0.76]	2.90 (d) 3.54 (d) {15.2} [0.64]
	-CH ₂ -	<i>d</i>	2.77 (d) 2.91 (d) {14.3} [0.14]	2.79 (d) 2.89 (d) {14.4} [0.10]
	-OCH ₃	<i>e, f</i>	3.73 (s), 3.82 (s)	3.72 (s), 3.81 (s)
2b	-CH ₃	<i>a, b</i>	1.64 (s), 2.02 (s)	1.57 (s), 2.00 (s)
	-CH ₂ -	<i>c</i>	3.33 (d) 4.09 (d) {15.6} [0.76]	2.95 (d) 3.58 (d) {15.2} [0.63]
	-CH ₂ -	<i>d</i>	2.50 (d) 2.84 (d) {14.8} [0.34]	2.50 (d) 2.85 (d) {14.9} [0.35]
	-OCH ₃	<i>e, f</i>	3.71 (s), 3.81 (s)	3.70 (s), 3.80 (s)
3a	-CH ₃	<i>a, b, c</i>	1.42 (s), 0.95 (s), 1.83 (s)	1.35 (s), 0.95 (s), 1.83 (s)
	-CH ₂ -	<i>d</i>	3.18 (d) 3.95 (d) {15.5} [0.77]	2.80 (d) 3.44 (d) {15.2} [0.64]
	-CH ₂ -	<i>e</i>	2.01 (d) 2.14 (d) {14.1} [0.13]	2.04 (d) 2.12 (d) {14.2} [0.08]
	-CH ₂ -	<i>f</i>	2.71 (d) 2.79 (d) {14.2} [0.08]	2.70 (d) 2.79 (d) {14.2} [0.09]
	-OCH ₃	<i>g, h, i</i>	3.71 (s), 3.70 (s), 3.78 (s)	3.70 (s), 3.69 (s), 3.78 (s)
3c	-CH ₃	<i>a, b, c</i>	1.59 (s), 1.11 (s), 1.81 (s)	
	-CH ₂ -	<i>d</i>	3.20 (d) 4.10 (d) {15.6} [0.90]	
	-CH ₂ -	<i>e</i>	1.69 (d) 2.16 (d) {14.4} [0.47]	
	-CH ₂ -	<i>f</i>	2.77 (d) 2.85 (d) {14.2} [0.08]	
	-OCH ₃	<i>g, h, i</i>	3.71 (s), 3.71 (s), 3.79 (s)	

^a { }, coupling const. *J* in Hz; [], differences in chemical shifts Δδ in ppm.

neighboring methylene protons (c) and (d), respectively, whereas the quaternary carbon (h) connectivity to the methyl protons (b) and only the methylene protons (d). Furthermore, the carbonyl carbon (i) showed ³J_{CH} connectivity to the methyl protons (a), the methylene protons (d), and the methoxy protons (e), respectively, whereas the carbonyl carbon (j) connectivity to the methyl protons (b), the

methylene protons (d), and the methoxy protons (f). Though we have already presented the ¹H NMR spectra (60 MHz, in CCl₄) of the homologues from BTCM in the previous paper,⁸ these 2D-NMR data prove that assignments on the methyl- and methoxy-proton signals of linear adducts (*n* = 2, 3) and cyclic diadducts should be corrected.

In general, ¹H and ¹³C NMR data of the

Table V. ¹H NMR parameters of cyclic adducts^a

Adduct	Proton	Symbol	Chemical shift in CDCl ₃ δ/ppm	
			X = Br	X = Cl
2c	-CH ₃	<i>a</i>	1.32 (s)	1.34 (s)
	-CH ₃	<i>b</i>	1.74 (s)	1.71 (s)
	-CH ₂ -	<i>c</i>	3.47 (d) 3.93 (d) {15.9} [0.46]	3.15 (d) 3.38 (d) {15.6} [0.23]
	-CH ₂ -	<i>d</i>	2.78 (d) 3.06 (d) {13.9} [0.28]	2.76 (d) 2.88 (d) {13.9} [0.12]
	-OCH ₃	<i>f</i>	3.83 (s)	3.83 (s)
	2d	-CH ₃	<i>a</i>	1.60 (s)
-CH ₃		<i>b</i>	1.74 (s)	1.73 (s)
-CH ₂ -		<i>c</i>	3.58 (d) 3.77 (d) {15.9} [0.19]	3.21 (d) 3.27 (d) {15.6} [0.06]
-CH ₂ -		<i>d</i>	2.22 (d) 3.51 (d) {14.4} [1.29]	2.18 (d) 3.36 (d) {14.4} [1.18]
-OCH ₃ -		<i>f</i>	3.81 (s)	3.81 (s)

^a { }, coupling const. *J* in Hz; [], differences in chemical shifts Δδ in ppm.

homologues from CTB are analogous to those of homologues from BTCM, respectively, but differences between them are characterized by the nonequivalence of geminal methylene protons adjacent to a trihalomethyl group. That is, the corresponding proton signals of the homologues from CTB resonated in lower magnetic fields relative to those of the homologues from BTCM, without exception, and exhibited stronger geminal coupling patterns (doublet-doublet) due to magnetic nonequivalence. This orderly shift may be attributable to differences in the steric behavior of the two groups bonded to the methylene group. On the other hand, a regular shift into higher magnetic fields was observed on the carbon signal corresponding to a trihalomethyl group in the ¹³C NMR spectra (δ: Cl₃C-, av. 96.0 ppm; Br₃C-, av. 32.6 ppm), and this tendency would be interpreted by so-called heavy halogen effects.

Stereochemistry of Diadducts

As shown in Table VIII, the conversion of the linear diadducts into cyclic ones was induced by heating in the absence of solvent

and by the catalytic action of silica gel. This cyclization selectively proceeded according to the routes shown in Scheme 3. The validity of the estimated conformations of the two linear diadducts and configuration of the resulting two cyclic ones may be supported by the results deduced in the previous paper.^{8,9} As can be seen from Table VIII, individual linear diadducts from CTB showed a higher cyclization in comparison with those from BTCM under similar conditions. Furthermore, isotactic **2b** showed a higher yield than syndiotactic **2a** in both diadduct systems. This tendency would be due to differences in the conformations of two linear diadducts as shown in Scheme 3.

Table IX shows the ratios of two dimeric diastereoisomers obtained in the telomerization of MMA using CTB, in which the ratios are compared with those of MMA-BTCM system. The telomerization of MMA gave **2a** in preference to **2b** regardless of the kind of telogen. On the other hand, the formation of cyclic diadducts increased with increasing reaction temperature as shown in Table II, as opposed to that of linear diadducts. It is

Table VI. ¹³C NMR assignments of linear adducts

Adduct	Carbon	Symbol	Chemical shift in CDCl ₃ δ/ppm	
			X = Br	X = Cl
1	-CH ₃	<i>a</i>	26.0	26.4
	-CH ₂ -	<i>b</i>	65.8	62.6
	-OCH ₃	<i>c</i>	53.4	53.4
	>C<	<i>d</i>	57.4	55.2
	-CO-	<i>e</i>	170.5	170.5
	X ₃ C-	<i>f</i>	31.1	94.9
2a	-CH ₃	<i>a, b</i>	17.6, 26.2	17.9, 26.1
	-CH ₂ -	<i>c, d</i>	66.2, 51.9	62.8, 51.6
	-OCH ₃	<i>e, f</i>	52.5, 53.2	52.4, 53.1
	>C<	<i>g, h</i>	49.5, 57.8	47.3, 57.8
	-CO-	<i>i, j</i>	175.1, 171.5	175.1, 171.5
	X ₃ C-	<i>k</i>	32.3	96.0
2b	-CH ₃	<i>a, b</i>	18.9, 29.7	19.3, 29.9
	-CH ₂ -	<i>c, d</i>	65.1, 51.6	61.9, 51.3
	-OCH ₃	<i>e, f</i>	52.5, 53.3	52.4, 53.3
	>C<	<i>g, h</i>	49.3, 58.3	47.2, 58.3
	-CO-	<i>i, j</i>	174.6, 171.3	174.7, 171.3
	X ₃ C-	<i>k</i>	32.8	96.2
3a	-CH ₃	<i>a, b, c</i>	17.2, 16.8, 25.9	17.4, 16.7, 25.9
	-CH ₂ -	<i>d, e, f</i>	67.0, 52.1, 53.2	63.6, 51.8, 53.2
	-OCH ₃	<i>g, h, i</i>	52.4, 52.1, 53.0	52.3, 52.1, 53.0
	>C<	<i>j, k, l</i>	48.4, 45.6, 58.2	46.2, 45.6, 58.2
	-CO-	<i>m, n, o</i>	175.7, 176.8, 171.7	175.7, 176.8, 171.6
	X ₃ C-	<i>p</i>	32.6	96.2
3c	-CH ₃	<i>a, b, c</i>	19.3, 19.0, 25.8	
	-CH ₂ -	<i>d, e, f</i>	65.1, 52.4, 51.4	
	-OCH ₃	<i>g, h, i</i>	52.3, 52.1, 53.1	
	>C<	<i>j, k, l</i>	48.6, 45.9, 58.2	
	-CO-	<i>m, n, o</i>	174.9, 175.9, 171.8	
	X ₃ C-	<i>p</i>	33.4	

considered that the telomerization of MMA in both systems is accompanied by the conversion of **2a** into **2c**, while that of **2b** into **2d** through a S_Ni intramolecular cyclization as discussed in the previous paper.⁹ Therefore, it is necessary to take the formation of two cyclic diadducts **2c** and **2d** into account for a more exact estimation of tacticity. As shown in Table IX, the yield of (**2a** + **2c**) was of greater advantage than that of (**2b** + **2d**) in both systems, but the decrease in the production ratio of (**2a** + **2c**) to (**2b** + **2d**) was observed with increasing reaction

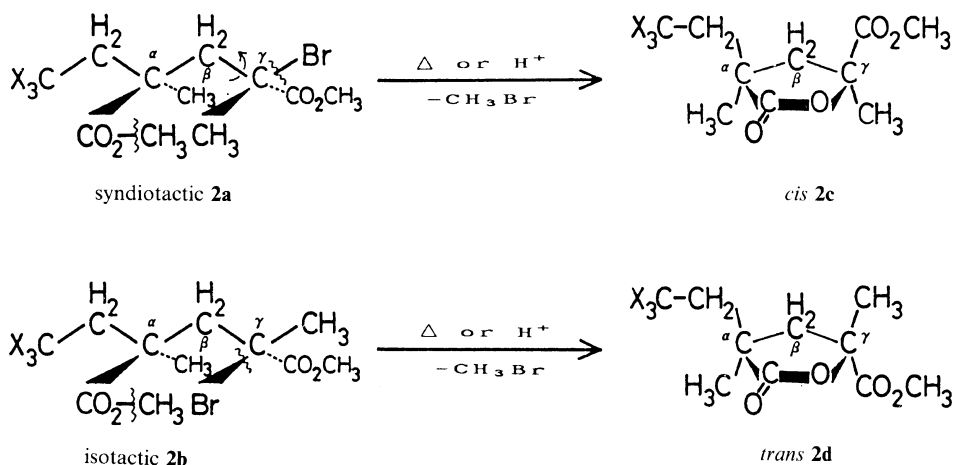
temperature. Consequently, the linear diadducts from CTB showed a lowering of the priority of syndiotacticity than the ones from BTCM.

CONCLUSIONS

MMA telomers (*n* = 1–3) were prepared by using CTB as the telogen, and the telomerization behavior of MMA and characterization of the resulting adducts were compared with those in MMA–BTCM system. The

Table VII. ^{13}C NMR assignments of cyclic adducts

Adduct	Carbon	Symbol	Chemical shift in CDCl_3 δ/ppm	
			X = Br	X = Cl
2c	$-\text{CH}_3$	<i>a, b</i>	25.0, 25.8	24.5, 25.8
	$-\text{CH}_2-$	<i>c, d</i>	63.0, 42.1	59.7, 43.2
	$-\text{OCH}_3$	<i>f</i>	53.0	53.0
	$>\text{C}<$	<i>g, h</i>	46.6, 81.4	44.6, 81.2
	$-\text{CO}-$	<i>i, j</i>	178.4, 173.0	178.3, 172.8
	$\text{X}_3\text{C}-$	<i>k</i>	33.1	96.2
2d	$-\text{CH}_3$	<i>a, b</i>	26.7, 25.7	26.5, 25.5
	$-\text{CH}_2-$	<i>c, d</i>	63.0, 42.0	59.4, 42.8
	$-\text{OCH}_3$	<i>f</i>	53.0	53.0
	$>\text{C}<$	<i>g, h</i>	46.9, 81.1	44.9, 81.0
	$-\text{CO}-$	<i>i, j</i>	178.7, 172.2	178.7, 172.2
	$\text{X}_3\text{C}-$	<i>k</i>	32.7	96.2



differences in both systems may be summarized as follows:

1) The telomerization of MMA using CTB gave preferentially the adducts with a lower degree of telomerization than that using BTCM.

2) The MMA-CTB system resulted in the preferential formation of cyclic diadducts than linear ones with increasing temperature.

3) E_a for this system was lower than that for MMA-BTCM system, while the chain transfer constant of PMMA radical to CTB was higher than that to BTCM.

Table VIII. Cyclization of linear diadducts

Type	Condition	Temp	Time	Conversion/%	
		$^{\circ}\text{C}$	h	X = Br	X = Cl
2a \rightarrow 2c	i)	100	2	89	46
	ii)	30	72	87	79
2b \rightarrow 2d	i)	100	0.5	53	41
			2	100	100
	ii)	30	4	43	40
			72	100	100

i), heated without solvent; ii), a solution of sample (0.3 g) in benzene (9 ml) was stirred with 3 g of silica gel (Wakogel C-300, dried at 180–200 $^{\circ}\text{C}$ for 3 h).

Table IX. Production ratios of dimeric diastereoisomers

Telogen	Temp	%		%		%		(2a + 2c)
	°C	2a	2b	2c	2d	(2a + 2c)	(2b + 2d)	(2b + 2d)
CBr ₄	50	93	7	49	51	76	24	3.17
	70	80	20	50	50	72	28	2.57
	90	93	7	60	40	63	37	1.70
Cl ₃ CBr	50	85	15			85	15	5.67
	70	78	22	71	29	77	23	3.35
	90	75	25	57	43	72	28	2.57

4) The homologous adducts from CTB had higher boiling or melting points than the homologous ones from BTCM, except for **2b**.

5) The differences of the ¹H NMR spectra between homologues in both system are characterized by the nonequivalence of the geminal methylene protons adjacent to a trihalomethyl group. That is, the corresponding proton signals of the homologues from CTB resonated in lower magnetic fields relative to those of the homologues from BTCM, without exception, and exhibited stronger geminal coupling patterns.

6) Because of the strong halogen effect, a regular shift into higher magnetic fields was observed on the carbon signal corresponding to a trihalomethyl group in the ¹³C NMR spectra.

7) The linear diadducts from CTB showed a lowering of the priority of syndiotacticity and higher extent of cyclization in comparison with those from BTCM.

REFERENCES

1. C. M. Starks, "Free Radical Telomerization," Academic Press, Inc., New York, N.Y., 1974.
2. B. Boutevin, *Adv. Polym. Sci.*, **94**, 69 (1990).
3. J. M. Bessiere, B. Boutevin, and L. Sarraf, *Polym. Bull.*, **18**, 253 (1987).
4. J. M. Bessiere, B. Boutevin, and L. Sarraf, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 3275 (1988).
5. K. Ute, T. Nishimura, and K. Hatada, *Polym. J.*, **21**, 1027 (1989).
6. C. A. Barson, A. R. Luxton, and J. C. Robb, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1666 (1972).
7. C. A. Barson and R. Ensor, *Eur. Polym. J.*, **13**, 53 (1977).
8. T. Kimura, T. Kodaira, and M. Hamashima, *Polym. J.*, **15**, 293 (1983).
9. T. Kimura and M. Hamashima, *Polym. J.*, **18**, 21 (1986).
10. T. Kimura, H. Morimoto, E. Sasaki, K. Tanji, and M. Hamashima, *Polym. J.*, **22**, 1015 (1990).
11. N. Fuhrman and R. B. Mesrobian, *J. Am. Chem. Soc.*, **76**, 3281 (1954).
12. F. R. Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943).