Separation and Structure of Methyl Methacrylate Telomers Synthesized in the Presence of Bromotrichloromethane

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ABSTRACT: The radical telomerization of methyl methacrylate (MMA) was carried out at 50—90°C using bromotrichloromethane (BTCM) as a chain transfer agent, and the n[MMA]:[BTCM] adducts, that is, the n-mers, where, $n = 1$—3, were separated by silica-gel column chromatography. The tacticities of two dimers and three trimers were estimated by ^{1}H NMR spectroscopy. *Syndiotactic* diastereoisomers were formed preferentially, and no *isotactic* trimer was found. The most stable conformations of the *syndiotactic-* and *isotactic-*dimers were presumed from the results of induced reactions.

KEY WORDS   Radical Telomerization / Methyl Methacrylate / Bromotrichloromethane / Telomers / Silica-Gel Column Chromatography / Diastereoisomer / ^{1}H NMR / Tacticity / Conformation /

The addition reactions of bromotrichloromethane (BTCM) with various olefins have been studied by several workers,[1,2] and BTCM has been pointed out to be an excellent radical addition reagent.

Furthermore, BTCM is known as a strong telogen for the radical telomerization of vinyl monomers. Kharasch *et al.*[2-6] investigated kinetically the photoinitiated reaction between styrene and BTCM, and proposed a reaction mechanism. Barson *et al.*[7-10] carried out the telomerizations of styrene and methyl methacrylate (MMA) in similar systems, and determined transfer constants for the telomeric radical intermediates using gel-permeation chromatography (GPC).

However, the separation and structural analysis of telomers synthesized using BTCM as a telogen have rarely been reported except some 1:1 adducts.[2] Since the corresponding telomers have labile substituent groups on both ends, they can be considered as the starting materials for subsequent reactions. These studies on lower polymers afford valuable data as model compounds of higher polymers.

Recently, Fujishige[11,12] studied the ^{1}H NMR spectra of MMA oligomers prepared through anionic oligomerization initiated with sodium methoxide. Bledzki *et al.*[13-15] isolated MMA oligomers obtained by radical oligomerization using 1,1,2,2-tetraphenyl-1,2-diphenoxyethane as the initiator, and identified two kinds of dimers and three kinds of trimers by ^{1}H NMR spectroscopy.

This article deals with the separation and structure of MMA telomers up to trimers synthesized in the presence of BTCM as the telogen. The tacticity and the conformation of the diastereoisomers are discussed in reference to the data obtained through ^{1}H NMR spectroscopy and induced reactions.

EXPERIMENTAL

Measurements

GPC analysis of the telomers was carried out with a Hitachi 635 chromatograph (column, Shodex A-80M, -803, -802; eluent, THF). Melting points were measured with a MP-21 (Yamato) and uncorrected. IR spectra were obtained by the KBr-method using a Hitachi 295 spectrophotometer. ^{1}H NMR spectra

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were recorded on a JNM-C-60HL (60 MHz) spectrometer (JEOL) using Me_4Si as an internal reference. Mass spectra were measured with a D-3000 (JEOL) and a M-80 (Hitachi) apparatus using a chemical ionization method [20 eV (3.2×10^{-18} J)]. Satisfactory patterns were obtained for all isotope peaks resulting from bromine and chlorine atoms in the mass spectra. The spectra corresponding only to ^{79}Br and ^{35}Cl have been treated in this paper.

Telomerization Procedure

Telomerization was carried out at 50, 70, and 90°C, for 24, 8, and 4 h respectively under the conditions of [BTCM]/[MMA] = 8, [AIBN]$^{0.5}$/[MMA] = 0.5 (AIBN is the abbreviation for azobisisobutyronitrile). Appropriate amounts of MMA and BTCM were placed in a three-necked round bottom flask equipped with a vacuum stirrer. The mixture was heated at a prescribed temperature with stirring under a nitrogen atmosphere. AIBN was then added to the solution to initiate the reaction. After the reaction was over, the mixture was cooled to below 20°C, and the unreacted MMA and BTCM were evaporated in vacuo. The residual viscous liquid afforded a low-polymeric product. MMA was purified by the conventional method. BTCM was distilled under reduced pressure before use, and AIBN was recrystallized from methanol.

Separation and Identification of Telomers

The n-mers (n = 1—3) were separated by silica-gel column chromatography with benzene. The development was achieved rapidly by pressing with nitrogen to avoid any side reactions in the column.

The first eluate contained 1-mer, methyl 2-bromo-4,4,4-trichloro-2-methylbutyrate (1). It was purified by distillation under reduced pressure; bp 111—113°C [8 mmHg (1.07 kPa)]; IR 1750 cm^{-1} (C=O); mass spectrum m/z (relative intensity) 297 (QM$^+$, 34), 261 (34), and 181 (100).

The second eluate was evaporated and the residue was recrystallized from hexane to afford syndiotactic (st)-dimer, dimethyl st-2-bromo-2,4-dimethyl-4-(2,2,2-trichloroethyl)glutarate (2a); mp 58—59.5°C; IR 1735 cm^{-1} (C=O); mass spectrum m/z (relative intensity) 397 (QM$^-$, 16), 365 (77), 317 (48), and 101 (100).

The third eluate, eluted immediately after the second one, was isotactic (it)-dimer, dimethyl it-2-bromo-2,4-dimethyl-4-(2,2,2-trichloroethyl)gluta-

rate (2b); mp 79—80°C; IR 1730 cm^{-1} (C=O); mass spectrum m/z (relative intensity) 397 (QM$^-$, 15), 365 (58), 317 (26), and 101 (100).

The fourth eluate afforded st-trimer, dimethyl st-2-bromo-4-methoxycarbonyl-2,4,6-trimethyl-6-(2,2,2-trichloroethyl)heptanedioate (3a) by a procedure similar to the above; mp 111—112°C; IR 1745, 1725 cm^{-1} (C=O); mass spectrum m/z (relative intensity) 497 (QM$^+$, 54), 465 (100), 461 (36), 437 (23), and 417 (82).

The production ratio in the unisolated part was determined from ^{1}H NMR spectrum data.

Induced Reactions of Telomers

Elimination Reaction of 1-mer (1) with Triethylamine (TEA). A mixture of 1 (6 g) and TEA (30 ml) was refluxed for 13 h. After cooling, the precipitated salt was removed, and the unreacted TEA was evaporated off. The residue was chromatographed in 2 : 1-benzene : cyclohexane on a silicagel column and purified by distillation in vacuo to obtain 3.6 g (83%) of methyl β-(trichloromethyl)-methacrylate (4); bp 65—67°C [1 mmHg (0.13 kPa)]; IR 1735 (C=O) and 1640 cm^{-1} (C=C); ^{1}H NMR (CCl$_4$) δ 7.26 (quartet, 1H, J = 1.5 Hz, CH), 3.77 (s, 3H, CO$_2$CH$_3$), and 2.21 ppm (d, 3H, CH$_3$); mass spectrum m/z (relative intensity) 217 (QM$^+$, 40), 181 (100), and 153 (28).

Reaction between st-Dimer (2a) and TEA. A mixture of 2a (3 g) and TEA (60 ml) was refluxed for 60 h. The reaction mixture was treated in a manner similar to that used for 1, and the following products were isolated by silica-gel column chromatography with benzene: 1.05 g (44%) of dimethyl 2-methyl-4-methylene-2-(2,2,2-trichloroethyl)glutarate (5a), a colorless viscous liquid; IR 1720 (C=O) and 1640 cm^{-1} (C=C); ^{1}H NMR (CCl$_4$) δ 6.19 (d, 1H, J = 1.5 Hz, =CH$_2$), 5.51 (s, 1H, =CH$_2$), 3.72 (s, 3H, CO$_2$CH$_3$), 3.64 (s, 3H, CO$_2$CH$_3$), 3.64 (d, 1H, J = 15 Hz, CH$_2$), 2.80 (d, 1H, CH$_2$), 2.59 (s, 2H, CH$_2$), and 1.38 ppm (s, 3H, CH$_3$); mass spectrum m/z (relative intensity) 317 (QM$^+$, 46), 285 (100), and 247 (43), and 0.5 g (22%) of trans-4-methoxycarbonyl-2,4-dimethyl-2-(2,2,2-trichloroethyl)-4-butanolide (6b); mp 94—95.5°C (recrystallized from hexane); IR 1765, 1735 cm^{-1} (C=O); mass spectrum m/z (relative intensity) 303 (QM$^+$, 100), 267 (70), 243 (40), 231 (5), and 207 (18).

Reaction of it-Dimer (2b) and TEA. A mixture of

2b (1.2 g) and TEA (24 ml) was treated in a manner similar to that used for **2a** to yield the following products: 0.12 g (13%) of **5a**, 0.24 g (26%) of **6b**, and 0.23 g (24%) of dimethyl 2,4-dimethyl-4-(2,2,2-trichloroethyl)-2-pentenedioate (**5b**), a colorless viscous liquid; IR 1725 (C=O) and 1625 cm^{-1} (C=C); ^{1}H NMR (CCl$_4$) δ 6.71 (quartet, 1H, $J=$ 1.5 Hz, C$\underline{H}$), 3.71 (s, 6H, CO$_2$C$\underline{H}_3$), 3.64 (d, 1H, $J=$ 15 Hz, C$\underline{H}_2$), 3.17 (d, 1H, C$\underline{H}_2$), 1.75 (d, 3H, C$\underline{H}_3$), and 1.64 ppm (s, 3H, C$\underline{H}_3$); mass spectrum m/z (relative intensity) 317 (QM$^+$, 100), 285 (91), and 247 (43).

Pyrolysis of Dimers. The two dimers were separately heated at 200°C for 2 h. Lactone **6b** was quantitatively obtained from **2b**. Similarly, **2a** produced *cis*-4-methoxycarbonyl-2,4-dimethyl-2-(2,2,2-trichloroethyl)-4-butanolide (**6a**); mp 73.5—75°C (recrystallized from hexane); IR 1770, 1740 cm^{-1} (C=O); mass spectrum m/z (relative intensity) 303 (QM$^+$, 100), 267 (48), 243 (37), 231 (42), and 207 (5).

Cyclization of Dimers by Silica Gel. To a benzene solution of a dimer (0.5 g in 15 ml), 5 g of silica gel was added, and the suspension was stirred for 72 h at room temperature. The conversions were calculated to be 11% (**2a**→**6a**) and 100% (**2b**→**6b**), respectively, from the ^{1}H NMR data.

Reaction of Trimers with Silica Gel. Silica gel was added to a benzene solution of a trimer, and the suspension was heated at 50°C for 24 h. Compound **3a** afforded *cis*-4-methoxycarbonyl-2-(2-methoxycarbonyl-2-methyl-4,4,4-trichlorobutyl)-2,4-dimethyl-4-butanolide (**7a**) in a 75% yield; mp 65.5—67°C (recrystallized from 3 : 1-cyclohexane : ethyl acetate); IR 1780, 1755, and 1740 cm^{-1} (C=O); ^{1}H NMR (benzene-d_6) δ 3.53 (d, 1H, $J=15.6$ Hz, C$\underline{H}_2$), 3.28 (s, 3H, CO$_2$C$\underline{H}_3$), 3.24 (s, 3H, CO$_2$C$\underline{H}_3$), 2.48 (d, 1H, C$\underline{H}_2$), 2.38 (d, 1H, $J=13.5$ Hz, C$\underline{H}_2$), 2.00 (d, 1H, C$\underline{H}_2$), 1.65 (s, 2H, C$\underline{H}_2$), 1.45 (s, 3H, C$\underline{H}_3$), 1.38 (s, 3H, C$\underline{H}_3$), and 1.09 ppm (s, 3H, C$\underline{H}_3$); mass spectrum m/z (relative intensity) 403 (QM$^+$, 100), 371 (63), and 367 (12). Trimers containing *heterotactic* (*ht*)-trimer (**3b**) produced primarily *trans*-4-methoxycarbonyl-2-(2-methoxycarbonyl-2-methyl-4,4,4-trichlorobutyl)-2,4-dimethyl-4-butanolide (**7b**) in a reasonable yield; mp 174—175°C (recrystallized from methanol); IR 1780, 1755, and 1740 cm^{-1} (C=O); ^{1}H NMR (benzene-d_6) δ 3.31 (d, 1H, $J=13.2$ Hz, C$\underline{H}_2$), 3.21 (s, 6H, CO$_2$C$\underline{H}_3$), 2.41 (d, 2H, $J=14.4$ Hz, C$\underline{H}_2$), 2.17 (d, 1H, C$\underline{H}_2$),

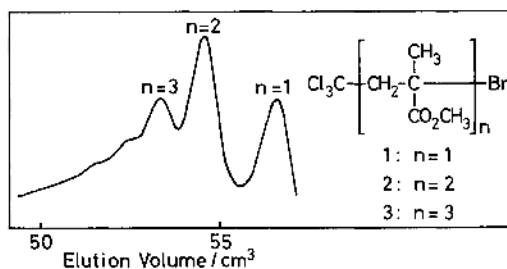**Figure 1.** GPC chromatogram of the product obtained at 90°C.
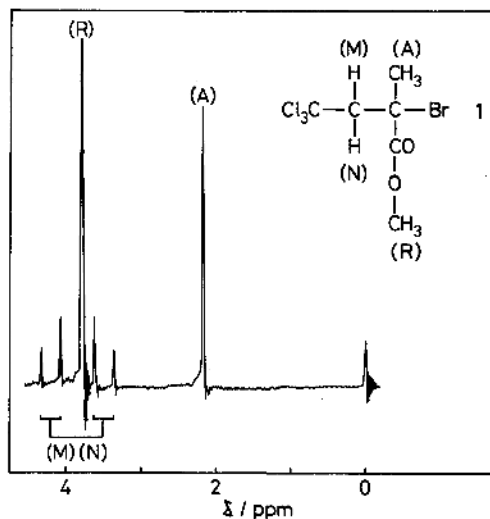
Figure 2. ^{1}H NMR spectrum of 1-mer (**1**) in CCl$_4$.

1.86 (d, 1H, C$\underline{H}_2$), 1.40 (s, 6H, C$\underline{H}_3$), 1.36 (d, 1H, C$\underline{H}_2$), and 1.01 (s, 3H, C$\underline{H}_3$) ppm; mass spectrum m/z (relative intensity) 403 (QM$^+$, 100), 371 (66), and 367 (34).

RESULTS AND DISCUSSION

Figure 1 shows a typical GPC chromatogram of the product obtained through the present telomerization. The yield of *n*-mers ($n=1$—3) was about 70% of the overall one, and an increase in the reaction temperature tended to decrease the molecular weight.

^{1}H NMR Structural Analysis of Telomers

1-mer (1). The ^{1}H NMR spectrum of **1** is shown in Figure 2. The singlets at 2.19 and 3.81 ppm correspond to the methyl protons (A) and those of

the ester group (R), respectively. Since the two geminal methylene protons (M) and (N) are expected to exhibit a typical AB pattern due to the magnetic nonequivalence, the quartet broadened at 3.85 ppm may be assigned to the (M)- and (N)-protons.

Dimers (2). Since **2** has two asymmetric carbon atoms, there are two possible diastereoisomers, **2a** and **2b**.

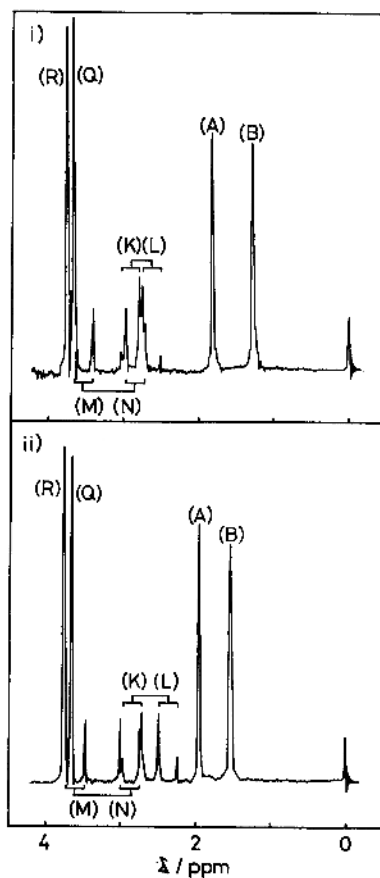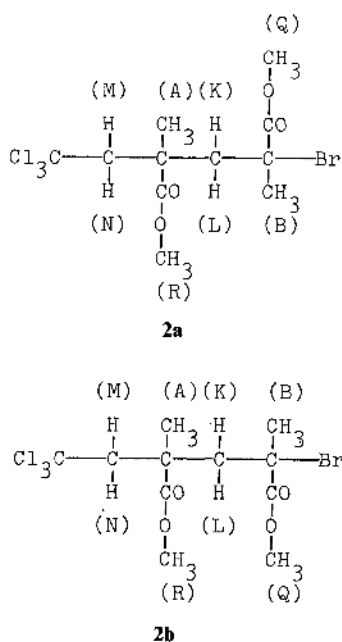^{1}H NMR spectroscopy is an effective method for

Figure 3. ^{1}H NMR spectra of dimers (**2**) in CCl$_4$: i) *st*-dimer (**2a**); ii) *it*-dimer (**2b**).

Table I. ^{1}H NMR parameters of 1-mer (**1**), *st*- (**2a**), and *it*- (**2b**) dimers

Proton	Symbol	Chemical shift δ/ppm		
		1	2a	2b
–CH$_3$	A	2.19	1.83	1.97
–CH$_3$	B		1.29	1.55
–CH$_2$–	K, L		3.02 2.78	2.97 2.72
			2.75 2.51	2.49 2.24
			[16.2] (14.4)	[28.8] (15.0)
–CH$_2$–	M, N	4.34 4.08	3.64 3.40	3.71 3.46
		3.63 3.37	2.96 2.72	2.99 2.74
		[42.6][a] (15.6)[b]	[40.8] (14.4)	[43.2] (15.0)
CO$_2$CH$_3$	Q		3.68	3.66
–CO$_2$CH$_3$	R	3.81	3.77	3.76

[a] [ ]: Difference in chemical shifts $\Delta\delta$ in Hz.

[b] ( ): Coupling const J in Hz.

determining the tacticities of telomers. The magnetic environment about the two geminal methylene protons (K) and (L) is obviously different for **2a** and **2b**. Therefore, the corresponding signals should show characteristic differences with each other. That is, **2a** will indicate signals resembling a singlet owing to the nearly equivalent protons, whereas **2b** will exhibit an AB pattern similar to that of other methylene protons (M) and (N) owing to nonequivalent protons.

Figure 3 shows the ^{1}H NMR spectra of two diastereoisomers of isolated dimers. On the basis of the assignment of the proton signals summarized in Table I, spectra i) and ii) in Figure 3 were found to correspond to **2a** and **2b**, respectively.

The methyl protons (A) and (B) of **2a** resonated in higher magnetic fields relative to those of **2b**. This tendency may be explained by a shielding effect of

the ester groups toward the methyl protons of **2a**. Although an electronegative effect of the trichloromethyl groups on the methyl protons (A) and (R) is weakened by the methylene groups between them, this effect will be even larger than a similar effect of the bromine atoms on the methyl protons (B) and (Q). Consequently, the signals of the methyl protons (A) and (R) must shift to magnetic fields lower than those of the methyl protons (B) and (Q), respectively.

Table II. Temperature dependence of the production ratio of *st*- (**2a**) and *it*- (**2b**) dimers

	Dimer	Temp/°C		
		50	70	90
Production	**2a**	85	78	75
ratio/%	**2b**	15	22	25

Figure 4. ^{1}H NMR spectrum of *st*-trimer (**3a**) in CCl$_4$.

Table III. ^{1}H NMR parameters of
st-trimer (**3a**)

Proton	Symbol	Chemical shift δ/ppm
–CH$_3$	A	1.77
–CH$_3$	B	0.87
–CH$_3$	C	1.28
–CH$_2$–	I, J	2.90 2.67 2.64 2.41
		[15.6][a] (13.8)[b]
–CH$_2$–	K, L	2.02
–CH$_2$–	M, N	3.53 3.28 2.85 2.60
		[40.8] (15.0)
–CO$_2$CH$_3$	P	3.67
–CO$_2$CH$_3$	Q	3.67
–CO$_2$CH$_3$	R	3.75

[a] [ ]: Difference in chemical shifts $\Delta\delta$ in Hz.
[b] ( ): Coupling const J in Hz.

The formation of **2a** was favored over that of **2b** as shown in Table II, but the production ratio of **2b** increased with the reaction temperature. It is considered that the temperature dependence of **2b** is larger than that of **2a** due to steric hindrance.

Trimers (3). Since **3** has three asymmetric carbon atoms, four possible diastereoisomers can be formed, **3a**, **3b**, *ht*- (**3c**), and *it*- (**3d**) trimers.

However, the diastereoisomer isolated was **3a** only. Figure 4 shows the ^{1}H NMR spectrum of **3a**, and the assignment of the proton signals is given in Table III.

Among the three methyl protons (A), (B), and (C) of **3a**, the (A) protons are located in a magnetic environment similar to the methyl protons (A) of **2a**. The singlet at 1.77 ppm was therefore assigned to the (A) protons. Furthermore, since the (C) protons correspond to the methyl protons (B) of **2a**, the singlet at 1.28 ppm is assignable to the (C) protons and the central methyl protons (B) resonate at 0.87 ppm as a singlet. The assignment of the two methylene protons on both sides may be estimated also on the basis of the corresponding methylene protons of **2a**. The ambiguous AB pattern consisting of signals at 2.90, 2.67, 2.64 and 2.41 ppm is due to the (I) and (J) protons, and the typical AB pattern consisted of signals at 3.53, 3.28, 2.85 and 2.60 ppm is due to the (M) and (N) protons. The central methylene protons (K) and (L) resonate at 2.02 ppm as a singlet, indicating that they are not influenced by the end groups.

The ^{1}H NMR spectrum of the whole unisolated **3**
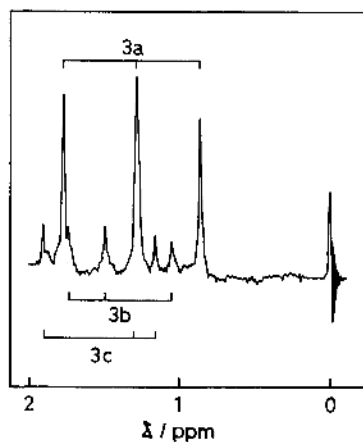
Figure 5. ^{1}H NMR spectrum of methyl proton resonance region of trimers (**3**) obtained at 70°C (CCl$_4$).

Table IV. Chemical shifts δ in ppm of methyl protons of the resulting trimers

Symbol	δ		
	3a	**3b**	**3c**
A	1.77 (1.83)[a]	1.74 (1.83)	1.90 (1.97)
B	0.87	1.04	1.15
C	1.28 (1.29)	1.49 (1.55)	1.30 (1.29)

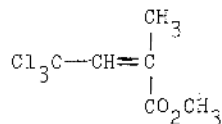[a] ( ): Chemical shifts estimated from the (A)- and (B)-proton signals of the dimers (see Table I).

in the methyl proton region is shown in Figure 5.

The formation of two diastereoisomers is predictable besides that of **3a**, since some smaller signals are present in addition to the signals corresponding to **3a** in Figure 5. The magnetic environment about the (A)- and (C)-protons of **3** resembles that about the (A)- and (B)-protons of **2**, respectively. Therefore, all the signals can be assigned as shown in Table IV. The production ratio of the resulting three trimers was **3a** : **3b** : **3c** = 58 : 21 : 21 as determined by the area ratio of the corresponding signals in Figure 5. However, the presence of **3d** was not confirmed, and the formation of **3d** seems difficult in this system.
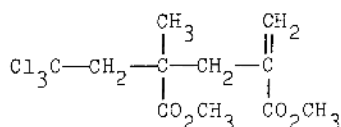
Induced Reactions of Telomers

1-mer (1). The reaction of **1** with TEA gave **4** in good yield, and the elimination of hydrogen chloride was not observed in this reaction. These results demonstrate that the trichloromethyl radical
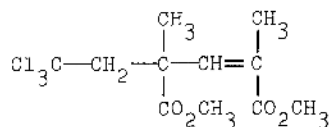
298

$$Cl_3C—CH \!=\! \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CO_2CH_3}{|}}{C}}$$

4

$$Cl_3C—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CO_2CH_3}{|}}{C}}—CH_2—\overset{\overset{\displaystyle CH_2}{||}}{\underset{\underset{\displaystyle CO_2CH_3}{|}}{C}}$$

5a

$$Cl_3C—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CO_2CH_3}{|}}{C}}—CH \!=\! \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CO_2CH_3}{|}}{C}}$$

5b
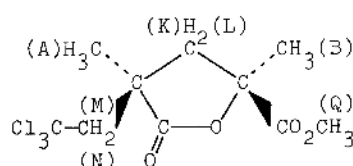
6a
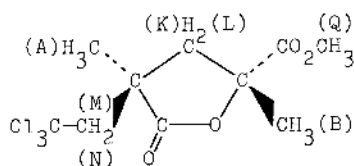
6b

resulting from BTCM is selectively attached to the β-position of the double bond of MMA and that the bromine atom on **1** is eliminated much more easily than the chlorine atom on **1**.

Dimers (2). The reaction between **2** and TEA was carried out in a manner similar to that with **1**, and **5a** and **6b** were obtained from **2a**, whereas **2b** gave **5a**, **6b** and **5b**. Since this reaction with TEA proceeds through a *trans* elimination mechanism, the conformation between the leaving hydrogen and
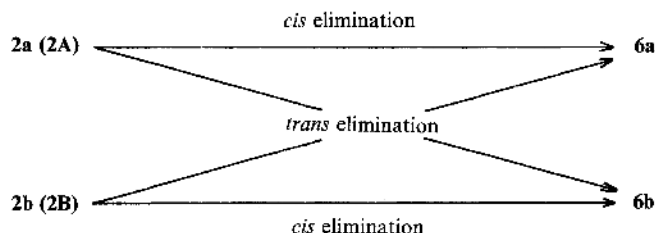
2A   **2B**

bromine atoms must be a *trans* form to produce **5b** according to Saytzeff's law. Olefin **5b** was produced in preference to **5a** in the reaction of **2b**, but **5b** was not obtained at all in the reaction of **2a**. That the *it*-poly(methyl methacrylate) (PMMA) has a 5_1 helical conformation, and that the *st*-PMMA has the 1 : 1-mixture of $T.T$ and T-*cis* coformations have already been reported by Amiya, *et al.*[16] If similar conformations are applied to **2a** and **2b**, the difference in reactivity may be satisfactorily explained. That is, the most stable conformations of **2a** and **2b** are **2A** and **2B**, respectively.

Lactone **6b** is a ring compound formed through the elimination of the methyl radical at the γ-ester group and the bromine atom of dimers. If the production of **6b** occurs by *trans* elimination as in the case of the olefins **5a** and **5b**, different lactones
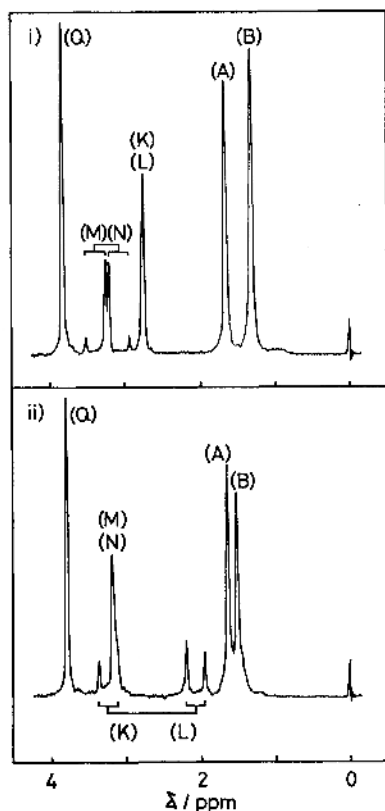
2a (2A) ⟶ *cis* elimination ⟶ **6a**

trans elimination
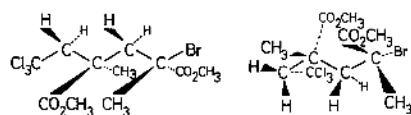
2b (2B) ⟶ *cis* elimination ⟶ **6b**

Scheme I.

Figure 6. ¹H NMR spectra of dimer-lactones in CCl₄: i) *cis*-type (6a); ii) *trans*-type (6b).

Table V. ¹H NMR parameters of *cis*- (6a) and *trans*- (6b) lactones

Proton	Symbol	Chemical shift δ/ppm		
		6a		6b
–CH₃	A	1.67		1.66
–CH₃	B	1.32		1.53
–CH₂–	K, L	2.75		3.36 3.12
				2.20 1.96
				[69.6] (14.4)
–CH₂–	M, N	3.51	3.24	3.18
		3.20	2.93	
		[18.6]ᵃ	(16.2)ᵇ	
–CO₂CH₃	Q	3.82		3.80

ᵃ [ ]: Difference in chemical shifts $\Delta\delta$ in Hz.

ᵇ ( ): Coupling const J in Hz.

7a

7b

will be generated by the following pathway: **2a**→**6b** and **2b**→**6a**. But both starting materials gave lactone **6b**. This may be explained by the difference in the conformations of **2a** and **2b**. In the conformational **2A**, the *trans* elimination tends to occur since the ethereal oxygen at the γ-ester group is situated on the opposite side of the bromine atom. In contrast, the *cis* elimination is dominant in the conformational **2B** since the oxygen is situated on the same side of the bromine atom (Scheme I).

Furthermore, heating of **2** without any solvent resulted in the *cis* elimination quantitatively, and **2a** and **2b** afforded **6a** and **6b**, respectively.

Similar reactions were also observed by the catalytic action of silica gel. However, the reactivities of **2a** and **2b** were greatly different in this case and the conversion of **2b** was larger than that of **2a**. The validity of the two estimated dimer conformations may be supported by the difference in reactivity.
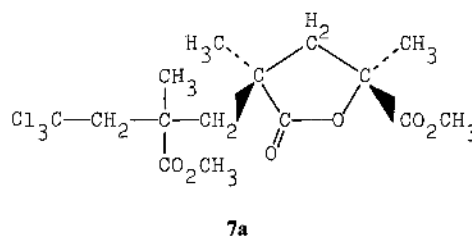
The ¹H NMR spectra of the dimer-lactones, **6a** and **6b**, are shown in Figure 6, and the assignment of the proton signals is summarized in Table V.

Since the free rotation of the trichloroethyl groups becomes possible by the ring formation, the signals of the methylene protons (M) and (N) may be equivalent. Actually, the corresponding signal of **6b** assumed a singlet. However, that of **6a** assumed an ambiguous AB pattern, since the new rotational hindrance of the methyl proton (A) against the trichloroethyl group is brought about by the repulsive force between the trichloroethyl and the ester groups. On the other hand, the methylene protons (K) and (L) will show a distinct AB pattern due to the magnetic nonequivalence, since they are situated apart from each other on either side of the

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five-membered ring. The predicted pattern of the methylene protons was observed for **6b**, but **6a** showed a singlet. In the case of **6a**, there is a repulsive force between the trichloroethyl and the ester groups.

It is therefore anticipated that isolation of the methylene protons (K) and (L) is promoted and that they are equivalent.

Trimers (3). As in the case of **2**, trimers **3** were successfully converted to the corresponding lactones by the catalytic action of silica gel. For instance, **7a** was obtained by the reaction of **3a**. A similar reaction was attempted with a mixture of **3** containing primarily **3b**. As a result, **7b** was obtained as the main product and was easily isolated because of the poorer solubility of **7b** in organic solvents than that of other components. The ^{1}H NMR spectra of **7a** and **7b** were consistently analyzed using the results in Tables III and V.

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