Cyclopolymerization of ether dimers of α-(hydroxymethyl)acrylic acid and its alkyl esters: substituent effect on cyclization efficiency and microstructures

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Free-radical cyclopolymerization of six ether dimers of α-(hydroxymethyl)acrylic acid and its alkyl esters was kinetically investigated to evaluate the factors that control the cyclopolymerizability. A strong effect of ester substituent on cyclopolymerizability was observed and cyclization efficiency at 80°C increased in the following order: methyl, ethyl, isobornyl, t-butyl and adamantyl esters. That is, cyclization efficiency is found to be affected by the number of carbons linked to the central ester carbon (which defines the 'effective' bulkiness) rather than by the 'apparent' bulkiness, which encompasses the total mass or size of the whole substituent. Kinetic considerations of the temperature dependence of cyclization efficiency indicated that a strong contribution of the steric factor for bulky substituents (which inhibits intermolecular monomer addition) resulted in high cyclization efficiency despite a disadvantage in activation energy for cyclization. A linear relationship between the difference of activation energies ($E_c - E_i$) and the logarithm of the ratio of collision frequency factors ($\ln(A_c/A_i)$) observed for various esters led to recognition of an iso-efficiency point at which all esters show the same cyclization efficiency ($k_c/k_i = 2.0\,\mathrm{mol\,l^{-1}}$ at -45°C). This phenomenon is caused by the fact that both parameters change in proportion to the bulkiness of the ester substituent. The ether dimer of α-(hydroxymethyl)acrylic acid showed unexpectedly high cyclization efficiency (intermediate between secondary and tertiary esters) despite having the lowest substituent bulkiness. The kinetic parameters obtained showed some deviation from the linearity observed for the ester derivatives. The large A_c/A_i obtained was attributed to the capability of hydrogen-bond formation between acid groups, which causes a favourable conformation for cyclization. Microstructures of the cyclopolymers were investigated by observation of carbonyl carbon peaks in the ^{13}C nuclear magnetic resonance spectra. The peaks observed were assigned to four microstructures based on the combination of *trans/cis* configuration of the tetrahydropyran ring and racemic/meso configuration between the rings. Both the *trans* and racemic ratios increased with the bulkiness of the ester substituent. The values of $E_{cis} - E_{trans}$ and A_{trans}/A_{cis} for the t-butyl ester cyclopolymer indicated that *trans* formation is slightly favourable in both activation energy and steric factor, a result similar to that reported for the racemic/meso ratio in radical polymerization of some alkyl methacrylates. On the other hand, racemic formation between rings was suggested to be sterically unfavourable by the $A_{racemic}/A_{meso}$ ratio = 0.55. The glass transition temperatures for the cyclopolymers were found to be much higher than for the corresponding acrylates or methacrylates, and the thermal stabilities of some of the derivatives, especially the adamantyl compound, were also high.

(Keywords: cyclopolymerization; ether dimers; substituent effect)

INTRODUCTION

It is well known that the polymerization of 2,6-disubstituted 1,6-heptadienes proceeds through sequential intramolecular–intermolecular propagation to give soluble cyclopolymers under the appropriate conditions[1]. The cyclopolymers obtained are known to possess many advantageous properties such as high glass transition temperatures, excellent thermal stabilities and less shrinkage during polymerization than non-cyclic linear polymers. Major obstacles encountered in synthesizing cyclopolymers arise from imperfect cyclization, which leads to pendent-group unsaturation and crosslinking. For the successful synthesis of cyclopolymers, it is important to understand and control the factors that affect cyclization efficiency and configuration.

As shown in an early study on cyclopolymerization of α,α′-dimethylenepimelates (**2**)[2–4], diacrylates having the general formula shown in *Figure 1* should be excellent cyclomonomers, giving high polymerization rates and high cyclization efficiencies. Consideration of the polymerizability of monofunctional analogues of the cyclomonomers should provide an indication of the effect of the central X moiety on the reactivity of this type of cyclomonomer. For example, α-(alkoxymethyl)acrylates polymerize well, while α-(alkyl)acrylates other than the methacrylates do not polymerize at room temperature with radical initiators owing to steric inhibition[5].

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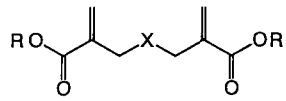

1 X = O
2 X = CH_2
3 X = $C(CN)_2$

Figure 1 General formula for cyclopolymerizable diacrylates

Therefore, ether dimers (having oxygen atom as the X moiety, **1**) are expected to show higher overall polymerizability than **2**.

We have been investigating radical cyclopolymerization of some ether dimers of α-(hydroxymethyl)acrylates (**1**)[6–8] that give novel cyclopolymers containing tetrahydropyran units in the polymer backbone as confirmed by ^{13}C nutation n.m.r. spectroscopy[9]. Especially interesting is the ether dimer containing bulky t-butyl ester groups, which cyclopolymerized spontaneously in bulk at >120°C to give soluble, high-molecular-weight polymer[7]. Stansbury also reported the effect of the bulky t-butyl ester in raising cyclization efficiency[10]. The enhancement of cyclization by bulky substituents was also observed in the cyclopolymerization of *N*-allylacrylamide and *N*-allylmethacrylamide, which yielded almost completely cyclized polymers for the *N*-t-butyl derivatives[11,12]. Substituent effects on cyclization efficiency observed to date have been attributed qualitatively to steric effects, which either inhibit intermolecular monomer addition or promote intramolecular cyclization. However, the substituent effect has not been fully evaluated and understood. In addition, although the kinetic approach is essential for the quantitative estimation of cyclopolymerizability, few examples of kinetic evaluations have been reported concerning acrylic dimers.

In addition to the kinetics of cyclopolymerization, we have also evaluated ring and inter-ring configurations for the diacrylate ethers. Tacticity of vinyl polymers is well known to influence physical properties. For cyclopolymerizations, much attention has been given to the elucidation of the ring formation mechanism and cyclopolymer microstructure. To our knowledge, however, few studies on the configuration along the cyclopolymer backbones have been reported, mainly due to the complexity of cyclopolymer structures, which may include residual double bonds, different ring sizes as well as intra- and inter-ring configurations. Cyclopolymers containing a single ring size and few residual double bonds are therefore of considerable interest for microstructure study.

We describe here the results to date of the kinetic study on the cyclopolymerization of monomers shown in *Figure 2* and characterization of microstructures of the resulting cyclopolymers.

EXPERIMENTAL

Overall synthetic procedures for the ether dimers investigated here are illustrated in *Figure 3*. The ethyl ester (**1b**) and t-butyl ester (**1d**) ether dimers were prepared using previously published procedures[6–8]. The adamantyl ester ether dimer (**1e**) was prepared by the procedure reported recently[13] and the isobornyl ester ether dimer (**1c**) was prepared in a similar manner. The methyl ester ether dimer (**1a**) and carboxylic acid ether dimer (**1f**) were derived from the t-butyl ester **1d** according to the procedure shown in *Figure 3*. Isobornyl acrylate (manufactured by Kyoeisha Yushi Chemical Industry Ltd) and adamantyl acrylate (manufactured by Hakusui Chemical Industry Ltd) were kindly supplied from Toagosei Chemical Industry Co. Ltd. Paraformaldehyde, 1,4-diazabicyclo[2.2.2]octane (DABCO), t-butyl alcohol and trifluoroacetic acid were purchased from Aldrich Chemical Co. and used as obtained. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol before use. Other reagents and solvents were used as obtained. ^1H and ^{13}C n.m.r. spectra were obtained on a Bruker AC-300 spectrometer. Thermal transitions were measured with a DuPont 9900 thermal analyser using a model 910 d.s.c. cell at a heating rate of 10°C min^{-1} under nitrogen flow.

*Synthesis of ethyl ester ether dimer (**1b**)*

To a 250 ml three-necked round-bottomed flask were added ethyl acrylate (150 g, 1.5 mol), paraformaldehyde (45 g, 1.5 mol) and DABCO (9.8 g, 4.8 wt%). This solution was stirred at 95°C for 4 days. After adding 250 ml of n-hexane, the mixture was washed three times with 100 ml of 3% HCl, and then with 100 ml of water. The organic layer was separated and evaporated under reduced pressure to give 120.6 g of crude **1b** (yield 66%). Repeated vacuum distillation gave pure **1b** as a clear liquid in 44% yield. ^1H n.m.r. ($CDCl_3$): $\delta = 6.29$ (s, 1H), 5.90 (s, 1H), 4.26 (s, 2H), 4.20 (t, 2H) and 1.30 ppm (t, 3H). ^{13}C n.m.r. ($CDCl_3$): $\delta = 165.6, 137.5, 125.4, 69.0, 60.7$ and 14.3 ppm.

*Synthesis of t-butyl ester ether dimer (**1d**)*

To a 250 ml three-necked round-bottomed flask were added t-butyl acrylate (137.7 g, 1.08 mol), paraformaldehyde (32.3 g, 1.08 mol), DABCO (5.38 g, 2.9 wt%) and t-butyl alcohol (8.61 g, 4.7 wt%). The mixture was stirred at 95°C for 4 days. After adding 200 ml of CH_2Cl_2, the mixture

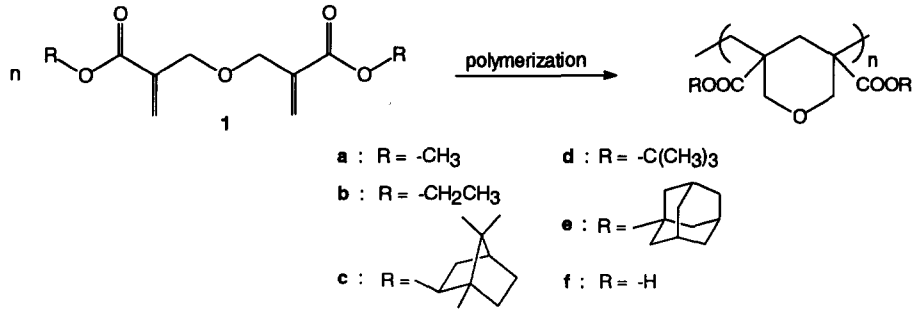

Figure 2 Cyclopolymerization of ether dimers of α-(hydroxymethyl)acrylic acid and its alkyl esters

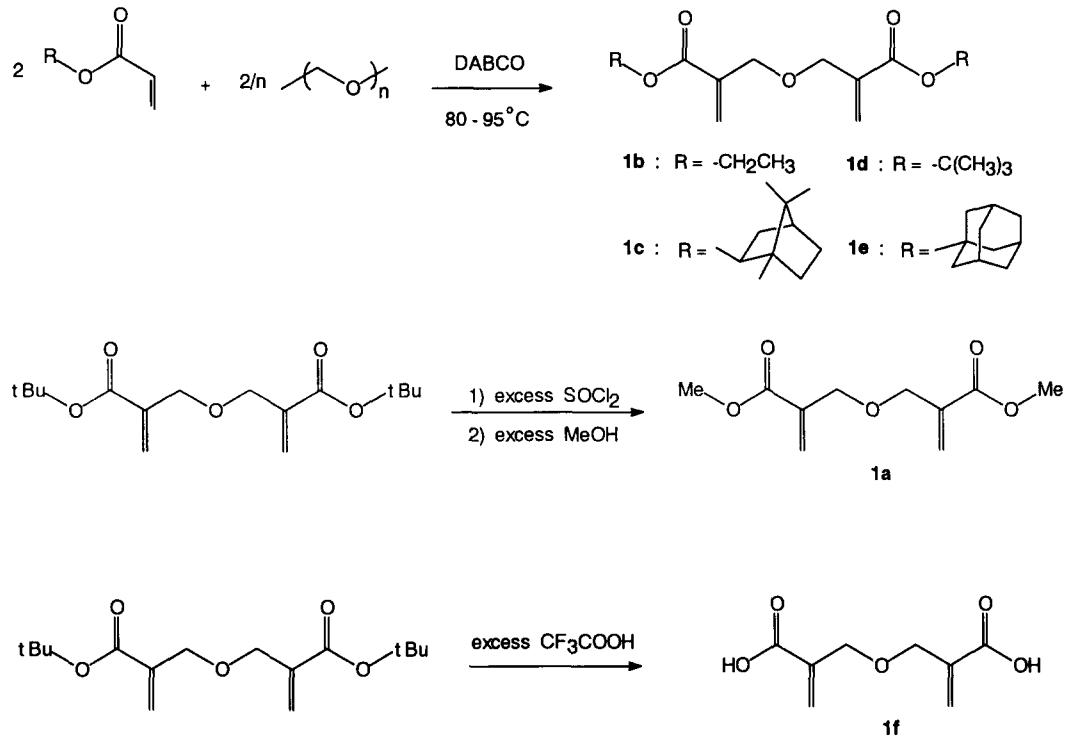

Figure 3 Synthesis of ether dimers of α-(hydroxymethyl)acrylic acid and its alkyl esters

was washed three times with 100 ml of 3% HCl, and then with 100 ml of water. The organic layer was separated and evaporated under reduced pressure to give 134.5 g of crude **1d** (yield 84%). Vacuum distillation gave the pure **1d** as a clear liquid in 74% yield. ^{1}H n.m.r. ($CDCl_3$): $\delta = 6.21$ (s, 1H), 5.82 (s, 1H), 4.21 (s, 2H) and 1.50 ppm (s, 9H). ^{13}C n.m.r. ($CDCl_3$): $\delta = 165.1$, 138.7, 124.5, 80.9, 69.0 and 28.1 ppm.

Synthesis of isobornyl ester ether dimer (1c)

To a 250 ml three-necked round-bottomed flask were added isobornyl acrylate (104.0 g, 0.5 mol), paraformaldehyde (15.0 g, 0.5 mol), DABCO (7.5 g, 4.8 wt%) and t-butyl alcohol (30.0 g, 19.2 wt%). The mixture was stirred at 80°C for 7 days. The resulting solution was poured into 1400 ml of methanol and placed in a refrigerator at −12°C overnight. The precipitant was filtered and dried *in vacuo* to give pure **1c** in 45% yield; m.p. 54°C. ^{1}H n.m.r. ($CDCl_3$): $\delta = 6.27$ (s, 1H), 5.87 (s, 1H), 4.75 (t, 1H), 4.24 (s, 2H), 1.7–1.9 (m, 1H), 1.57 (m, 1H), 1.05–1.25 (m, 2H), 1.02 (s, 3H) and 0.86 ppm (s, 6H). ^{13}C n.m.r. ($CDCl_3$); $\delta = 165.0$, 137.5, 125.2, 81.2, 68.9, 48.8, 46.9, 45.0, 38.7, 33.6, 27.0, 20.1, 19.9 and 11.5 ppm.

Synthesis of methyl ester ether dimer (1a)

To a 500 ml one-necked round-bottomed flask were added t-butyl ester ether dimer **1d** (54.8 g, 0.184 mol), thionyl chloride (437.6 g, 3.68 mol) and five drops of *N,N*-dimethylformamide. The mixture was stirred at 40°C for 2 days. The mixture was evaporated *in vacuo* to give crude acid chloride, which was then mixed with 200 ml of dried methanol and stirred at 40°C for 2 days. The mixture was evaporated under reduced pressure to give crude **1a** in 95% yield. The crude **1a** was diluted with 100 ml of CH_2Cl_2 and extracted three times with 50 ml of 0.5 M KOH. The organic layer was separated, evaporated and distilled *in vacuo*. The product was purified by recrystallization from n-hexane twice at −12°C to give pure **1a** in 45% yield; m.p. 47–48°C. ^{1}H n.m.r. ($CDCl_3$): $\delta = 6.32$ (s, 1H), 5.92 (s, 1H), 4.27 (s, 2H) and 3.77 ppm (s, 3H). ^{13}C n.m.r. ($CDCl_3$): $\delta = 166.2$, 137.0, 126.0, 68.9 and 51.8 ppm.

Synthesis of carboxylic acid ether dimer (1f)

To a 250 ml one-necked round-bottomed flask were added t-butyl ester ether dimer **1d** (57.0 g, 0.191 mol) and trifluoroacetic acid (62.7 g, 0.550 mol). After mixing at ambient temperature for 24 h, the precipitate formed was filtered and washed with diethyl ether. The filter cake was dried *in vacuo* to give white crystals of **1f** in 97% yield; m.p. 166°C. ^{1}H n.m.r. (DMSO-d_6): $\delta = 6.18$ (s, 1H), 5.85 (s, 1H) and 4.17 ppm (s, 2H). ^{13}C n.m.r. (DMSO-d_6): $\delta = 166.7$, 137.9, 124.8 and 68.3 ppm.

Typical polymerization conditions

To a 50 ml three-necked round-bottomed flask equipped with a small magnetic stirring bar were added ether dimer (4 g) and solvent as indicated in *Table 1*. After heating for 15 min in an oil bath preheated to the temperature indicated in *Table 1*, the mixture was subjected to nitrogen deaeration, which was continued during the polymerization. Small amounts of AIBN were added when polymerization was slow. On the other hand, benzoquinone was added as retarder when polymerization was too fast. The resulting polymer solution was poured into the precipitant indicated below. The precipitate was filtered and dried *in vacuo*. The polymer obtained was purified by reprecipitation at least one more time before n.m.r. measurements. Polymer conversion was determined from the product weight after the first precipitation. The fraction of cyclized units in the cyclopolymer was calculated from the intensity ratio of double-bond protons (5.6–6.5 ppm) to the other protons (0.5–5.0 ppm) in the ^{1}H n.m.r. spectra of purified

Table 1 Results of low-conversion cyclopolymerization of ether dimers (*Figure 1*, X = O, R as shown)

Substituent R	Feed ($mol\ l^{-1}$) [M]	[I][a]	[R][b]	Solvent	Temp. (°C)	Time (min.)	Conv. (%)	f_c[c]	k_c/k_1[d]
Methyl	0.6	0.016		Benzene	40	135	2.3	0.889	9.6
	0.6	0.0039			48	140	4.7	0.902	11.0
	0.6	0.0006			65	60	2.7	0.913	12.6
	0.6	0.0004			80	14	3.1	0.936	16.7
Ethyl	0.42	0.0003		Toluene	80	20	3.5	0.961	20.7
	1.27				80	30	5.0	0.880	18.7
	2.25				80	30	2.3	0.808	18.9
	1.27	0.0019		Xylene	60	30	7.4	0.863	16.0
	1.27				80	15	2.7	0.889	20.3
	1.27				80	130	12.0	0.883	21.2
	1.27				100	25	5.8	0.905	24.2
	1.27		0.007		120	40	5.1	0.918	28.4
	1.27		0.014		140	20	2.2	0.889	38.4
Isobornyl	0.5			Toluene	80	45	8.8	0.982	54.4
	0.9				80	15	6.1	0.968	55.1
	1.27				80	15	16.3	0.951	49.1
	1.27		0.0007		80	160	9.3	0.950	47.7
	2.0		0.0028		80	40	3.1	0.892	33.1
	1.27				50	150	5.0	0.918	28.5
	1.27				66	30	9.3	0.935	36.7
	1.27		0.0067		93	420	11.1	0.958	57.3
t-butyl	0.42	0.0002		Toluene	80	40	13.8	0.990	83.2
	0.83	0.0015			80	20	17.8	0.981	85.6
	1.27				80	90	11.9	0.972	88.2
	1.27				80	75	2.9	0.973	91.7
	1.70				80	15	15.2	0.964	90.0
	2.25				80	90	4.1	0.947	80.4
	3.26				80	20	8.7	0.906	62.8
	1.27				50	900	9.1	0.949	47.3
	1.27				65	180	2.4	0.957	56.6
	1.27				95	12	11.4	0.978	113
Adamantyl	0.42	0.0006		Toluene	80	10	11.8	0.987	63.6
	1.27				80	50	2.5	0.974	95.2
	1.27	0.0035			65	17	2.9	0.963	66.1
H	0.42	0.0001		DMSO	80	15	19.8	0.988	69.4
	0.83				80	140	16.3	0.983	95.6
	1.27				80	65	6.1	0.964	68.0
	1.79				80	20	4.8	0.952	71.0
	1.27	0.0007			60	25	7.0	0.953	51.5
	1.27		0.007		110	270	17.9	0.974	95.2
	1.27		0.011		130	50	8.4	0.975	99.1

[a] AIBN
[b] Benzoquinone
[c] Calculated from the intensity ratio in ^1H n.m.r. spectra
[d] Calculated from equations (1) and (2)

samples. The following solvents and precipitants were used for the purification of cyclopolymers: methylene chloride/n-hexane for methyl, ethyl and t-butyl esters (**1a**, **1b** and **1d**); methylene chloride/acetone for isobornyl and adamantyl esters (**1c** and **1e**); and methanol/acetone for the carboxylic acid derivative (**1f**).

Hydrolysis of cyclopolymers

For the ^{13}C n.m.r. study of the microstructure of the cyclopolymers, hydrolysis of the ester groups was carried out according to the following procedures. The methyl and ethyl ester polymers could not be completely hydrolysed with acid or base catalysis.

t-Butyl or adamantyl ester cyclopolymer. First, 0.25 g of cyclopolymer was dissolved in 4 g of trifluoroacetic acid and stirring was continued overnight at ambient temperature. The precipitate formed was filtered, washed with diethyl ether and dried *in vacuo*.

Isobornyl ester cyclopolymer. A mixture of 0.3 g of cyclopolymer, 1.5 g of trifluoroacetic acid and 3.0 g of conc. HCl was stirred at 60°C for 4 h. The resulting solution was evaporated under reduced pressure and the residue dried *in vacuo*.

RESULTS AND DISCUSSION

Synthesis and characterization of ether dimers

Ethyl, t-butyl, isobornyl and adamantyl ester ether dimers were successfully synthesized according to the procedure published before, although higher temperatures were needed. t-Butyl alcohol (5–20 wt%) was added for non-polar acrylates (t-butyl, isobornyl and adamantyl esters) in order to improve homogeneity of the reaction mixture and facilitate conversion. The conversions of acrylates to ether dimers were usually 60–90% as determined by g.c. or ^{1}H n.m.r. The purities of the ether dimers after distillation or recrystallization were >98% based on the results of ^{1}H n.m.r. analysis. The carboxylic acid ether dimer was easily obtained in good yield (>95%) from the t-butyl ester by mixing with trifluoroacetic acid, and no observable impurities were seen in the ^{13}C n.m.r. spectrum. The methyl ester ether dimer was derived from the t-butyl ester via the diacid chloride to avoid use of methyl α-(hydroxymethyl)acrylate, which was previously found to be a skin irritant.

Table 2 shows the chemical shifts of vinyl carbons for each ether dimer synthesized here together with those published for some ester derivatives. As previously described for allyl monomers[14], chemical shifts of vinyl carbons are considered to reflect or correlate with their reactivity through polarization effects. That is, electron-withdrawing substituents that enhance polymerizability cause a decrease in chemical-shift difference between the two vinyl carbon peaks. Although upfield shifts of the vinyl methylene carbon for the ether dimers having bulky substituents have been reported previously[10], the systematic change of the chemical-shift difference $\Delta\delta$ shown in *Table 2* allows consideration of the substituent effect. The values of $\Delta\delta$ clearly show that chemical shift is not affected by the 'apparent' bulkiness (total mass of the whole substituent) but rather by the number of carbons attached to the carboxyester carbon; that is, by its 'effective' bulkiness in terms of steric interactions. The chemical shift of the vinyl carbons arises from both inductive effects and through-space shielding effects of the ester substituent. While the former is related to energetic factors in polymerization, the latter correlates to the steric factor. Therefore, the larger values of $\Delta\delta$ observed for bulky substituents may lead to lower polymerizability due to lower propagation enthalpy or steric hindrance. In fact, the reverse effect on polymerization was observed for the bulkiest adamantyl ester as previously reported[13]. Moreover, the occurrence of spontaneous polymerization during monomer synthesis forced a lowering of reaction temperature (from 95 to 80°C). This fact is explained by a reduction in the termination reaction caused by steric hindrance of the bulky substituent, as suggested also in the polymerization of t-butyl fumarate[15] and adamantyl methacrylate[16]. In terms of cyclopolymerizability, however, more emphasis is given to the relative contributions of substituent effects to cyclization *versus* monomer addition reactions. Further consideration of substituent effects will be given later, based on the experimental results on cyclopolymerizations described next.

Table 2 ^{13}C n.m.r. shifts of ether dimers in ($CDCl_3$)

Ester substituent		Chemical shift (ppm)		
		-C=	$=CH_2$	$\Delta\delta$
	Methyl	137.0	126.0	11.0
	Methyl[a]	136.9	126.0	10.9
Primary	Ethyl	137.5	125.4	12.1
	Ethyl[a]	137.2	125.5	11.7
	n-Butyl[a]	137.2	125.5	11.7
	Isobutyl[a]	137.2	125.6	11.6
Secondary	Isobornyl	137.5	125.2	12.3
	Trimethylcyclohexyl[a]	137.6	125.2	12.4
Tertiary	t-Butyl	138.7	124.5	14.2
	t-Butyl[a]	138.6	124.4	14.2
	Adamantyl[b]	138.8	124.5	14.3
Carboxylic acid[c]		137.9	124.8	13.1

[a] Published data from ref. 10
[b] Published data from ref. 13
[c] Solvent DMSO-d_6

Cyclopolymerization

In most cases, polymerization of ether dimers proceeded spontaneously without initiator. The results of the cyclopolymerizations carried out are listed in *Table 1*. Conversions were kept low for the purpose of kinetic evaluation. In the cyclopolymerization of ether dimers, the reaction rate of intermolecular monomer addition R_i and intramolecular cyclization R_c shown in *Figure 4* are expressed by equations (1) and (2):

$$R_i = k_i[P^*]2[M] \quad (1)$$

$$R_c = k_c[P^*] \quad (2)$$

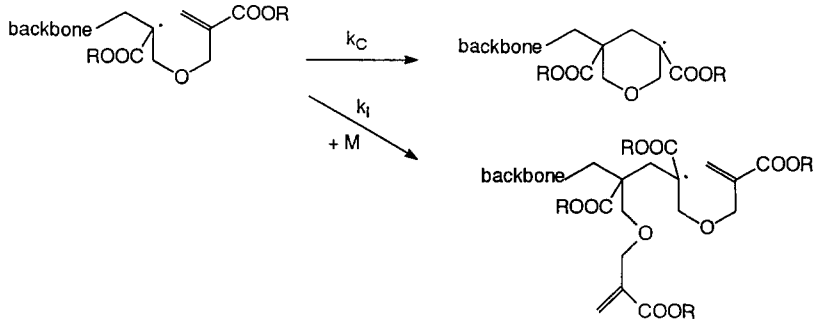

Figure 4 Intramolecular cyclization and intermolecular monomer addition

[P•] symbolizes concentration of uncyclized radical. The ratio R_i/R_c is accordingly given by:

$$R_i/R_c = 2k_i[M]/k_c \quad (3)$$

When polymerization conversion is kept low, R_i/R_c can be calculated from f_c (the fraction of cyclized units in cyclopolymers formed) using the relationship:

$$R_i/R_c = (1-f_c)/f_c \quad (4)$$

A plot of R_i/R_c *versus* [M] should give a straight line with a slope of $2k_i/k_c$ according to equation (3). *Figure 5* shows the plots for the cyclopolymerization of ether dimers carried out at 80°C. All plots showed a linear relationship, although small deviations were observed at high monomer concentrations for isobornyl and t-butyl esters. Two tertiary alkyl esters (t-butyl and adamantyl) fell on the same straight line, which means virtually identical cyclization efficiencies. As shown in *Figure 5*, deviation from linearity becomes evident at concentrations above 1.27 mol l^{-1} (for isobornyl ester) or 2.25 mol l^{-1} (for t-butyl ester). These concentrations correspond to 50–70% volume fraction of the monomers. The reason for this deviation is not clear, although some type of interaction between monomers and propagating polymers at higher monomer concentration might be responsible. In conclusion, linear relationships between R_i/R_c and monomer concentrations were observed for all ether dimers investigated except for two at high monomer concentration, with the result that the validity of equation (3) at a concentration below 1.27 mol l^{-1} was confirmed.

The values of k_c/k_i calculated from the plots in *Figure 5* (experimental data at a volume fraction above 0.6 were omitted) are listed in *Table 3*. Cyclization efficiency was clearly found to increase with the bulkiness of the substituents. Careful observation of the k_c/k_i values listed, however, leads to the following conclusions. First, the value of k_c/k_i depends on the number of carbons that are linked to the carboxyester carbon (effective bulkiness as mentioned before), rather than on the apparent bulkiness of the whole substituent; compare the value for

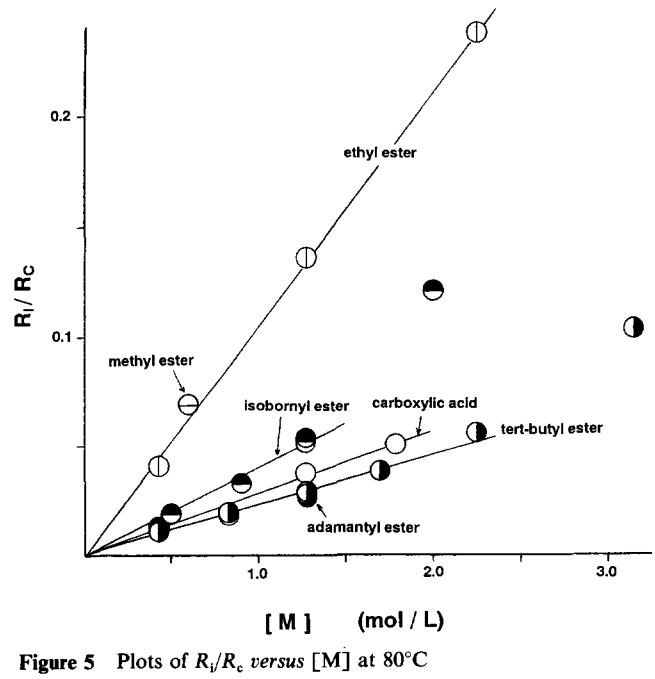

Figure 5 Plots of R_i/R_c *versus* [M] at 80°C

Table 3 Kinetic parameters estimated

Substituent R	k_c/k_i at 80°C (mol l^{-1})	A_c/A_i (mol l^{-1})	E_c-E_i (kcal mol^{-1})
Methyl	16.7[a]	807	2.75
Ethyl	19.0	1110	2.81
Isobornyl	50.0	11 700	3.87
T-butyl and adamantyl	87.0	94 100	4.89
H	70.5	2810	2.63

[a] One-point data calculated from equation (1)

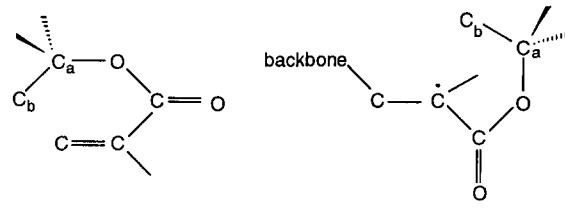

Figure 6 Through-space shielding effects of ester substituents

Table 4 Solvent effect on cyclization efficiency in the cyclopolymerization of ethyl ester ether dimer at 60°C and 1.27 mol l^{-1}

Solvent	Conv. (%)	f_c
Benzene	3.9	0.84
Toluene	2.6	0.85
Xylene	7.4	0.86
Methyl ethyl ketone	6.4	0.86
Tetrahydrofuran	5.0	0.86
Chloroform	9.4	0.88
Acetonitrile	4.0	0.87
Dimethylsulfoxide	13.0	0.83
Ethanol	9.1	0.84

the apparently more bulky isobornyl ester with that for the effectively more bulky t-butyl ester. This implies that the C_b carbon shown in *Figure 6* plays an important role in the substituent effect on cyclization efficiency. That is, vinyl carbons of monomer or propagating radical are considered to be sterically shielded mainly by C_b carbons. Secondly, the carboxylic acid monomer shows an unexpectedly high cyclization efficiency despite the lowest bulkiness of the series. This result suggests that specific interactions among carboxylic acid groups and solvent molecules can influence the cyclization efficiency. The examination of solvent effect was carried out for the ethyl ester ether dimer, with the results listed in *Table 4*. Clearly, differences in solvent caused only minor changes in the f_c value. We conclude that cyclization efficiency is not markedly affected by the solvent used for the radical cyclopolymerization of alkyl ester ether dimers.

Studies on the temperature dependence of cyclization efficiency gave useful kinetic information on the cyclization and monomer addition steps. Arrhenius equations for the two reactions are combined to give the relationship:

$$\ln(k_c/k_i) = \ln(A_c/A_i) - (E_c-E_i)/RT \quad (5)$$

Plots of $\ln(k_c/k_i)$ *versus* $1000/T$ for the ether dimers are shown in *Figure 7*. The methyl ester was polymerized at 0.6 mol l^{-1} while all the other esters and carboxylic acid monomers were polymerized at 1.27 mol l^{-1}. All plots showed linear relationships, which imply that reversible

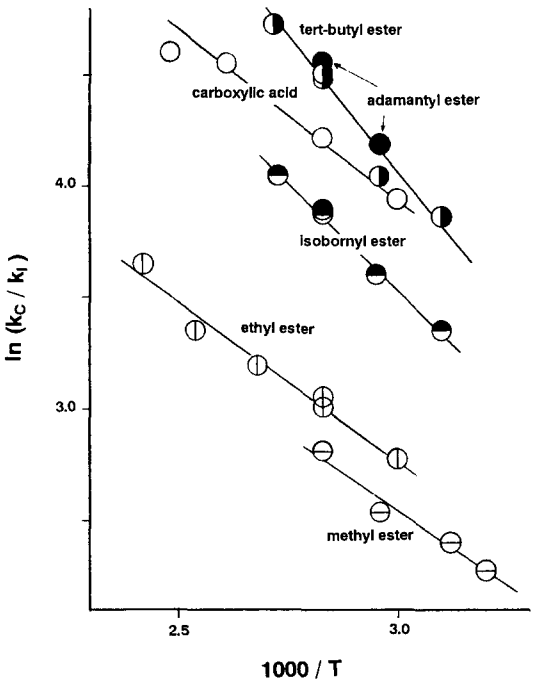

Figure 7 Plots of $\ln(k_c/k_i)$ *versus* $1000/T$

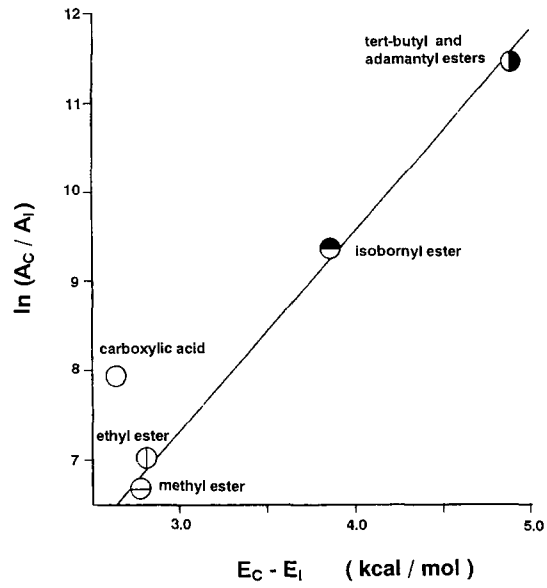

Figure 8 Plots of $\ln(A_c/A_i)$ *versus* E_c-E_i

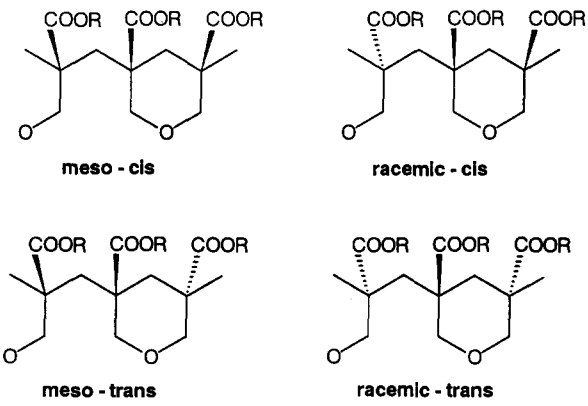

Figure 9 Possible microstructures of cyclopolymers from ether dimers

intermolecular monomer addition (as reported for acrylic and methacrylic anhydride[17]) is not important in this cyclopolymerization. Differences of activation energies E_c-E_i and ratios of collision frequency factors A_c/A_i were estimated as listed in *Table 3*. Clearly, both E_c-E_i and A_c/A_i values increase with the effective bulkiness of the ester substituent, except for the carboxylic acid derivative, which showed an unexpectedly high A_c/A_i value in spite of having the lowest bulkiness. The increase of A_c/A_i with bulkiness of the substituent implies that increasing substituent size sterically inhibits intermolecular monomer addition much more than intramolecular cyclization. On the other hand, the increase of E_c-E_i with bulkiness can be explained by hindrance of transition-state orbital overlap. As a result, the advantage in the steric factor dominates over the disadvantage in activation energy such that the bulkiness of the substituent contributes to the improved cyclization efficiency. The fact that a larger A_c/A_i value was obtained for the carboxylic acid derivative in comparison to methyl or ethyl esters may be explained by a restricted favourable conformation of the uncyclized radical with respect to the residual double bond caused by hydrogen bonding between carboxylic acid groups. This ordered conformation would raise the A_c value significantly.

Values of both A_c/A_i and E_c-E_i changed in proportion to the effective bulkiness of the ester substituent, with the result that a linear relationship was observed between $\ln(A_c/A_i)$ and E_c-E_i, with the exception of carboxylic acid as shown in *Figure 8*. The slope and intercept of this line give critical values for T and k_c/k_i ($k_c/k_i=2.0$ at -45°C) according to the transformed equation (5) shown in equation (6):

$$\ln(A_c/A_i)=\ln(k_c/k_i)+(E_c-E_i)/RT \qquad (6)$$

Theoretically, all alkyl ester dimers should show the same k_c/k_i value at -45°C and the order of cyclization efficiency for various esters should be reversed below this temperature. This temperature is a transition point at which the controlling steric factor is replaced by the energetic factor. The occurrence of an iso-efficiency temperature is considered to be a general phenomenon for cyclopolymerizations, at least as far as substituent effects on cyclization efficiency are concerned. Viewed in this light, the enhancement of cyclization efficiency observed for bulky ester derivatives is due to the low iso-efficiency temperature for this family of monomers.

Microstructures of the cyclopolymers

The microstructures of interest involve intra- and inter-ring and repeat-unit configurations represented by the four structures shown in *Figure 9*. *Cis/trans* isomerization across the ring was reported to have a larger effect on chemical-shift differences than meso/racemic isomerization through the methylene bridge for poly(1,5-hexadiene)[18]. Therefore, it is reasonable to expect four peaks in the ^{13}C n.m.r. spectrum, which correspond to the four structures in *Figure 9* for the substituent on the backbone quaternary carbon. In addition, the assumption of Bernoullian behaviour, which is valid in a normal free-radical polymerization, gives the relationship in equation (7) for the probabilities (or peak intensity ratios in n.m.r. spectrum) of the four structures:

$$P_{\text{racemic-}trans}/P_{\text{meso-}trans}=P_{\text{racemic-}cis}/P_{\text{meso-}cis} \qquad (7)$$

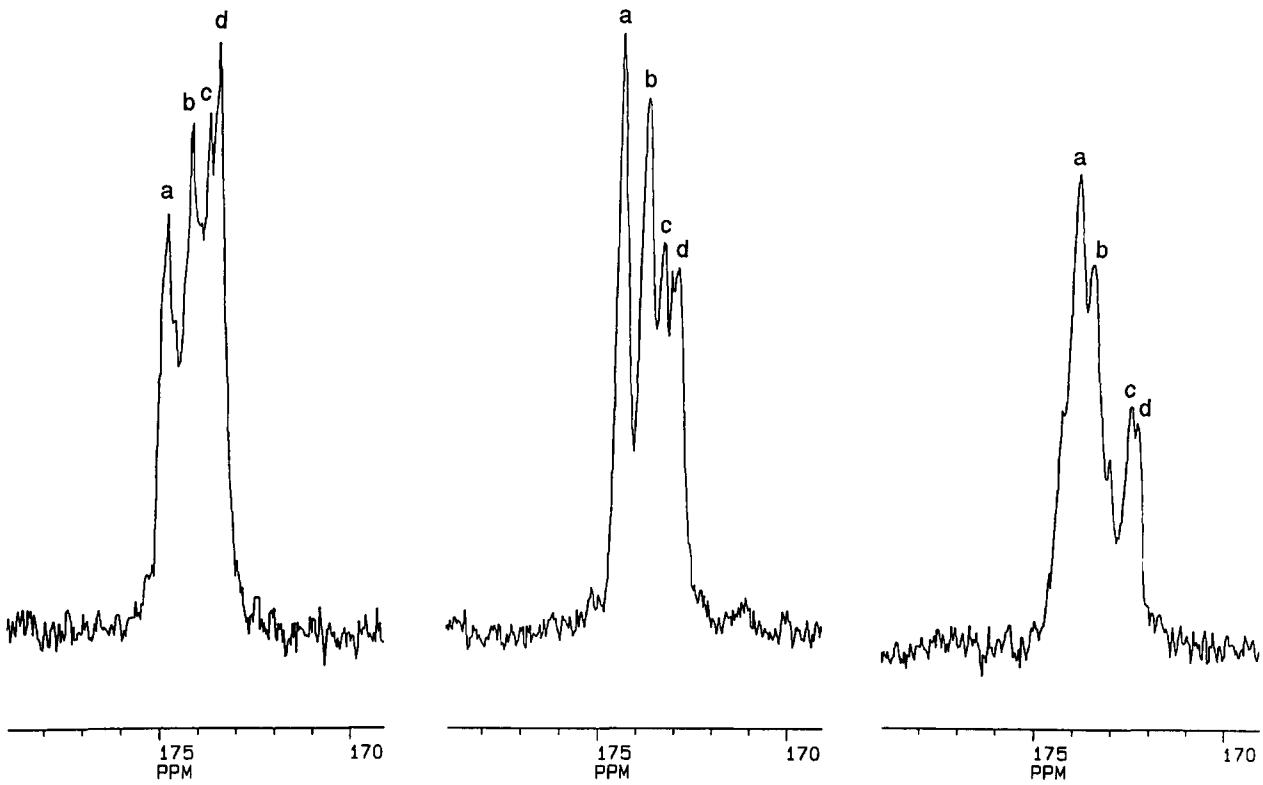

Figure 10 ^{13}C n.m.r. spectra of cyclopolymer carbonyl regions: methyl ester (left), ethyl ester (middle), t-butyl ester (right)

Figure 10 shows typical ^{13}C n.m.r. spectra of the carbonyl region for methyl, ethyl and t-butyl ester cyclopolymers. In all cases, the four major peaks expected from the above considerations are seen with reasonable intensity ratios (denoted by a, b, c and d in the spectra), although complicated by minor peaks due to longer-range structural-unit effects. The four peaks were assigned to racemic-*trans*, meso-*trans*, racemic-*cis* and meso-*cis* structures for a–d, respectively. *Table 5* gives the chemical-shift data for the three esters. Consistent changes of the chemical shifts and chemical-shift differences between peaks support these peak assignments. Further support for the validity of these assignments is given by comparison of the spectrum of the *gem*-dinitrile-containing cyclopolymer derived from diacrylate **3** (shown in *Figure 1*), for which *cis*-dominated configurations were confirmed by the peak ratios in the cyano carbon region[19]. *Figure 11* shows the carbonyl regions of the ^{13}C n.m.r. spectra for both methyl ester polymers. The assignments made for the ether cyclopolymers given here are in good agreement with those for the dicyano-containing cyclopolymer. *Figure 10* clearly shows that both *trans* and racemic configurations increase with the bulkiness of the ester substituent. The fraction of *trans* configuration for the t-butyl ester polymer was estimated to be ca. 80% based on peak intensity ratios, with a slight decrease with an increase in polymerization temperature as shown in *Table 6*. The data on the temperature dependence of the *trans/cis* ratio allowed the calculation of kinetic parameters for *trans* and *cis* formation. The difference of activation energies ($E_{cis}-E_{trans}$) and the ratio of collision frequency factors (A_{trans}/A_{cis}) were estimated to be 0.51 kcal mol^{-1} and 1.9, respectively, from the plot shown in *Figure 12* by using the equation:

$$\ln(k_{trans}/k_{cis})=\ln(A_{trans}/A_{cis})+(E_{cis}-E_{trans})/RT \quad (8)$$

These values imply that the *trans* addition of incoming monomer to the terminal cyclized radical is slightly favourable compared to *cis* addition as illustrated in *Figure 13*. Similar behaviour has been observed for the tacticity of poly(alkyl methacrylate)s prepared under free-radical conditions in which usually 70–90% of racemic configurations are obtained[16]. The disadvantage

Table 5 Chemical shifts of multiple peaks in carbonyl region of ^{13}C n.m.r. spectrum

	trans			*cis*			
	racemic *a*	meso *b*	$\Delta\delta^a$	racemic *c*	meso *d*	$\Delta\delta^b$	$\Delta\delta_{trans-cis}{}^c$
Methyl	174.8	174.1	0.7	173.7	173.4	0.3	0.9
Ethyl	174.4	173.8	0.6	173.3	172.9	0.4	1.0
t-Butyl	173.9	173.5	0.4	172.5	172.3	0.2	1.3

[a] $a-b$
[b] $c-d$
[c] $(a+b-c-d)/2$

Table 6 Temperature dependence of *trans/cis* and racemic/meso ratio for t-butyl ester cyclopolymer

Polymerization temp. (°C)	*trans/cis*[a]	racemic/meso[b]
50	81.0/19.0	67.2/32.8
80	79.8/20.2	64.6/35.4
110	79.1/20.9	63.4/36.6
140	78.0/22.0	60.1/39.9

[a] Calculated from intensity ratio (a+b)/(c+d) of ^{13}C n.m.r. spectrum shown in *Figure 10* for neat cyclopolymer
[b] Calculated from intensity ratio e/f of ^{13}C n.m.r. spectrum shown in *Figure 15* for hydrolysed cyclopolymer

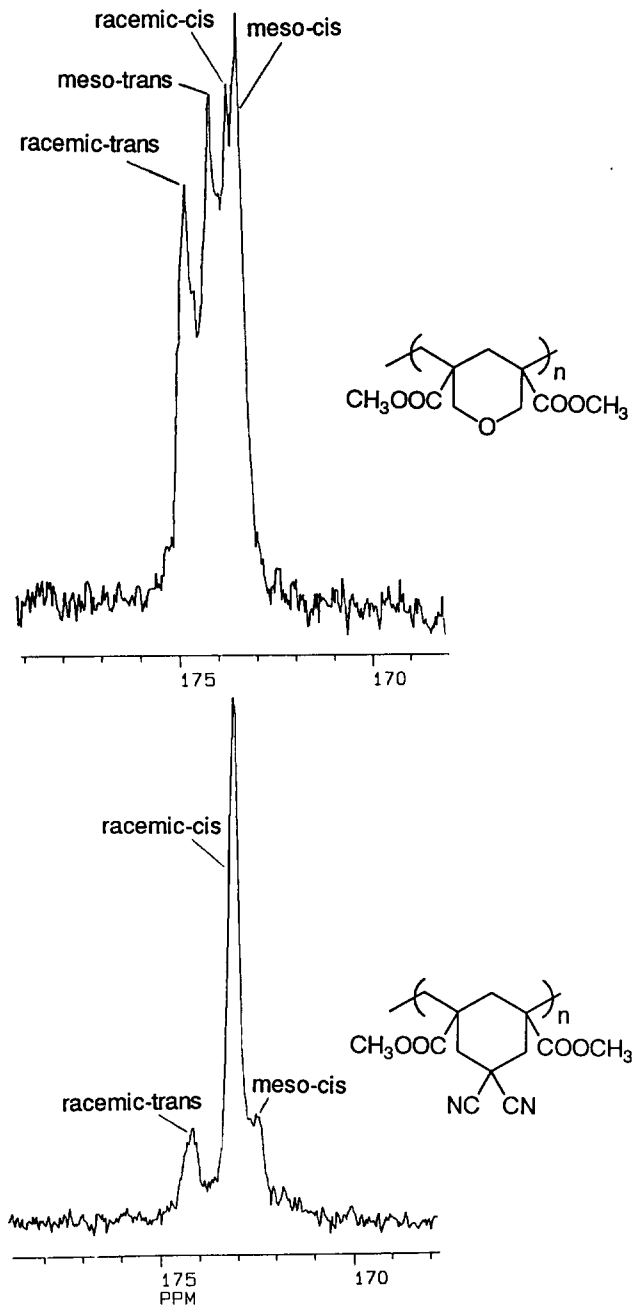

Figure 11 ^{13}C n.m.r. spectra of cyclopolymer carbonyl regions for methyl ester cyclopolymers derived from ether dimer (top) and *gem*-dinitrile diacrylate (bottom)

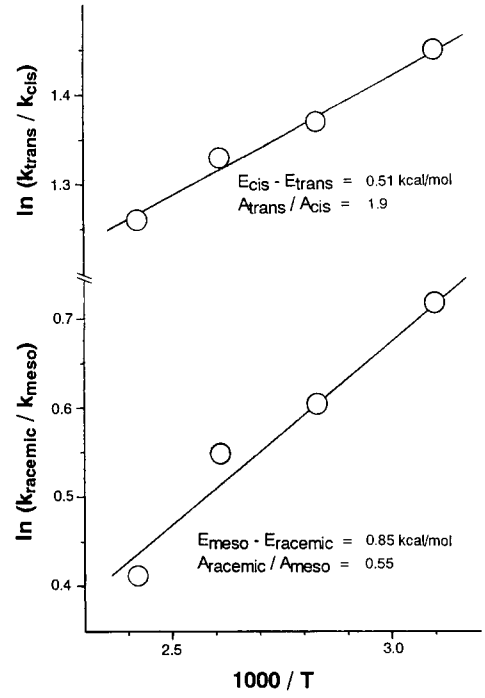

Figure 12 Arrhenius plots for *trans/cis* incorporation (top) and racemic/meso placement (bottom)

of *cis* addition observed is attributable to the presence of the bulky polymer backbone on the same side of the tetrahydropyran ring as the incoming monomer, as illustrated in *Figure 13*. This propensity for *trans* dominance increases with the bulkiness of the ester substituent (as mentioned before in *Figure 10*). Although the selectivity for *trans* formation is lower, the decrease of *trans* formation with increase in temperature was also observed for the methyl ester derivative as shown in *Figure 14*. This indicates a lower activation energy for *trans* formation than *cis* formation similarly to the bulkier esters. The other esters (isobornyl and adamantyl esters) showed only broad peaks without clear splitting for the carbonyl carbons, apparently due to the lower mobility of the ester substituents in solution.

Figure 15 shows the carbonyl regions of ^{13}C n.m.r. spectra for carboxylic acid cyclopolymer and three hydrolysed cyclopolymers derived from isobornyl, t-butyl

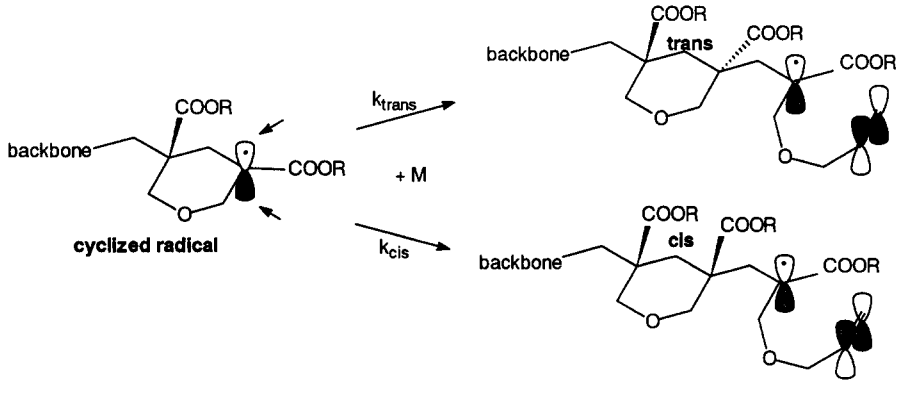

Figure 13 Possible addition mechanism resulting in *trans* and *cis* rings

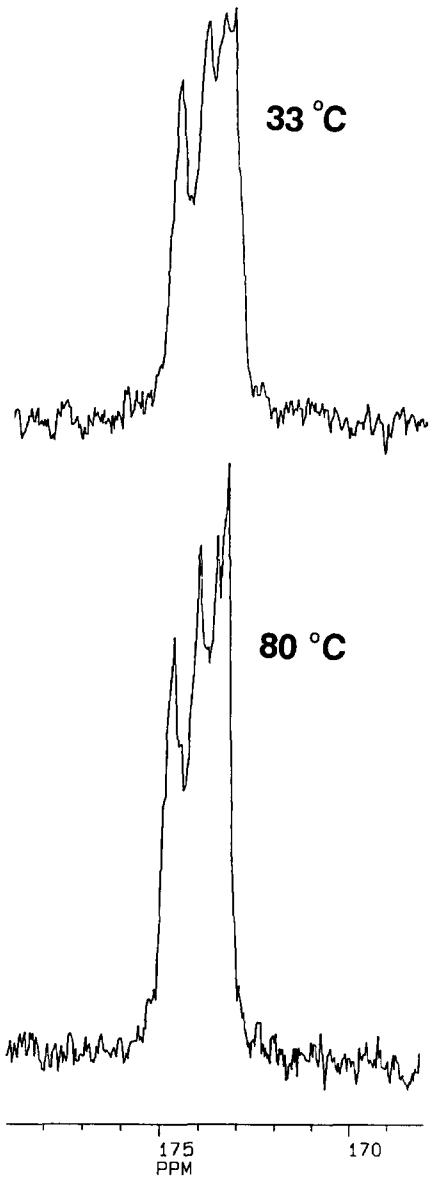

Figure 14 ^{13}C n.m.r. spectra of methyl ester cyclopolymer carbonyl regions polymerized at 33°C (top) and at 80°C (bottom)

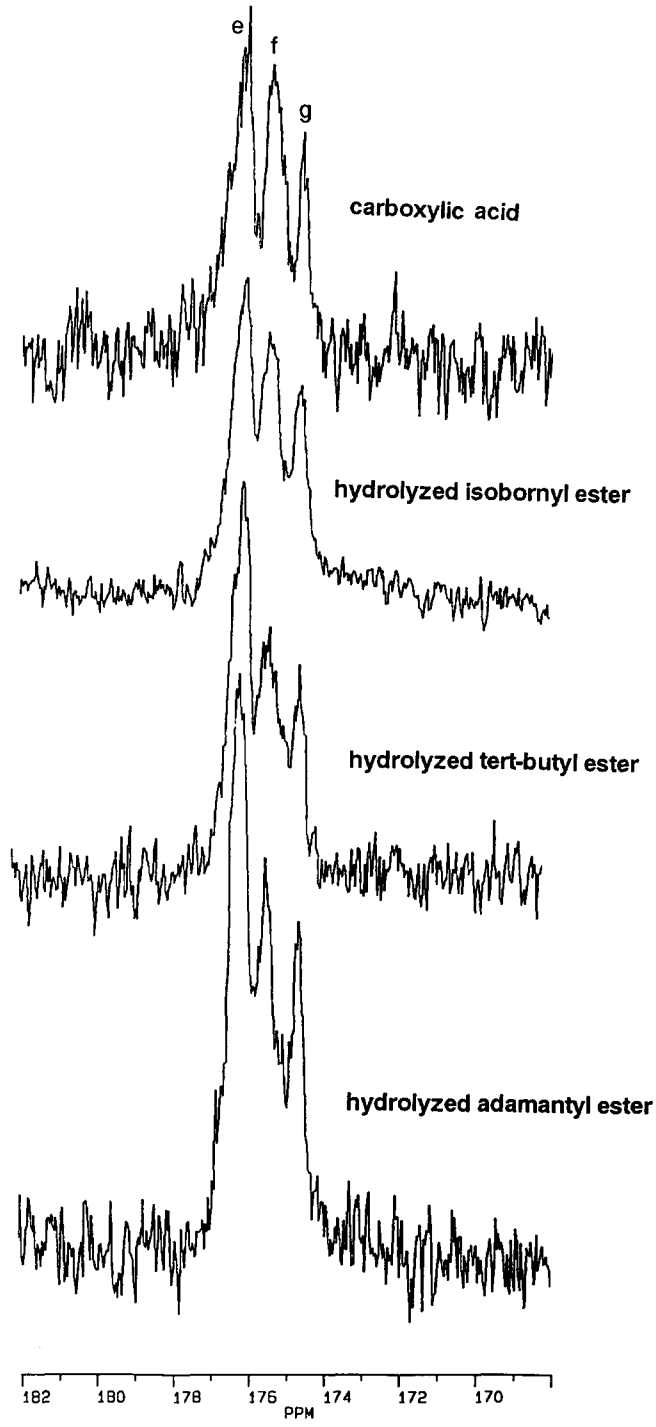

Figure 15 ^{13}C n.m.r. spectra of carbonyl region of carboxylic acid cyclopolymers (all polymerized at 80°C) for carboxylic acid (top), hydrolysed isobornyl ester (second), hydrolysed t-butyl ester (third) and hydrolysed adamantyl ester (bottom)

and adamantyl esters. The attempts to hydrolyse methyl and ethyl esters under acidic and basic conditions were not successful because of the high stability of the *cis* configuration. The three peaks observed were assigned to racemic-*trans*, meso-*trans* and *cis* carbonyl carbons (peaks denoted e, f and g in *Figure 15*) by referring to the corresponding spectrum of the t-butyl ester polymer, as well as by considering the temperature dependence of the relative intensity of each peak. The larger peak ratio of e/f observed for hydrolysed t-butyl and adamantyl esters indicates higher racemic selectivity in comparison to isobornyl ester and carboxylic acid. Thus, microstructure also was affected by the effective bulkiness of the ester substituents just as was cyclization efficiency. Peak ratio e/f for hydrolysed t-butyl ester cyclopolymer decreased with an increase in temperature as shown in *Figure 16*. The temperature dependence of the peak ratio (racemic/meso ratio listed in *Table 6*) allowed the calculation of the kinetic parameter for racemic/*cis* formation in the same way as for *trans*/*cis* formation. As shown in *Table 6* and *Figure 12*, lower stereoselectivity, larger activation-energy difference and smaller frequency factor ratio were observed compared with *trans*/*cis* incorporation. Racemic/meso configuration is determined by the intramolecular cyclization of the terminal uncyclized radical as illustrated in *Figure 17*. The characteristics of intramolecular cyclization are higher activation energy, higher frequency factor and the consequent higher reaction rate in comparison with intermolecular monomer addition, as concluded before. These features should affect the

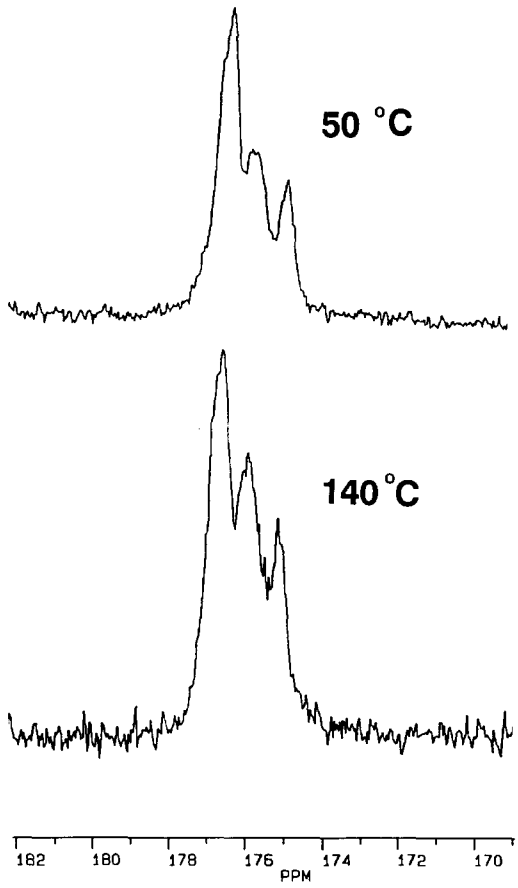

Figure 16 ^{13}C n.m.r. spectra of carbonyl region of hydrolysed t-butyl ester cyclopolymers polymerized at 50°C (top) and at 140°C (bottom)

Table 7 Glass transition temperatures of cyclopolymers and related polymers

Substituent R	T_g (°C)		
	Acrylate	Methacrylate	Cyclopolymer
Methyl	10[a]	104[a]	165[c]
Ethyl	−24[a]	65[a]	70–90
t-Butyl	43–107[a]	113[b]	138[d]
Isobornyl	94[a]	110[a]	ca. 230
Adamantyl	153[b]	>254[b]	260[e]

[a] Published data from ref. 20
[b] Published data from ref. 16
[c] Published data from ref. 6
[d] Published data from ref. 7
[e] Published data from ref. 13

selection of racemic or meso isomers during cyclization. The larger activation-energy difference observed for racemic/meso formation might be related to the high activation energy of the overall cyclization reaction. However, the reason for the unusual $A_{racemic}/A_{meso}$ ratio (a value <1 means meso formation is sterically favourable) is not clear. As a result of a small $A_{racemic}/A_{meso}$ value, lower selectivity for racemic/meso formation was observed compared with *trans/cis* formation. This propensity for low stereoregularity caused by the small $A_{racemic}/A_{meso}$ values is also presumed to be true for the less bulky methyl ester system based on the carbonyl carbon peaks in *Figure 14*. The low tacticity observed for the methyl and ethyl esters is in sharp contrast to the high stereoregularity of the cyclopolymers from the corresponding dicyano-containing dimers, in which polymerization at room temperature gave almost exclusive racemic-*cis* structures.

Glass transition temperatures

The glass transition temperatures of the cyclopolymers are listed in *Table 7* along with those for the corresponding acrylates and methacrylates. The T_g values of the cyclopolymers are much higher than those for the acrylate and methacrylate analogues. Thermal decomposition of isobornyl ester groups was suggested to occur above the T_g (ca. 230°C) by the d.s.c. thermogram, similar to behaviour of the t-butyl ester cyclopolymer reported before[7].

CONCLUSIONS

In the cyclopolymerization of the ether dimers of α-(hydroxymethyl)acrylates, the effective bulkiness of the ester substituent was found to affect both the cyclization efficiency and the microstructures in a consistent manner. Bulky substituents increased cyclization efficiency and the content of *trans*/racemic microstructures. The carboxylic acid derivative showed some deviation from the linear relationship between energetic and steric factors observed for the various esters, apparently due to its ability to form intramolecular hydrogen bonds.

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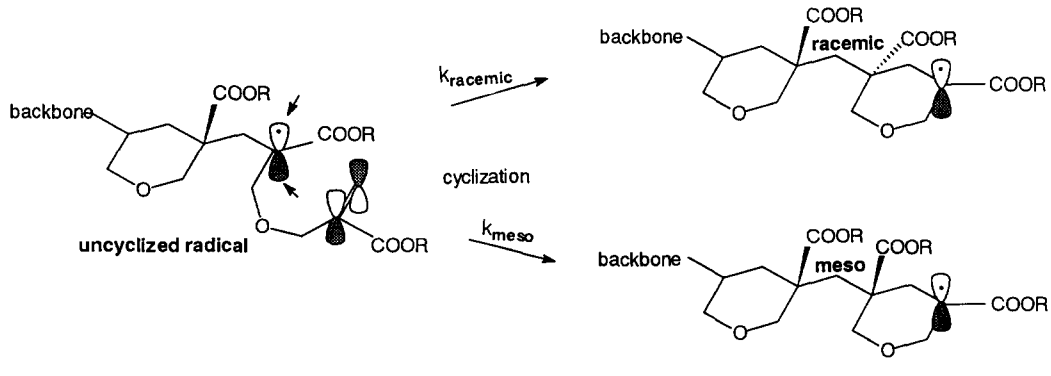

Figure 17 Possible cyclization mechanism resulting in racemic and meso configurations

K. Maeda of Toagosei Chemical for isobornyl and adamantyl acrylates. T. T. wishes to thank the Mathias Research Group, and especially Dr C. P. Jariwala and R. D. Thompson for help and advice during this research.

REFERENCES

1 Butler, G. B. 'Cyclopolymerization and Cyclocopolymerization', Marcel Dekker, New York, 1992
2 Marvel, C. S. and Vest, R. D. *J. Am. Chem. Soc.* 1957, **79**, 5771
3 Marvel, C. S. and Vest, R. D. *J. Am. Chem. Soc.* 1959, **81**, 984
4 Milford, G. N. *J. Polym. Sci.* 1959, **41**, 295
5 Penelle, L., Collot, J. and Rufflard, G. *J. Polym. Sci., Polym. Chem. Edn.* 1993, **31**, 2407
6 Mathias, L. J., Kusefoglu, S. H. and Ingram, J. E. *Macromolecules* 1988, **21**, 545
7 Mathias, L. J., Warren, R. M. and Huang, S. *Macromolecules* 1991, **24**, 2036
8 Tsuda, T. and Mathias, L. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1993, **34** (1), 499
9 Mathias, L. J., Colletti, R. F. and Bielecki, A. *J. Am. Chem. Soc.* 1991, **113**, 1550
10 Stansbury, J. W. *Macromolecules* 1991, **24**, 2029
11 Fukuda, W., Suzuki, Y. and Kakiuchi, H. *J. Polym. Sci., Polym. Lett. Edn.* 1988, **26**, 305
12 Kodaira, T., Okumura, M., Urushisaki, M. and Isa, K. *J. Polym. Sci., Polym. Chem. Edn.* 1993, **31**, 169
13 Tsuda, T. and Mathias, L. J. *Macromolecules* 1993, **26**, 4734
14 Vaidya, R. A. and Mathias, L. J. *J. Polym. Sci., Polym. Symp.* 1986, **74**, 243
15 Otsu, T., Yasuhara, T. and Matsumoto, A. *J. Macromol. Sci., Chem. (A)* 1988, **25**, 537
16 Matsumoto, A., Tanaka, S. and Otsu, T. *Macromolecules* 1991, **24**, 4017
17 Matsumoto, A., Terada, T. and Oiwa, M. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 775
18 Cheng, H. N. and Khasat, N. P. *J. Appl. Polym. Sci.* 1988, **35**, 825
19 Tsuda, T. and Mathias, L. J. *Macromolecules* 1993, **26**, 6359
20 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', 3rd Edn., Wiley, New York, 1989