

Study on Radical Telomerization of Esters of Methacrylic Acid Using Bromotrichloromethane and Characteristics of the Resulting Telomers IV.[†] Branched Alkyl Methacrylates

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ABSTRACT: The radical telomerization of isopropyl (IPMA) and *t*-butyl (TBMA) methacrylates was carried out using bromotrichloromethane as a telogen at 50, 70, and 90°C, and compared with that of ethyl methacrylate (EMA). The telomerization behavior of these monomers and reactivity of the resulting telomers were greatly dependent on the kinds of alkyl substituents in the ester groups. The average degree of telomerization decreased, whereas the yield of lactones increased, with increasing degree of branching in the alkyl chain. The telomerization of IPMA gave the *syndiotactic* (*st*) dimeric telomer in preference to the *isotactic* one in a ratio around 85 : 15, which was almost identical with the value in the telomerization of EMA. In the telomerization of TBMA, however, all the dimeric telomer which was produced at reaction temperature below 70°C, was the *st* one. Furthermore, the formation of carboxylic acid compounds was observed only in the telomerization of TBMA. The lactonization of dimeric- and trimeric-telomers was induced by the catalytic action of silica gel and heat. The IPMA telomers resembled EMA ones in the reactivities of lactonization. On the other hand, the TBMA telomers were greatly subject to lactonization in comparison with others. Lactones resulting from the TBMA telomers were further transformed into corresponding carboxylic acids. The carboxylation of TBMA lactones was promoted by the catalytic action of *t*-butyl bromide.

KEY WORDS Telomerization / Isopropyl Methacrylate / *t*-Butyl Methacrylate / Bromotrichloromethane / Reactions of Telomers / Diastereoisomer / Lactonization / Carboxylation / Effect of Substituent /

Bromotrichloromethane (BTCM) is known to be a strong telogen for the radical telomerization of vinyl monomers by kinetic studies.¹⁻⁵ However, there have been reported few studies on the separation and the characterization of telomers synthesized by using BTCM as a telogen.⁶

The resulting telomers can be utilized as "reactive oligomers" by way of chemical modification of both functional end groups. Furthermore, studies on the stereochemistry and the reactivity of the telomers provide valuable data as model compounds for oligomers, and detailed analyses of the telomers are

available for molecular design of new oligomers.

In previous papers,^{7,8} we reported the radical telomerization of a series of primary alkyl (C₁—C₄) methacrylates in the presence of BTCM and the characteristics of the resulting telomers. A significant effect of the alkyl chain length of the ester group was not observed in the telomerization behavior. *Syndiotactic* (*st*) diastereoisomers were formed preferentially, and no *isotactic* (*it*) trimer was found. The most stable conformations of the *st*- and *it*-dimers were suggested to be zigzag and helical, respectively. The increase in

[†] Part I, II, and III of this series are ref 7, 8, and 9.

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molecular flexibility by increasing the alkyl chain length of the ester group caused a decrease in the melting points of the homologous telomers. The pyrolysis of dimeric- and trimeric-telomers and the catalytic reaction of those with silica gel resulted in the lactonization, which was proposed to proceed through a cationic S_N1 mechanism.

As a part of the study, the present work deals with the radical telomerization of branched alkyl methacrylates, that is, isopropyl (IPMA) and *t*-butyl (TBMA) methacrylates using BTCM. The telomerization behavior of these monomers and reactivity of the resulting telomers are compared on the basis of those of ethyl methacrylate (EMA), and the effects of degree of branching in the alkyl chain are discussed.

EXPERIMENTAL

Measurements

The instruments and methods used in this experiment have been described elsewhere.⁸

Telomerization Procedure

Telomerization was carried out at 50, 70, and 90°C for 24, 8, and 4 h, respectively, under the conditions of $[BTCM]_0/[Monomer]_0 = 8$ and $[AIBN]_0^{0.5}/[Monomer]_0 = 0.5$ (AIBN is the abbreviation for 2,2'-azobisisobutyronitrile). The reaction mixture was treated essentially as in case of the previous paper.⁷ Commercial IPMA and TBMA were purified by a conventional method.¹⁰ Commercial BTCM was purified by distillation under reduced pressure, and AIBN by recrystallization from methanol.

Separation and Identification of Telomers

The separation⁸ and identification⁷ of IPMA telomers were carried out in a manner similar to that of the previous papers.

The TBMA telomers were extracted with 3% aqueous sodium hydroxide to remove the

carboxylic acid component. The unextracted ester component was separated in a manner similar to that of the IPMA telomers, whereas the following carboxylic acids were separated by silica gel column chromatography with ethyl acetate as an eluent: **6a**, mp 177–179°C (dec.)⁸ and **7a**, mp 169–171°C (dec.); IR 2900 (OH) and 1765, 1725, 1680 cm^{-1} (C=O); mass spectrum m/z 431 (QM⁺); ¹H NMR (CDCl₃) δ 1.32 (3H, s, -CH₃), 1.52 (9H, s, -*t*-Bu), 1.58 (3H, s, -CH₃), 1.61 (3H, s, -CH₃), 2.03 (2H, s, -CH₂-), 2.22 (1H, d, $J = 13.2$ Hz, -CH₂-), 2.59 (1H, d, -CH₂-), 2.94 (1H, d, $J = 15.0$ Hz, -CH₂-) and 3.68 ppm (1H, d, -CH₂-).

Esterification of Carboxylic Acid Component

Azeotropic esterification of carboxylic acids (ca. 2 g) was carried out using dry methanol (20 ml), dry toluene (10 ml), and conc. sulfuric acid (8 drops) according to the procedure of Brewster *et al.*¹¹

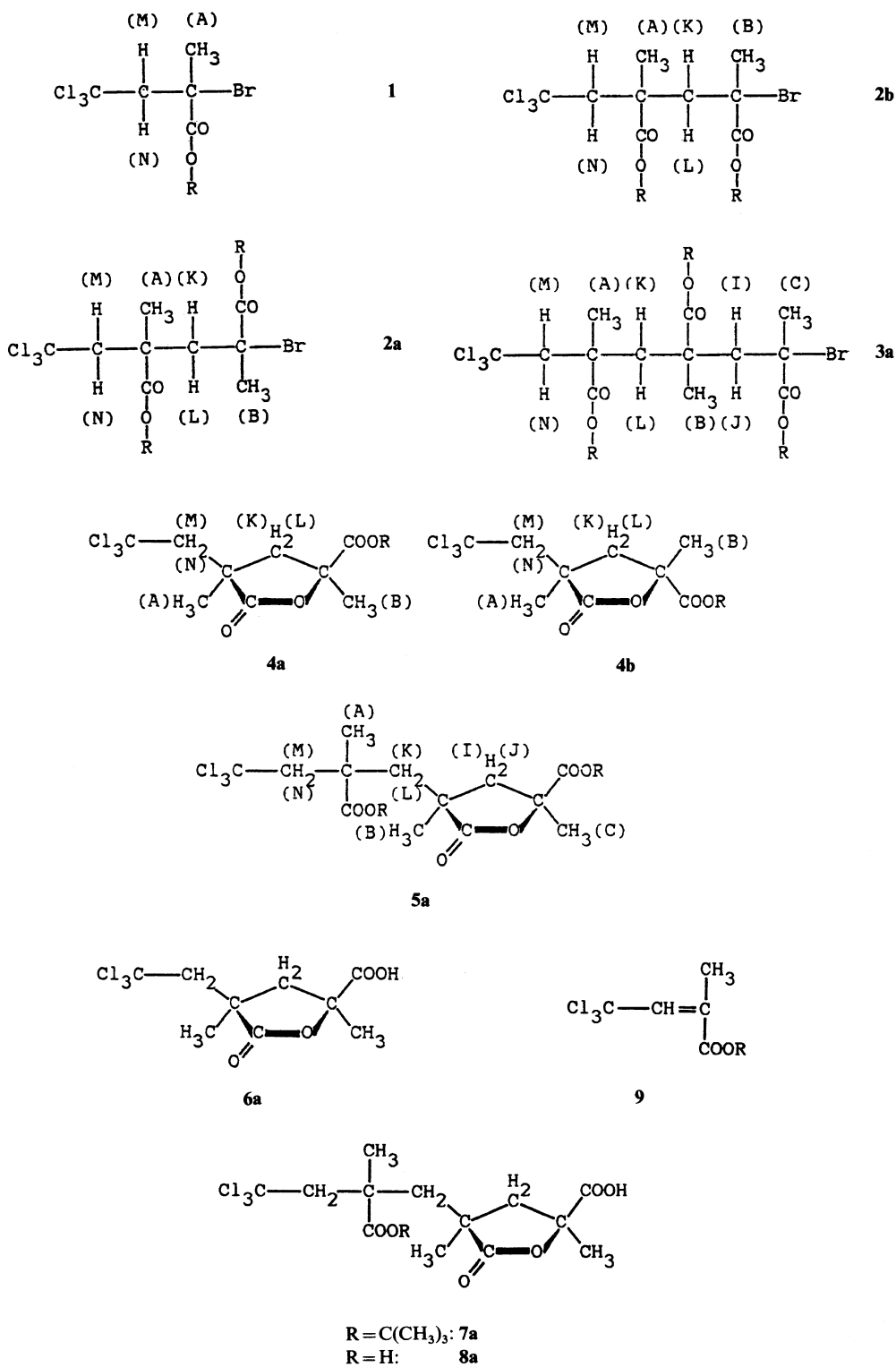
Reactions of Telomers

Elimination Reaction by Triethylamine (TEA). A mixture of a telomer sample and TEA (1 g in 10 ml) was refluxed for a prescribed time. The reaction mixture was treated as in the previous paper.⁷

Catalytic Reaction by Silica Gel. To a solution of a telomer sample (0.3 g in 9 ml dry benzene), 3 g of silica gel (Wakogel C-300, dried at 180–200°C for 3 h) were added, and the suspended mixture was stirred at 30°C for 72 h. The reaction mixture was treated in a manner similar to that in the previous paper,⁸ and when necessary, the resulting carboxylic acid was separated by extraction with 3% aqueous sodium hydroxide.

Pyrolysis. (a) *Open System.* A sample was directly heated at a given temperature for 2 h. The product was separated by silica gel column chromatography with benzene as an eluent, and when necessary, the following carboxylic acids were separated by extraction with 3% aqueous sodium hydroxide: **6a** and

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8a, mp 201–204°C (dec.); IR 3000 (OH) and 1770, 1700 cm^{-1} (C=O); mass spectrum m/z 375 (QM^+).

(b) *Closed System*. Dimeric lactone **4a** ($\text{R} = t\text{-Bu}$) was sealed in a glass tube under reduced pressure, and heated at 100°C for a prescribed time. The product was analyzed by HPLC (column: 2.6 i.d. \times 500 mm; packing material: Hitachi Gel #3010; eluent: methanol).

RESULTS AND DISCUSSION

Telomerization of Branched Alkyl Methacrylates with BTCM

The results of the radical telomerization of branched alkyl methacrylates along with that of EMA are summarized in Table I. The apparent rate of telomerization (R'_p) of these alkyl methacrylates was not appreciably dependent on the kinds of alkyl substituents in the ester group, but their product distribution (MWD) was so to a considerable degree. The average degree of telomerization (\bar{n}) decreased, whereas the yield of lactones increased, with increasing degree of branching in the alkyl chain. In particular, the telomerization of TBMA preferentially gave lactones. Furthermore, the formation of carboxylic acids was only observed in the telomeriza-

tion of TBMA, and their yield gradually increased with increasing reaction temperature. Figure 1 shows GPC diagrams of the ester- and carboxylic acid-components obtained in the telomerization of TBMA. The MWD of ester component shifted to $n = 1$, whereas that of carboxylic acid component to $n \geq 2$, regardless of the reaction temperature.

Identification of Telomers and Lactones

The characterizations of the resulting telomers and lactones are summarized in Tables II and III, respectively. The melting points of homologous telomers increased in the order: $\text{R} = t\text{-Bu} > \text{Et} > i\text{-Pr}$. The IR absorption maxima corresponding to the C=O stretching vibration of a lactone ring appeared at constant wavenumber near 1775cm^{-1} . Ion peaks based on an identical fragmentation pattern were generally detected in the mass spectra of the homologues. However, it was difficult to detect the parent ion peaks of **2a** ($\text{R} = t\text{-Bu}$) due to rapid lactonization at the time of measurement.

The ^1H NMR parameters of the telomers and lactones are listed in Tables IV and V. Some methyl- and methylene-proton signals marked with the same symbol shifted to higher magnetic fields in the order: $\text{R} = t\text{-Bu} > i\text{-Pr} > \text{Et}$. However, the majority of the

Table I. Radical telomerization of branched alkyl methacrylates

Monomer	Temp	$R'_p \times 10^6$ $\text{mol l}^{-1} \text{s}^{-1}$	Esters/wt%			Carboxylic acids/wt%
	°C		$n = 1$	$n = 2^a$	$n \geq 3$	
EMA	50	8	6	16 [0]	78	—
	70	70	23	30 [4]	47	—
	90	147	33	28 [5]	39	—
IPMA	50	22	22	31 [5]	47	—
	70	70	32	31 [7]	37	—
	90	131	38	33 [14]	29	—
TBMA	50	18	45	21 [12]	26	8
	70	66	51	19 [19]	21	9
	90	129	54	21 [21]	15	10

^a [], content of dimeric lactones.

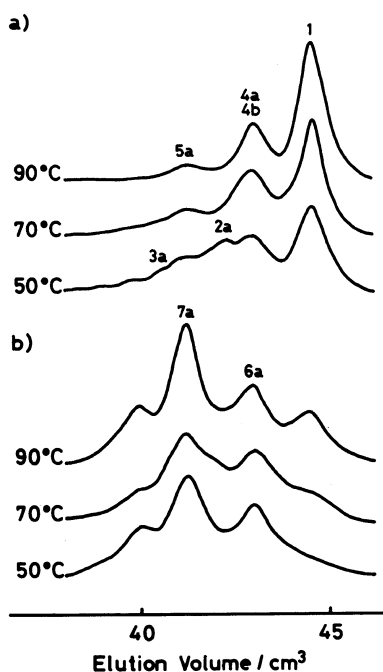


Figure 1. GPC diagrams of products obtained in the telomerization of TBMA: a) ester component; b) carboxylic acid component.

proton signals gave nearly the same chemical shifts regardless of the bulkiness of the alkyl chain in the ester groups. The proton signals of the ester groups, which are omitted in the tables, appeared in the expected resonance regions.

Ratios of Dimeric Diastereoisomers in the Products

Table VI shows the ratio of two dimeric diastereoisomers obtained in the telomerization of branched alkyl methacrylates along with EMA. The telomerization of IPMA gave **2a** ($R = i\text{-Pr}$) in preference to **2b** ($R = i\text{-Pr}$) in a similar ratio as that of EMA, and temperature dependence on the ratio was not clearly observed. On the other hand, telomerization of TBMA gave only **2a** ($R = t\text{-Bu}$), and the dimeric telomers were not observed at a reaction temperature above 70°C. It is necessary to take the formation of two lactones **4a** and **4b** into account for a more exact estimation of tacticity. The formation of dimeric lactones increased with increasing re-

Table II. Characterization of telomers

Telomer	R ^a	Shape ^b	mp [bp]	$\nu_{(\text{C}=\text{O})}$	m/z (QM ⁺)
			°C	cm ⁻¹	
1	Et	C	[77— 78/1 mmHg]	1745	311
	<i>i</i> -Pr	C	[89— 91/2 mmHg]	1745	325
	<i>t</i> -Bu	C	[123—125/8 mmHg]	1740	339
2a	Et	A	48—49	1740	425
	<i>i</i> -Pr	B	— ^c	1740	453
	<i>t</i> -Bu	A	100.5—102 (dec.)	1740	(481) ^d
2b	Et	A	17.5—19	1735	425
	<i>i</i> -Pr	B	— ^c	1735	453
3a	Et	A	62.5—64.5	1725	539
	<i>i</i> -Pr	B	— ^c	1730	581
	<i>t</i> -Bu	A	111—113 (dec.)	1735	623

^a Et, ethyl; *i*-Pr, isopropyl; *t*-Bu, *t*-butyl.

^b A, colorless crystals; B, colorless viscous oil; C, colorless liquid.

^c Not solidified at -10°C.

^d No parent ion peak was detected.

Table III. Characterization of lactones

Lactone	R ^a	Shape ^b	mp	$\nu_{(C=O)}$	m/z (QM ⁺)
			°C	cm ⁻¹	
4a	Et	A	72 — 73.5	1775, 1730	317
	<i>i</i> -Pr	A	122 — 123.5	1775, 1750	331
	<i>t</i> -Bu	A	134.5—136	1775, 1750	345
4b	Et	A	48.5— 50	1770, 1735	317
	<i>i</i> -Pr	A	43 — 45	1780, 1745	331
	<i>t</i> -Bu	A	82.5— 84	1780, 1750	345
5a	Et	B	— ^c	1775, 1730	431
	<i>i</i> -Pr	A	91.5— 93	1780, 1735	459
	<i>t</i> -Bu	A	74 — 77	1775, 1750, 1735	(487) ^d

^a See Table II.^b A, colorless crystals; B, colorless viscous oil.^c Not solidified at -10°C.^d No parent ion peak was detected.Table IV. ¹H NMR parameters of telomers in CCl₄

Telomer	Proton	Symbol	Chemical shift δ /ppm		
			EMA	IPMA	TBMA
1	-CH ₃	A	2.19	2.16	2.09
	-CH ₂ -	M, N	4.24 3.51 (15.6) ^a	4.25 3.51 (15.6)	4.13 3.40 (15.0)
2a	-CH ₃	A	1.86	1.85	1.85
	-CH ₃	B	1.32	1.29	1.28
	-CH ₂ -	K, L	2.91 2.62 (14.4)	2.94 2.65 (15.0)	2.92 2.60 (14.4)
	-CH ₂ -	M, N	3.53 2.83 (15.6)	3.58 2.85 (15.0)	3.50 2.69 (15.6)
2b	-CH ₃	A	1.96	1.98	
	-CH ₃	B	1.54	1.54	
	-CH ₂ -	K, L	2.83 2.36 (15.0)	2.82 2.36 (15.0)	
	-CH ₂ -	M, N	3.59 2.88 (15.6)	3.62 2.92 (15.6)	
3a	-CH ₃	A	1.78	1.75	1.79
	-CH ₃	B	0.92	0.91	0.98
	-CH ₃	C	1.33	1.30	1.34
	-CH ₂ -	I, J	2.81 2.55 (13.8)	2.63	2.65
	-CH ₂ -	K, L	2.04	1.98	2.00
	-CH ₂ -	M, N	3.42 2.74 (15.0)	3.38 2.68 (15.0)	3.43 2.74 (15.0)

^a (), coupling const. J in Hz.

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Table V. ^1H NMR parameters of lactones in CCl_4

Lactone	Proton	Symbol	Chemical shift δ /ppm		
			EMA	IPMA	TBMA
4a	$-\text{CH}_3$	A	1.66	1.64	1.62
	$-\text{CH}_3$	B	1.32	1.32	1.34
	$-\text{CH}_2-$	K, L	2.73	2.69	2.64
	$-\text{CH}_2-$	M, N	3.36 3.05 (16.2) ^a	3.33 3.02 (15.6)	3.28 2.98 (15.0)
4b	$-\text{CH}_3$	A	1.67	1.64	1.66
	$-\text{CH}_3$	B	1.55	1.52	1.58
	$-\text{CH}_2-$	K, L	3.28 2.06 (14.4)	3.26 2.02 (15.0)	3.28 2.03 (14.4)
	$-\text{CH}_2-$	M, N	3.19	3.17	3.20
5a	$-\text{CH}_3$	A	1.59	1.56	1.54
	$-\text{CH}_3$	B	1.59	1.56	1.54
	$-\text{CH}_3$	C	1.20	1.18	1.19
	$-\text{CH}_2-$	I, J	1.91	1.87	1.87
	$-\text{CH}_2-$	K, L	2.45 2.17 (13.2)	2.45 2.14 (13.2)	2.50 2.18 (13.2)
	$-\text{CH}_2-$	M, N	3.69 2.86 (15.0)	3.68 2.83 (15.0)	3.63 2.86 (15.0)

^a (), coupling const. J in Hz.

Table VI. Ratios of dimeric diastereoisomers in the products

Monomer	Temp °C	% (2a, 2b)		% (4a, 4b)		% (2a+4a, 2b+4b)	
		2a	2b	4a	4b	2a+4a	2b+4b
EMA	50	83	17	—	—	83	17
	70	83	17	66	34	80	20
	90	86	14	52	48	79	21
IPMA	50	85	15	52	48	78	22
	70	83	17	61	39	77	23
	90	85	15	54	46	69	31
TBMA	50	100	0	48	52	65	35
	70	—	—	65	35	65	35
	90	—	—	53	47	53	47

action temperature as shown in Table I, as opposed to that of dimeric telomers. It is considered that the heat of telomerization results in the conversion of **2a** into **4a**, while that of **2b** into **4b**, through a cationic $\text{S}_{\text{N}}1$ mechanism as discussed in the previous paper.⁸ Consequently, the yield of (**2a** + **4a**) was

larger than that of (**2b** + **4b**) as shown in Table VI, and the production ratio of (**2b** + **4b**) to (**2a** + **4a**) increased with increasing bulkiness of the alkyl chain in the ester groups.

Reactivity of Telomers

Elimination Reaction by TEA. The reac-

tion of **1** with TEA gave **9** exclusively after 20 h in the following yields: R=Et, 64%⁸; *i*-Pr, 75%; *t*-Bu, 87%. But the recovery of **1** unexpectedly increased with increasing bulkiness of the alkyl chain in the ester group. In the reaction of **1** (R=*t*-Bu), elongation of the reaction time led to the decrease of **9** (R=*t*-Bu) as follows: 76%, 48 h; 52%, 72h, as opposed to the disappearance of starting material. Therefore, the resulting unsaturated compound **9** is considered to be liable to damage under these conditions. On the other hand, the elimination reaction of dimeric telomers with TEA was found to be labile and complicated with bulkiness of the alkyl chain in the ester group. In the reaction of **2a** (R=*t*-Bu), the expected elimination products, as well as unreacted material, were not entirely observed after 60 h.

Catalytic Reaction by Silica Gel. As shown in Tables VII and VIII, the lactonization

Table VII. Catalytic reactions of dimeric telomers with silica gel

Telomer	R ^a	Yield of products/%			Recovd.
		4a	4b	6a	%
2a	Et	87	—	—	13
	<i>i</i> -Pr	100	—	—	—
	<i>t</i> -Bu ^b	17	—	71	—
	—	—	—	94	—
2b	Et	—	100	—	—
	<i>i</i> -Pr	—	100	—	—

^a See Table II.

^b Reaction time, 24 h.

Table VIII. Catalytic reactions of *st*-trimeric telomers with silica gel

Telomer	R ^a	Yield of products/%		Recovd.
		5a	7a	%
3a	Et	69	—	31
	<i>i</i> -Pr	69	—	31
	<i>t</i> -Bu	—	96	—

^a See Table II.

of dimeric- and trimeric-telomers selectively proceeded by the catalytic action of silica gel in the following routes: **2a**→**4a**, **2b**→**4b**, and **3a**→**5a**. The IPMA telomers resembled EMA telomers in the reactivities of lactonization. On the other hand, the TBMA telomers were greatly subject to lactonization in comparison with other ones. Lactones resulted from the TBMA telomers were further transformed into **6a** or **7a** through carboxylation of the ester group directly bonded to a lactone ring.

Pyrolysis. Tables IX and X show the results of the pyrolysis of dimeric- and trimeric-telomers in the absence of solvent. Heating

Table IX. Pyrolysis of dimers

Dimer	R ^a	Temp	Yield of products/%		
		°C	4a	4b	6a
2a	Et	200	100	—	—
	<i>i</i> -Pr	200	99	—	—
	<i>t</i> -Bu	100 ^b	51 (49) ^c	—	—
		100 ^d	44	—	56
		100	25	—	74
		150	—	—	89
	200	—	—	— ^e	
4a	<i>t</i> -Bu	150	—	—	96
2b	Et	200	—	100	—
	<i>i</i> -Pr	200	—	74	—

^a See Table II.

^b Reaction time, 10 min.

^c Recovered.

^d Reaction time, 20 min.

^e Decomposed.

Table X. Pyrolysis of *st*-trimeric telomers at 200°C

Telomer	R ^a	Yield of products/%	
		5a	8a
3a	Et	100	—
	<i>i</i> -Pr	96	—
	<i>t</i> -Bu ^b	—	86

^a See Table II.

^b Heating temperature, 150°C.

of IPMA telomers, as well as EMA telomers, at 200°C exclusively gave the corresponding lactones by the same route as the catalytic lactonization with silica gel. On the other hand, heating of **2a** (R = *t*-Bu) at 100°C easily gave **4a** (R = *t*-Bu), which was transformed into **6a** as the reaction time proceeded. Furthermore, heating of **2a** at 150°C for 2 h gave only **6a**, via formation of **4a** (R = *t*-Bu), which was rapidly decomposed by heating at 200°C. Trimeric telomer **3a** (R = *t*-Bu) gave dibasic acid **8a** directly by heating at 150°C.

Mechanistic Consideration of Carboxylation

As shown in Tables IX and XI, some induced reactions of dimeric lactones were attempted to interpret mechanistically the processes of carboxylation of TBMA lactones. Under the conditions in Table XI, the formation of **6a** was only observed in the combination of **4a** (R = *t*-Bu) and *t*-butyl bromide. In the lactonization of **2a** (R = *t*-Bu) in closed pyrolysis, *t*-butyl bromide was simultaneously detected as an elimination product, which was identified with the use of an authentic sample by ¹H NMR. Therefore,

Table XI. Carboxylation of dimeric lactones in the presence of solvents^a

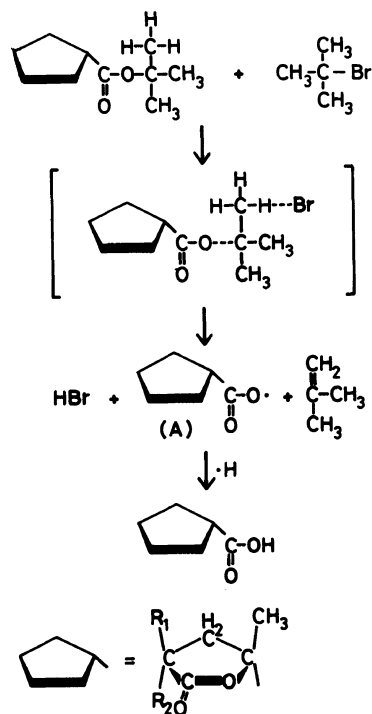
Lactone	R ^b	Solvent ^b	Temp	6a	
		ml			°C
4a	<i>t</i> -Bu	BTCM	20	90	0
	<i>t</i> -Bu	<i>t</i> -BuBr	10	Reflux	73
		BTCM	10		
	<i>t</i> -Bu	<i>t</i> -BuBr benzene	10	Reflux	20
			10		
	<i>t</i> -Bu ^c	<i>t</i> -BuBr benzene	10	Reflux	0
			10		
	<i>t</i> -Bu	<i>t</i> -BuBr	20	73	91
	<i>t</i> -Bu	BuBr	20	90	0
<i>i</i> -Pr	<i>t</i> -BuBr	20	73	0	

^a Sample, 0.5 g; Reaction time, 4 h.

^b *t*-Bu, *t*-butyl; *i*-Pr, isopropyl; BTCM, bromotrichloromethane.

^c An equimolar amount of 1,1-diphenyl-2-picrylhydrazyl was added.

the carboxylation of lactones during telomerization of TBMA is probably promoted by the catalytic action of *t*-butyl bromide formed as an elimination product during the lactonization of telomers. However, the carboxylation of **4a** (R = *t*-Bu) by *t*-butyl bromide was not observed in the presence of an equimolar



Scheme 1. Main route of carboxylation of TBMA lactones.

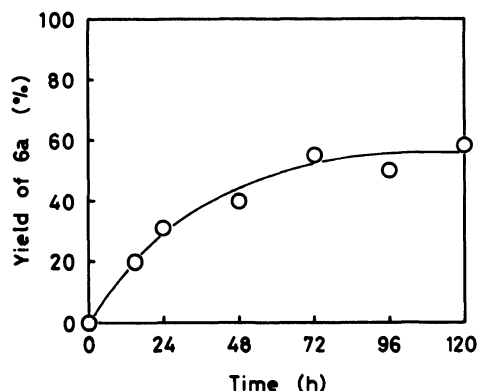


Figure 2. Time-conversion plots of carboxylation of dimeric lactone **4a** (R = *t*-Bu) in closed pyrolysis.

amount of 1,1-diphenyl-2-picrylhydrazyl as a radical scavenger. The carboxylation of TBMA lactones is considered to take place through a radical E2 mechanism as illustrated in Scheme 1. The formation of isobutene accompanied by that of carboxy radical (A) was confirmed by detection of the corresponding ion peak in the mass spectra of **2a** (R = *t*-Bu) and **4a** (R = *t*-Bu). The carboxylation of **4a** (R = *t*-Bu) was also observed in the absence of *t*-butyl bromide as shown in Table IX. Figure 2 shows the time-conversion plots of the carboxylation of **4a** (R = *t*-Bu) by heating at 100°C in a sealed tube. The yield of **6a** increased slowly to about 60% with the elapse of time and reached an equilibrium state. Therefore, the *t*-butyl ester group directly bonded to a lactone ring is considered to be greatly subject to carboxylation in comparison with the corresponding other alkyl ester groups.

REFERENCES

1. C. A. Barson, R. R. Mather, and J. C. Robb, *Trans. Faraday Soc.*, **66**, 2585 (1970).
2. D. A. J. Harker, R. A. M. Thomson, and I. R. Walters, *Trans. Faraday Soc.*, **67**, 3057 (1971).
3. C. A. Barson, A. R. Luxton, and J. C. Robb, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1666 (1972).
4. C. A. Barson, R. A. Batten, and J. C. Robb, *Eur. Polym. J.*, **10**, 97 (1974).
5. C. A. Barson and R. Ensor, *Eur. Polym. J.*, **13**, 53 (1977).
6. M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).
7. T. Kimura, T. Kodaira, and M. Hamashima, *Polym. J.*, **15**, 293 (1983).
8. T. Kimura and M. Hamashima, *Polym. J.*, **18**, 21 (1986).
9. T. Kimura, I. Nakanishi, and M. Hamashima, *Polym. J.*, **18**, 689 (1986).
10. T. Otsu and M. Kinoshita, "Kobunshi Gosei no Jikkenho (Experimental Methods of Polymer Synthesis)," Kagaku Dojin Co., Kyoto, 1976, pp 74—75.
11. R. Q. Brewster, C. A. Vanderwerf, and W. E. McEwen, "Unitized Experiments in Organic Chemistry," Van Nostrand Reinhold Co., New York, N. Y., 1970, pp 102—103.