Bull. Chem. Soc. Jpn., 65, 846—852 (1992) [Vol. 65, No. 3

Synthesis and Radical Polymerization of Itaconates Containing an Adamantyl Ester Group

Akikazu Matsumoto, Hiroyuki Watanabe, and Takayuki Otsu*
Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558
(Received October 21, 1991)

Itaconates containing a 1-adamantyl or a 3,5-dimethyl-1-adamantyl ester group were prepared and polymerized in the presence of a radical initiator. The polymerization reactivity has been investigated in relation to the structure of ester alkyl groups of the monomer. It has been clarified that the adamantyl-containing polyitaconates show high thermal stability, i.e., high glass transition temperatures and decomposition temperatures. The relationship between polymer structures and thermal properties of polymers from some α- and β-substituted acrylic esters, i.e., acrylates, methacrylates, crotonates, fumarates, and itaconates was discussed.

In the previous papers,[1] we have reported on synthesis and characterization of some vinyl polymers from adamantyl-containing acrylic derivatives such as acrylates,[1a,1b] methacrylates,[1a,1e] fumarates,[1c] crotonates,[1d] and sorbate[1f] bearing a 1-adamantyl or 3,5-dimethyl-1-adamantyl group as an ester alkyl group. These polymers show excellent thermal stability, e.g., high glass transition temperature (T_g) and high decomposition temperature on account of physical and chemical stabilities of an adamantyl moiety.[2]

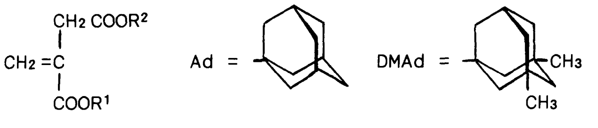
We have also reported since 1981 that dialkyl fumarates containing a bulky alkyl ester group such as *t*-butyl proceed by radical polymerization to give a less-flexible substituted polymethylene because of the decrease in the bimolecular termination rate between polymer radicals, despite of sterical hindrance in propagation between the substituted polymethylene radical and the 1,2-disubstituted ethylene monomer.[3,4] Similar high polymerization was also observed in radical polymerization of some dialkyl itaconates (DRI) as 1,1-disubstituted ethylenes on account of the slow termination.[5,6] Many studies have been intensively carried out on not only polymerization but also characterization and application of the resulting poly(DRI)s.[7—13]

In this paper, synthesis and radical polymerization of DRI containing adamantyl moieties as an ester alkyl group as shown in Scheme 1, and the thermal properties of the resulting polymers are described.

Results and Discussion

Preparation of Monomers. Compounds **1** and **2** were prepared by the reaction of itaconic anhydride with twofold moles of a respective adamantyl alcohol with reflux in cyclohexane for 40 h in the presence of an acidic catalyst. The yields were 50 and 66%, and melting points were 83 and 42 °C for **1** and **2**, respectively.

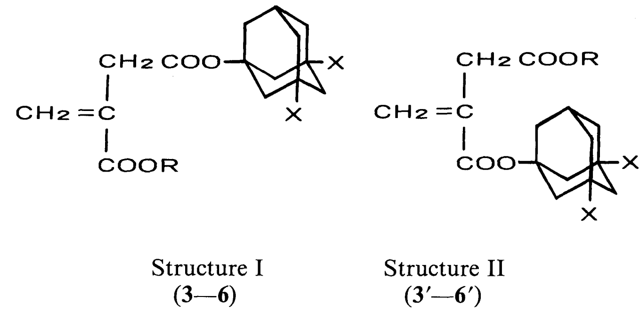
The monomers bearing two different alkyl groups, i.e., **3**—**6**, were obtained by the method as follows: Itaconic anhydride was reacted with an equimolar adamantyl alcohol, followed by the further reaction with an another alcohol, i.e., methanol or 2-propanol. From the monomer mixture consisting of the diadamantyl ester, the dimethyl or diisopropyl ester, and two kind of DRIs bearing different alkyl groups as shown in Fig. 1, one



DRI

No	R1	R2
1	Ad	Ad
2	DMAd	DMAd
3	Methyl	Ad
4	Methyl	DMAd
5	Isopropyl	Ad
6	Isopropyl	DMAd
7	Methyl	Methyl
8	Isopropyl	Isopropyl
3′	Ad	Methyl
4′	DMAd	Methyl
5′	Ad	Isopropyl
6′	DMAd	Isopropyl

Scheme 1.



Structure I (**3**—**6**) Structure II (**3′**—**6′**)

X=H or CH_3
R=CH_3 or $CH(CH_3)_2$

Fig. 1. Two possible structures of alkyl adamantyl itaconates.

isomer of alkyl adamantyl itaconates was isolated by column chromatography.

The partial ^1H and ^{13}C NMR spectra of the adamantyl-containing DRIs are depicted in Figs. 2 and 3, respectively, and a part of the chemical shifts determined is summarized in Tables 1 and 2. These results support strongly that DRIs bearing different ester groups isolated in this work have the structure I in Fig. 1. For example, the septets due to the two kind of methine protons of the isopropyl esters are observed at δ=5.01 and 5.07, respectively, in the spectrum of **8** (Fig. 2(c)), but in the spectrum of **5** only one septet at a higher field is observed. It has also been confirmed that the olefinic protons have different chemical shifts depending on the ester alkyl groups, i.e., δ=6.19 and 5.55 for **1**, δ=6.21 and 5.58 for **5**, and δ=6.28 and 5.65 for **8**. The spectrum of **5** has revealed that this monomer contains a small amount of another isomer, **5′** (see Scheme 1). The peaks at δ=6.25

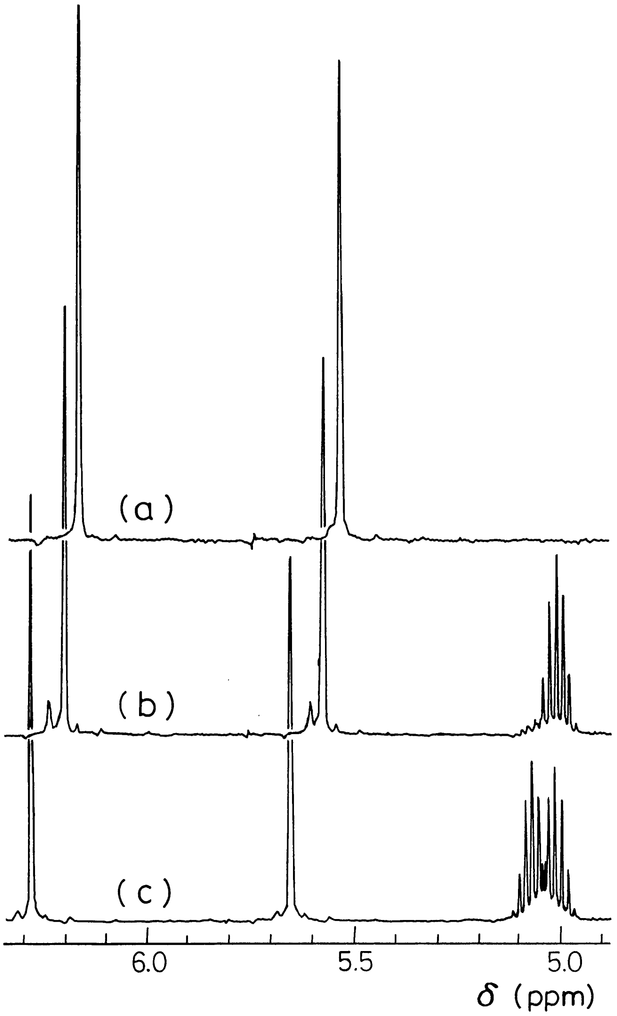


Fig. 2. Partial ^1H NMR spectra of DRIs: (a) **1**, (b) **5**, and (c) **8** in $CDCl_3$.

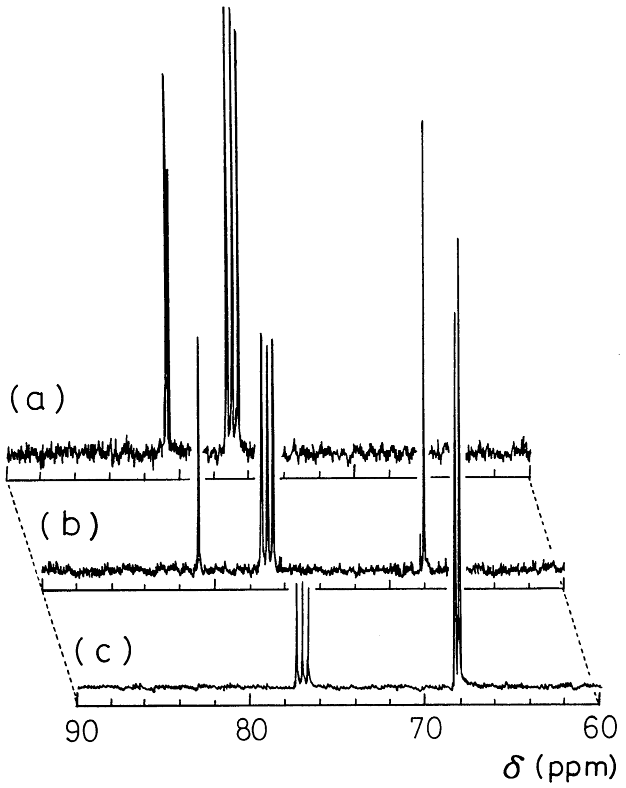


Fig. 3. Partial ^{13}C NMR spectra of DRIs: (a) **1**, (b) **5**, and (c) **8** in $CDCl_3$.

Table 1. ^1H NMR Chemical Shifts of DRIs[a)]

DRI	CH_2=	CH_2COO	$-OCH(CH_3)_2$	$-OCH_3$	CH_3 (adamantyl)
1	6.19, 5.55	3.19	—	—	—
2	6.17, 5.53	3.18	—	—	0.88 0.87
3	6.23, 5.61	3.29	—	3.70	—
4	6.22, 5.60	3.28	—	3.70	0.88
5	6.21, 5.58	3.24	5.02, 1.24	—	—
6	6.21, 5.58	3.24	5.02, 1.24	—	0.88
7	6.33, 5.73	3.35	—	3.77 3.70	—
8	6.28, 5.65	3.29	5.07, 1.27 5.01, 1.24	—	—

a) DRI: $CH_2=C(COOR^1)CH_2COOR^2$, chemical shifts in ppm from TMS, in $CDCl_3$.

Table 2. ^{13}C NMR Chemical Shifts of DRIs[a)]

DRI	$\underline{C}OOR^1$	$\underline{C}OOR^2$	$=C<$	$CH_2=$	$-O\overset{\vert}{\underset{\vert}{C}}-$	$-OCH<$	$-OCH_3$
1	169.72	165.09	136.10	126.51	80.83 80.72	—	—
2	169.78	165.19	136.05	126.61	82.24 82.14	—	—
3	171.24	164.82	135.38	127.21	81.07	—	51.80
4	171.26	164.98	135.41	127.28	82.52	—	51.84
5	170.31	164.97	135.69	126.93	80.97	68.07	—
6	170.32	165.05	135.62	127.02	82.36	68.08	—
7	170.98	166.46	133.59	128.39	—	—	51.97 51.87
8	170.10	165.55	134.56	127.43	—	68.26 68.04	—

a) DRI: $CH_2=C(COOR^1)CH_2COOR^2$, chemical shifts in ppm from TMS, in $CDCl_3$.

Table 3. Radical Polymerization of Adamantyl-Containing DRIs in Bulk

DRI[a)]			[AIBN]	Temp	Time	Yield	$M_n \times 10^{-4}$	M_w/M_n
No.	R^1	R^2	mol L^{-1}	°C	h	%		
1	Ad	Ad	0.02[b)]	85	10	47.3	0.22	1.7
1[c)]	Ad	Ad	0.02	60	10	12.9	0.20	1.6
2	DMAd	DMAd	0.02	60	10	15.5	0.69	2.2
2	DMAd	DMAd	0.01	50	65	14.9	1.2	2.3
3	Me	Ad	0.02	60	10	36.2	3.1	2.1
4	Me	DMAd	0.02	60	10	40.1	5.5	1.8
5	*i*-Pr	Ad	0.02	60	10	23.5	2.3	1.9
6	*i*-Pr	DMAd	0.02	60	10	43.6	3.8	1.8
7	Me	Me	0.02	60	10	33.5	3.6	2.0
8	*i*-Pr	*i*-Pr	0.02	60	10	38.1	2.7	2.0

a) DRI: $CH_2=C(COOR^1)CH_2COOR^2$, Ad=adamantyl, DMAd=3,5-dimethyl-1-adamantyl, Me=methyl, and *i*-Pr=isopropyl. b) ACN was used as an initiator. c) In benzene, [**1**]=1.0 mol L^{-1}.

and 5.61 seem to be due to the isomer **5′** of the structure II. Similar results were also observed for the ^{13}C NMR spectra. For the determination of the structure of the isomers I and II, data of two kind of methyl *t*-butyl itaconates, methyl 2-(*t*-butoxycarbonylmethyl)acrylate and *t*-butyl 2-(methoxycarbonylmethyl)acrylate, were also available.[14)] The structures of **3**, **4**, and **6** were similarly identified. The isomers with an alternating structure, **3′**—**6′**, were not isolated in this work.

Polymerization Reactivity. Radical polymerization of DRI containing an adamantyl ester group was performed in bulk with AIBN at 60 °C. The results are summarized in Table 3. It was found that polymerization reactivities (yield and M_n of the polymer produced) of **1** and **2** as diadamantyl esters were lower than those of other DRIs. Poly(**1**) obtained from bulk polymerization at 85 °C and solution polymerization at 60 °C was relatively low molecular weight. Bulk polymerization of **2** at 60 °C also gave a polymer with M_n less than 10^4. The yield and M_n of poly(**2**) was very close to those for di-*t*-butyl itaconate under the identical polymerization conditions,[6a,6b)] i.e., yield 13.7%, M_n 0.7×10^4, and M_w/M_n 1.8. In polymerization of DRI, it has been reported that the polymerization rate and M_n of the resulting polymer decrease in the following order: normal alkyl esters>secondary alkyl esters>tertiary alkyl esters, except for cycloalkyl esters with high viscosity. The polymerizations of cycloalkyl or cycloalkylmethyl esters proceed with a higher rate to give a high-molecular-weight polymer on account of the retardation of bimolecular termination by high viscosity of the polymerization medium.[6a)]

However, adamantyl alkyl itaconates, i.e., **3**—**6** were revealed to have a reactivity similar to dimethyl or diisopropyl esters, **7** and **8** and to give a polymer with M_n more than 10^4. It suggests that the structure of R^1 in the two ester alkyl groups dominates the polymerization reactivity of DRI more significantly rather than R^2, agreeing well with our previous results for monoalkyl itaconates,[6c)] methyl alkyl itaconates,[6d)] and methyl *t*-butyl itaconates.[6a,14)]

These results are different from those for polymerization of DRF,[3,4)] indicating that the polymerization reactivities of DRI are controlled by the steric effects of the two substituents at the 1-position on both propagation and termination. Recently, propagation and termination rate constants of several DRIs have been determined and related to the structure of the ester alkyl groups.[6e)]

Characterization of Poly(DRI). The structure of poly(DRI)s obtained was confirmed by NMR and IR spectroscopy. The ^1H and ^{13}C NMR spectra of poly(**3**) are depicted in Figs. 4 and 5, respectively. In these spectra, the peaks due to the carbon-to-carbon double bond were not observed. Similar results were also obtained by IR spectroscopy, i.e., the absorption due to stretching vibration of carbon-to-carbon double bond around 1630 cm^{-1} disappeared upon polymerization. The other DRIs gave similar results. These polymers are colorless powder and soluble in benzene, chloroform, and THF, and insoluble in methanol and hexane.

Thermal Property of Poly(DRI). The poly(DRI)s containing adamantyl moieties as an ester group were expected to show an excellent thermal stability. From DSC measurements, T_g was determined and are listed in Table 4. The adamantyl-containing poly(DRI)s have higher T_g (158—197 °C) than those for dimethyl or diisopropyl esters (88 and 95 °C). For poly(**1**) and poly(**2**) as diadamantyl esters, no transition was observed

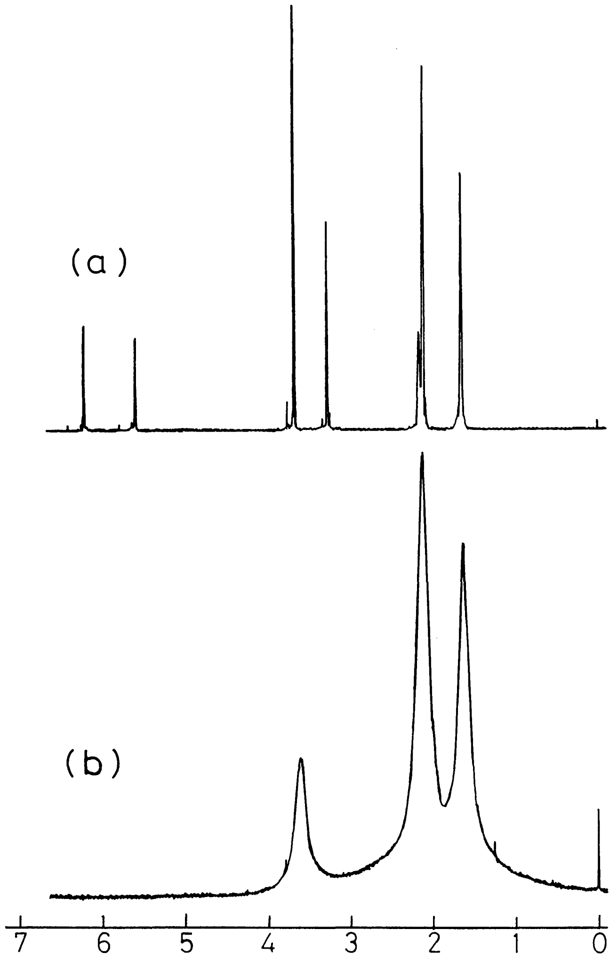


Fig. 4. ^1H NMR spectra of (a) **3** and (b) poly(**3**) in $CDCl_3$.

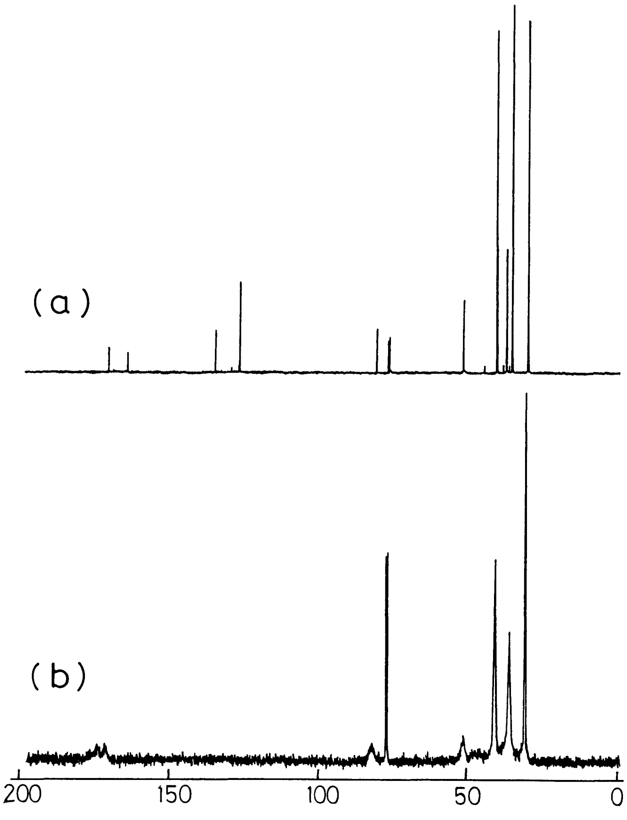


Fig. 5. ^{13}C NMR spectra of (a) **3** and (b) poly(**3**) in $CDCl_3$.

Table 4. Thermal Properties of Adamantyl-Containing Poly(DRI)s a)

Polymer	T_g / °C	T_{init} / °C	T_{max} b) / °C	Residue at 500 °C/%
Poly (**1**)	>Decomp	291	(354) (383) (401) 409	14.4
Poly (**2**)	>Decomp	299	354 (405)	7.5
Poly (**3**)	197	271	338 (366)	12.9
Poly (**4**)	144	264	(341) 391	6.9
Poly (**5**)	180	267	326	13.5
Poly (**6**)	158	266	(310) 353	14.3
Poly (**7**)	95	258	330	1.2
Poly (**8**)	88	236	288	6.1

a) Heating rate of 10 °C min^{-1}. b) The values in parentheses indicate the peaks other than T_{max} in derivative curves.

Table 5. Radical Copolymerization of DRI (M_2) with St (M_1) and Glass Transition Temperature of the Resulting Copolymers[a)]

M_2	Yield	$M_n \times 10^{-4}$	M_w/M_n	$[M_2]$ in copolymer	T_g
	%			mol%	°C
1	17.2	1.07	1.9	59.6	194
2	18.1	1.15	1.9	60.0	150
3	16.6	1.25	1.4	51.6	149
4	17.1	1.39	1.4	56.6	119
5	13.4	1.16	1.4	60.9	127
6	14.3	1.36	1.4	63.3	106

a) Copolymerization conditions: [DRI]=[St]=0.5 mol L^{-1}, [AIBN]=0.005 mol L^{-1}, in benzene at 60 °C for 15 h.

Table 6. Comparison of T_g of α- and β-Substituted Acrylic Polymers[a)]

Polymer	$\left(\text{CHZ-CY(COOR)} \right)_n$		T_g/°C	
	Y	Z	R=Ad	DMAd
Poly(RA)	H	H	153	105
Poly(RMA)	CH_3	H	>Decomp	194
Poly(DRI)	CH_2COOR	H	>Decomp	>Decomp
Poly(RCr)[b)]	H	CH_3	>Decomp	230
Poly(DRF)	H	COOR	>Decomp	>Decomp

a) Ad: 1-adamantyl, DMAd: 3,5-dimethyl-1-adamantyl; Prepared by radical polymerization at 60 °C.
b) Anionic polymerization in THF at −78 °C.

under their onset temperatures of decomposition. The isopropyl esters tend to show lower T_g than the methyl esters.

Since it has been reported that DRI copolymerizes alternatingly with styrene (St),[15)] T_g of the copolymers from these adamantyl-containing DRI with styrene was also examined. Radical copolymerization with styrene was carried out in benzene at 60 °C for 15 h. The copolymers containing 51—63 mol% of DRI units were produced in 13—18% yields from copolymerization of equimolar comonomers in feed as shown in Table 5. The M_n determined by GPC were 1.1—1.4×10^4 and M_w/M_n were 1.4—1.9. The copolymerization reactivities of **1** and **2** were resemble to the other DRIs, which is different from the case of homopolymerization. The T_g observed decreased in the following order: **1**>**2**>**3**>**5**>**4**>**6**, agreeing with the order of T_g of the homopolymers (Table 4).

Table 6 shows the comparison of T_g of the adamantyl-containing poly(DRI) with those of other α- and β-substituted acrylic polymers,[1a–1d)] in which polymers of acrylates (RA), methacrylates (RMA), crotonates (RCr), and fumarates (DRF) are included. For the adamantyl esters, no T_g was observed below their decomposition temperatures except for poly(RA) (T_g=153 °C).

For the 3,5-dimethyl-1-adamantyl esters, T_g depends on the structure of the polymers in the following order: poly(RA)<poly(RMA)<poly(RCr)<poly(DRI) and poly(DRF). The last two polymers, which have two

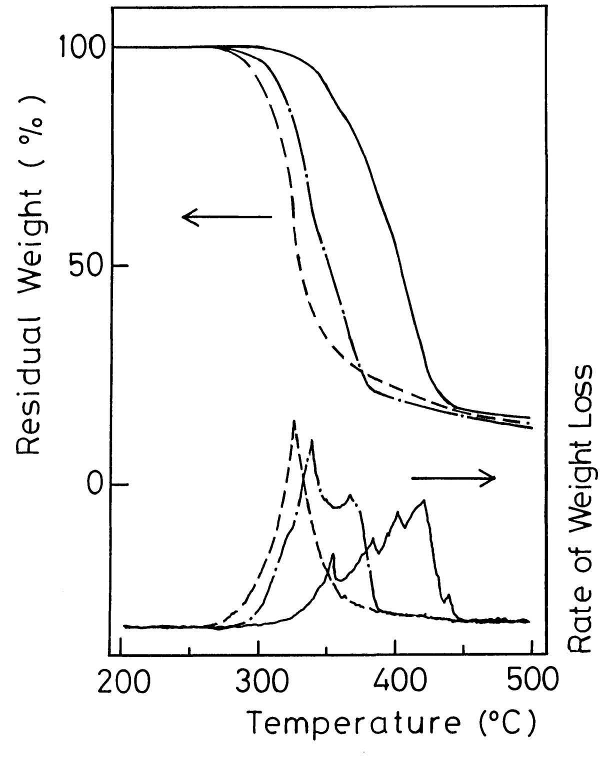


Fig. 6. TGA curves of adamantyl-containing poly(DRI)s in a nitrogen stream with a heating rate of 10 °C min^{-1}: (—) poly(**1**), (—·—) poly(**3**), and (-----) poly(**5**).

ester groups in the repeating monomer unit, show no T_g. This order reflects difference in the chain rigidity, i.e., poly(monosubstituted ethylene)<poly(1,1-disubstituted ethylene)<substituted polymethylene (≡poly(1,2-disubstituted ethylene).

The initial and maximum decomposition temperatures (T_{init} and T_{max}) were also determined by TGA under nitrogen with a heating rate of 10 °C min^{-1}. The typical thermograms obtained are shown in Fig. 6. All adamantyl-containing polymers exhibit high onset temperatures of decomposition, i.e., T_{init} at 264—299 °C, which were higher than 258 and 238 °C for the dimethyl and diisopropyl esters, respectively. Especially poly(**1**) and poly(**2**) were revealed to have T_{init} more than 290 °C. However, the introduction of methyl or isopropyl group decreased the decomposition temperatures, as shown in the thermograms.

Experimental

Monomers. Di-1-adamantyl itaconate (**1**) was prepared as follows: Itaconic anhydride (14.7 g) and 1-adamantanol (20 g) were refluxed in cyclohexane (400 mL) in the presence of sulfuric acid (1 mL) for 40 h on removing a resulting water. The reaction product was extracted with ether, dried and then recrystallized from methanol. The monomer **1** obtained was purified by column chromatography (silica gel/hexane) and repeating recrystallization. Yield 66%. Mp 83 °C. IR (KBr) 2900, 2850, 1730, 1720, 1635, 1340, 1295, 1200, 1175, 1155, 1105, 970, 960, and 815 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.19(s), 5.55(s), 3.19(s), 2.17(br), 2.15(br), 2.11(s), 2.10(s), 1.67(s), 1.66(s). ^{13}C NMR (CDCl$_3$, 100 MHz) δ=169.72, 165.09, 136.10, 126.51, 80.83, 80.72, 41.23, 39.24, 36.18, 30.81.

Bis(3,5-dimethyl-1-adamantyl) itaconate (**2**) was prepared similarly. Yield 50%. Mp 42 °C. IR (neat) 2930, 2890, 2840, 2820, 1720, 1705, 1625, 1445, 1325, 1310, 1260, 1195, 1170, 1145, 995, and 960 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.17(s), 5.53(s), 3.18(s), 2.22(br), 2.00(br), 1.98(br), 1.72—1.85(m), 1.11—1.41(m), 0.88(s), 0.87(s). ^{13}C NMR (CDCl$_3$, 100 MHz) δ=169.78, 165.19, 136.05, 126.61, 82.24, 82.14, 50.51, 50.48, 47.15, 47.11, 42.53, 39.70, 39.67, 39.33, 33.89, 33.86, 31.08, 29.90.

1-Adamantyl methyl itaconate (**3**) was prepared in the following procedure. A mixture of itaconic anhydride (60 g) and 1-adamantanol (81.4 g) was refluxed in cyclohexane in the presence of sulfuric acid for 4 h. After methanol (19.7 g) was added, it was further refluxed for 1 h on removing water. The monomer mixture was confirmed by gas chromatography to consist of **3**, the diadamantyl ester **1**, dimethyl ester **7**, and an another isomer of adamantyl methyl itaconate (**3′**) (see Scheme 1). The compound **3** was isolated by column chromatography on silica gel with chloroform as an eluent, followed by distillation under a reduced pressure. Colorless liquid. Yield 22.5 g (14%). Bp 147 °C (1.5 mmHg) (1 mmHg=133.322 Pa). IR (neat) 2890, 2830, 1735, 1710, 1700, 1630, 1445, 1430, 1415, 1340, 1325, 1290, 1250, 1190, 1145, 1055, 965, and 820 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.23(s), 5.61(s), 3.70(s), 3.29(s), 2.17(br), 2.14(br), 1.67(br). ^{13}C NMR (CDCl$_3$, 100 MHz) δ=171.24, 164.82, 135.38, 127.21, 81.07, 51.81, 41.10, 37.73, 36.08, 30.73.

1-Adamantyl isopropyl itaconate (**4**) was prepared similarly to the method for **3**. A mixture of hexane and chloroform was adopted as an eluent of column chromatography. Colorless liquid. Yield 24%. Bp 162 °C (1 mmHg). IR (neat) 2960, 2890, 2830, 1725, 1710, 1700, 1630, 1445, 1340, 1310, 1290, 1255, 1190, 1150, 1105, 1055, 965, 945, and 815 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.22(s), 5.60(s), 3.70(s), 3.28(s), 2.21—2.23(m), 1.98(br), 1.75—1.83(m), 1.12—1.41(m), 0.88(s). ^{13}C NMR (CDCl$_3$, 100 MHz) δ=171.26, 164.98, 135.41, 127.28, 82.52, 51.84, 50.48, 47.04,2 42.50, 39.62, 37.74, 33.87, 31.07, 29.84.

3,5-Dimethyl-1-adamantyl methyl itaconate (**5**) and 3,5-dimethyl-1-adamantyl isopropyl itaconate (**6**) were synthesized and purified similarly.

5: Colorless liquid. Yield 26%. Bp 155 °C (2 mmHg), IR (neat) 2930, 2890, 2840, 2820, 1735, 1715, 1705, 1630, 1445, 1340, 1315, 1250, 1195, 1170, 1145, and 995 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.21(s), 5.58(s), 5.02(sept, J=6.1 Hz), 3.24(s), 2.17(br), 2.15(br), 1.67(br), 1.24(d, J=6.1 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) δ=170.31, 164.97, 135.69, 126.93, 80.97, 68.07, 41.17, 38.29, 36.15, 30.78, 21.73.

6: Colorless liquid. Yield 30%, Bp 164 °C (1 mmHg). IR (neat) 2950, 2920, 2890, 2850, 2820, 1730, 1715, 1705, 1630, 1445, 1370, 1350, 1335, 1320, 1310, 1265, 1195, 1170, 1145, 1105, 995, 960, and 815 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.21(s), 5.58(s), 5.02(sept, J=6.1 Hz), 3.24(s), 2.21—2.23(m), 1.99(br), 1.75—1.84(m), 1.12—1.41(m), 1.24(d, J=6.1 Hz), 0.88(s). ^{13}C NMR (CDCl$_3$, 100 MHz) δ=170.32, 165.05, 135.62, 127.02, 82.36, 68.08, 50.47, 47.05, 42.48, 39.58, 38.27, 33.84, 31.06, 29.84, 21.74.

Dimethyl itaconate (**7**) was commercially available. IR (neat) 2970, 2930, 2820, 1730, 1715, 1630, 1430, 1335, 1315, 1255, 1200, 1145, 1010, and 815 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.33(s), 5.73(s), 3.77(s), 3.70(s), 3.35(s). ^{13}C NMR(CDCl$_3$, 100 MHz) δ=170.98, 166.46, 133.59, 128.39, 51.97, 51.87, 37.33.

Diisopropyl itaconate (**8**) was prepared from itaconic anhydride with isopropanol. Colorless liquid. IR (neat) 2980, 2940, 2880, 1735, 1715, 1640, 1375, 1310, 1260, 1200, 1150, 1010, 950, and 820 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz) δ=6.28(s), 5.65(s), 5.07(sept, J=6.1 Hz), 5.01(sept, J=6.1 Hz), 3.29(s), 1.27(d, J=6.1 Hz), 1.24(d, J=6.1 Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) δ=170.10, 165.55, 134.56, 127.43, 68.26, 68.04, 38.03, 21.60.

Other Materials. 2,2′-Azobis(isobutyronitrile) (AIBN) and 1,1′-azobis(cyclohexanecarbonitrile) (ACN) were recrystallized from methanol. The other reagents and solvents were purified by ordinary methods.

Polymerization. Radical polymerization was carried out in a sealed glass tube in the presence of an initiator. The resulting polymer was precipitated with a large amount of methanol or a mixture of methanol and water, filtered, and then dried under vacuum. The polymer yield was determined gravimetrically.

Radical copolymerization was carried out similarly to homopolymerization in benzene with AIBN at 60 °C. The composition of the copolymers was determined by ^{1}H NMR spectroscopy.

Measurements. IR spectra were recorded on a JASCO A-202 spectrometer. NMR spectra were taken on a JEOL GX-400 and Hitachi R-24B with deuteriochloroform as a solvent. Gel permeation chromatography (GPC) was performed by use of Tosoh 8000 series GPC system with TSK—gel columns in tetrahydrofuran (THF) at 38 °C. Number-average molecular weight (M_n) and weight-average molecular weights (M_w) were calibrated with standard polystyrenes. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream with a heating rate of 10 °C min^{-1} by means of Shimadzu TG-50. Differential scanning calorimetry (DSC) was performed with a heating rate of 10 °C min^{-1}.

The authors wish to thank Dr. Y. Matoba and Mr. S. Umano, Hakusui Chemical Industries, Ltd., for their experimental supports as to a part of the monomer preparation and the DSC measurements, and Mr. S. Mori, Osaka City University for the TGA measurements.

References

1) a) A. Matsumoto, S. Tanaka, and T. Otsu, *Macromolecules,* **24**, 4017 (1991); b) T. Otsu, A. Matsumoto, A. Horie, and S. Tanaka, *Chem. Lett.,* **1991**, 1145; c) A. Matsumoto and T. Otsu, *Chem. Lett.,* **1991**, 1361; d) A. Matsumoto, A. Horie, and T. Otsu, *Polym. J.,* **23**, 211 (1991); e) A. Matsumoto, S. Tanaka, and T. Otsu, *Colloid Polym. Sci.,* in press; f) A. Matsumoto, A. Horie, and T. Otsu, *Makromol. Chem., Rapid Commun.,* **12**, 681 (1991).

2) H. Stetter, *Angew. Chem.,* **74**, 361 (1962); b) R. C. Fort, Jr. and P. von R. Schleyer, *Chem. Rev.,* **64**, 277 (1964); c) R. C. Bringham and P. von R. Schleyer, *Top. Curr. Chem.,* **18**, 1 (1970).

3) T. Otsu, T. Yasuhara, and A. Matsumoto, *J. Macromol. Sci., Chem.,* **A25**, 537 (1988), and references cited therein.

4) As recent papers; a) A. Matsumoto, T. Tarui, and T. Otsu, *Macromolecules,* **23**, 5102 (1990); b) T. Otsu, B. Yamada, and T. Ishikawa, *Macromolecules,* **24**, 415 (1991); c) M. Yoshioka, A. Matsumoto, T. Otsu, and I. Ando, *Polymer,* **32**, 2741 (1991); d) M. Yoshioka, A. Matsumoto, and T. Otsu, *Polym. J.,* **23**, 1191, 1249 (1991).

5) a) T. Sato, S. Inui, H. Tanaka, T. Ota, M. Kamachi, and K. Tanaka, *J. Polym. Sci., Polym. Chem. Ed.,* **25**, 637 (1987); b) T. Sato, K. Morino, H. Tanaka, and T. Ota, *Makromol. Chem.,* **188**, 2951 (1987); c) T. Sato, N. Morita, H. Tanaka, and T. Ota, *J. Polym. Sci., Part A: Polym. Chem.,* **27**, 2497 (1989).

6) a) T. Otsu, H. Watanabe, J. Z. Yang, M. Yoshioka, and A. Matsumoto, *Makromol. Chem., Macromol. Symp.,* in press; b) T. Otsu, M. Okuo, H. Watanabe, and J. Z. Yang, *Chem. Express,* **5**, 953 (1990); c) J. Z. Yang and T. Otsu, *Polym, Bull.,* **25**, 145 (1991); d) J. Z. Yang and T. Otsu, *Makromol. Chem., Rapid Commun.,* **12**, 205 (1991); e) T. Otsu, K. Yamagishi, and M. Yoshioka, *Macromolecules,* in press.

7) a) B. E. Tate, *Adv. Polym. Sci.,* **5**, 214 (1967); b) B. E. Tate, "Vinyl and Diene Monomers Part 1," ed by E. C. Leonard, Wiley, New York (1970), p. 205.

8) a) S. Nagai, T. Uno, and K. Yoshida, *Kobunshi Kagaku,* **15**, 550 (1958); b) S. Nagai and K. Yoshida, ibid., **17**, 77, 79 (1960). c) S. Nagai, *Bull. Chem. Soc. Jpn.,* **37**, 369 (1964).

9) C. S. Marvel and T. H. Shepherd, *J. Org. Chem.,* **24**, 599 (1959).

10) a) J. M. G. Cowie, I. J. McEwen, and J. Velickovic, *Polymer,* **16**, 869 (1975); b) J. M. G. Cowie, S. A. E. Henshall, I. J. McEwen, and J. Velickovic, *Polymer,* **18**, 612 (1977); c) J. M. G. Cowie, M. Yazdani-Pedram, and R. Ferguson, *Eur. Polym. J.,* **21**, 227 (1985); d) J. M. G. Cowie and A. C. S. Martin, *Polym. Commun.,* **26**, 298 (1985); e) A. F. Miles and J. M. G. Cowie, *Eur. Polym. J.,* **27**, 165 (1991).

11) a) J. Velickovic and S. Vasovic, *Makromol. Chem.,* **153**, 207 (1972); b) J. Velickovic and J. Filipovic, *Macromolecules,* **17**, 611 (1984); c) I. G. Popovic, V. Galogaza, L. Katsikas, and J. Velickovic, *Polym. Bull.,* **23**, 5320 (1991).

12) a) L. Gargallo, D. Radic, M. Yazdani-Pedram, and A. Horta, *Eur. Polym. J.,* **25**, 1059 (1989); b) A. Leon, L. Gargallo, A. Horta, and D. Radic, *J. Polym. Sci., Part B: Polym. Phys.,* **27**, 2337 (1989); c) A. Leon, L. Gargallo, D. Radic, and A. Horta, *Polymer,* **32**, 761 (1991); d) A. Horta, L. Gargallo, and D. Radic, *Macromolecules,* **23**, 5320 (1991).

13) a) K. Shiraishi, K. Sugiyama, and T. Otsu, *Bull. Chem. Soc. Jpn.,* **62**, 4083 (1989); b) K. Sugiyama and K. Shiraishi, *Bull. Chem. Soc. Jpn.,* **64**, 1715 (1991).

14) T. Otsu and H. Watanabe, unpublished data.

15) J. Brundrup and E. Immergut, "Polymer Handbook," 3rd ed, Wiley, New York (1989).