Synthesis and Characterization of Thermally Stable Polymers through Anionic Polymerization of *tert*-Alkyl Crotonates

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(Received October 25, 1990)

ABSTRACT: Some alkyl crotonates bearing *tert*-alkyl groups, *i.e.*, *tert*-butyl, *tert*-amyl, 1-adamantyl and 3,5-dimethyl-1-adamantyl crotonates were prepared and polymerized with *sec*-butyllithium as an anionic catalyst in toluene or THF. The resulting polymers were confirmed to consist of poly(substituted methylene) structure by IR and NMR spectroscopies. The polymers bearing adamantyl groups had more resistance to hydrolysis, whereas the *tert*-butyl and amyl esters were readily hydrolyzed. The introduction of the adamantyl groups also increased glass transition temperature and decomposition temperature of the polymer. It was revealed that the polymers bearing the *tert*-butyl and amyl esters decomposed *via* a two-step mechanism, resulting in the formation of poly(crotonic acid) accompanied with elimination of corresponding olefins from the ester groups, but the polymers containing adamantyl groups showed excellent thermal stability.

KEY WORDS *tert*-Alkyl Crotonate / 1-Adamantyl Crotonate / 3,5-Dimethyl-1-adamantyl Crotonate / Anionic Polymerization / Poly(substituted methylene) / Hydrolysis / Glass Transition Temperature / Thermogravimetric Analysis / Thermolysis /

We have reported that dialkyl fumarates bearing bulky alkyl groups polymerize in the presence of a radical initiator to give high molecular weight polymers which consist of a poly(substituted methylene) structure (eq 1).^{1,2}

These polymers have a lessflexible structure because they have no methylene group as a spacer in the main chain, and are expected to show new properties different from ordinary flexible vinyl polymers.^{2–7} Polymers with a similar structure can be also obtained by polymerization of β -substituted acrylic esters such as alkyl crotonates (RCr) (eq 2), which give poly(substituted methylene) bearing alter-

natingly methyl and alkoxy carbonyl groups as a substituent.

RCr does not proceed radical polymerization on account of steric hindrance and degradative chain transfer due to the existence of the β -methyl group, and it has been also reported that anionic high polymerization of RCr with methyl or *n*-alkyl esters is difficult because of the occurrence of side reactions in preference to propagation, when Grignard reagents, alkyl-lithiums, and LiAlH_4 are used as an initiator.⁸ On the contrary, high molecular weight poly(RCr) was obtained in polymerization of RCr with bulky *sec*- and *tert*-alkyl esters.^{9,10} Nagasawa and coworkers studied on the

Scheme 1

synthesis of poly(*tert*-butyl crotonate) with a semiflexible backbone and a narrow molecular weight distribution by anionic polymerization with very careful procedures for purification and polymerization,¹¹ and they examined as to the rigidity of the polymer chain from molecular characteristics in dilute solution or in bulk.¹² However, polymerizations of other *tert*-alkyl esters of RCr have not been ever reported.

Recently, we have commenced the study on synthesis and characterization of polymers containing adamantyl groups. The introduction of an adamantyl moiety was found to induce great advancement of thermal property of the polymers because adamantane is a thermodynamically stable and highly symmetrical tricyclic hydrocarbon, which consists of fused chair-form cyclohexane rings with same structure as a diamond lattice.¹³ For example, polymers from 1-adamantyl or 3,5-dimethyl-1-adamantyl esters of methacrylate and acrylate have extremely high glass transition temperatures and decomposition temperature.¹⁴ Other polymers bearing adamantyl moiety in the main or side chain have been also developed by some workers.¹⁵

In this study, therefore, anionic polymerization of RCr bearing *tert*-alkyl groups, *i.e.*, *tert*-butyl, *tert*-amyl, 1-adamantyl, and 3,5-dimethyl-1-adamantyl (Scheme 1) was performed with *sec*-butyllithium (sBuLi) as an initiator in toluene or THF, and the resulting

polymers were characterized on the structure, hydrolysis and thermal properties.

EXPERIMENTAL

Materials

tBCr was commercially available. tACr was prepared from crotonic acid and 2-methyl-2-butene with an acidic catalyst at a room temperature, or from crotonyl chloride and *tert*-amyl alcohol at 0°C. AdCr and DMAdCr were obtained from crotonic acid with 1-hydroxyadamantane and 1,3-dimethyl-5-hydroxyadamantane, respectively, which were supplied from Hakusui Chemical Industries Co., Ltd., in cyclohexane in the presence of sulfuric acid with reflux for 7 h.

AdCr: Yield 84%, bp 95°C/1 mmHg, d_{20} 1.058, n_D^{24} 1.506; IR (neat) $\nu_{\text{C}=\text{O}}$ 1710, $\nu_{\text{C}=\text{C}}$ 1650 cm^{-1} ; ^{13}C NMR (CDCl_3) δ 165.2, 142.5, 124.5, 79.5, 41.1, 36.0, 30.6, and 17.4 ppm; ^1H NMR (CDCl_3) δ 6.85 (dq, $J=15.6$ Hz and 6.7 Hz, 1H, $\text{CH}_3\text{CH}=\text{CH}$), 5.76 (dq, $J=15.6$ Hz and 1.8 Hz, 1H, $\text{CH}_3\text{CH}=\text{CH}$), 2.16 (br, 3H, CH (adamantyl)), 2.14 (br, 6H, CH_2 (adamantyl)), 1.84 (dd, $J=6.7$ Hz and 1.8 Hz, 3H, $\text{CH}_3\text{CH}=\text{CH}$), and 1.67 ppm (br, 6H, CH_2 (adamantyl)).

DMAdCr: Yield 80%, bp 124°C/0.9 mmHg, d_{20} 1.025, n_D^{24} 1.493; IR (neat) $\nu_{\text{C}=\text{O}}$ 1710, $\nu_{\text{C}=\text{C}}$ 1650 cm^{-1} ; ^{13}C NMR (CDCl_3) δ 165.7, 143.0, 124.6, 81.4, 50.5, 47.3, 42.5, 39.8, 33.8, 31.1, 29.9, and 17.7 ppm; ^1H NMR (CDCl_3) δ 6.84

(dq, $J=15.6$ Hz and 6.7 Hz, 1H , $\text{CH}_3\text{CH}=\text{CH}$), 5.75 (dq, $J=15.6$ Hz and 1.8 Hz, 1H , $\text{CH}_3\text{CH}=\text{CH}$), 1.83 (dd, $J=6.7$ Hz and 1.8 Hz, 3H , $\text{CH}_3\text{CH}=\text{CH}$), 1.1 – 2.2 (m, 13H , adamantyl), and 0.8 ppm (s, 6H , CH_3 (adamantyl)).

RCr were distilled under a reduced pressure over calcium hydride or triethylaluminum before use.¹⁶ Commercial sBuLi (1.0 mol l^{-1} in cyclohexane, Kanto Chemical Co., Tokyo) was used without further purification. Other reagents and solvents were purified by ordinary methods.

Polymerization Procedures

All procedures for transfer of materials were carried out under dry nitrogen atmosphere by using a Y-shaped glass tube with a rubbery cap and a hypodermic syringe. Polymerization was performed under vacuum and stopped with methanol containing hydrochloric acid. Polymer was precipitated with a large amount of methanol, filtered, and dried under vacuum.

Hydrolysis and Methylation

Poly(RCr) was hydrolyzed in chloroform in the presence of a catalytic amount of H_2SO_4 with reflux for 24 h, or in concentrated H_2SO_4 at room temperature for 5 days. The resulting poly(crotonic acid) was isolated by pouring into a large amount of water after the solvent was removed. Then it was reprecipitated from methanol and diethyl ether.

Poly(crotonic acid) was converted to the methyl ester by reflux in methanol in the presence of an acidic catalyst for 24 h, followed by the reaction with diazomethane. The polymer obtained was purified by reprecipitation from benzene and methanol.

Measurements

IR spectra were recorded on a JASCO A202 spectrometer. NMR spectra were taken by means of JEOL GX-400 in CDCl_3 at an ambient temperature. Gel permeation chromatography (GPC) was carried out with THF as

eluent at 38°C , and number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were calibrated with standard polystyrenes. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out in a nitrogen stream with a heating rate of $10^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

Anionic Polymerization

The results of anionic polymerization of RCr with sBuLi are shown in Table I. In polymerization of tBCr in toluene, a high molecular weight polymer was obtained with a high yield, but its molecular weight distribution (MWD) was relatively broad ($\bar{M}_w/\bar{M}_n > 2$). The use of THF as a solvent resulted in the achievement of fast polymerization at -78°C . Furthermore, the resulting poly(tBCr) was found to have a considerably narrow MWD ($\bar{M}_w/\bar{M}_n < 1.2$), although the initiation efficiency was low. These results were in good agreement with the results previously reported by Kitano *et al.*¹¹

In polymerization of AdCr in toluene, the polymer yield was very low even at 0°C , but addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was effective for increasing of the polymer yield. The polymerization of AdCr in THF yielded the polymer quantitatively, as well as the polymerization of tBCr. However, the moderately broad MWD of the resulting poly(AdCr) ($\bar{M}_w/\bar{M}_n \sim 1.5$) was different from the case of polymerization of tBCr. Recently, we found that low dispersity polymer was obtained when the polymerization of AdCr was carried out in the presence of lithium chloride (LiCl),¹⁷ although its polymerization rate decreased drastically.

Since 1,2-disubstituted ethylenes including RCr are generally low-reactive because of the steric hindrance of the β -substituent, the contribution of unfavorable side reactions, *e.g.*, carbonyl attack and metalation at the α -position may be more important during

Table I. Anionic polymerization of RCr in toluene or THF with sBuLi

Monomer	sBuLi	Solvent	Temp.	Time	Yield ^a	$\bar{M}_n^b$	$\bar{M}_w/\bar{M}_n^b$
mmol	mmol	ml	°C	h	%		
tBCr (13.6)	0.88	Toluene (8.3)	-78	28	48.1	112000	2.75
tBCr (13.6)	0.88	Toluene (8.3)	0	28	95.9	— ^c	— ^c
tBCr (13.6)	0.87	THF (15)	-78	1	80.2	11300	1.17
tBCr (13.6)	0.87	THF (15)	-78	2	95.8	20200	1.21
tACr (8.32)	0.61	THF (1.8)	-78	50	28.8	11800	1.54
AdCr (10.9)	0.87	Toluene (56)	-78	3	0.6	—	—
AdCr (10.9)	0.87 ^d	Toluene (56)	-78	3	73.9	45000	3.48
AdCr (10.9)	0.87	Toluene (56)	0	3	16.1	11000	3.38
AdCr (9.44)	0.87	THF (56)	-78	0.5	84.0	5200	1.48
AdCr (10.9)	0.87	THF (56)	-78	1	99.1	8100	1.58
AdCr (9.44)	0.87 ^e	THF (56)	-78	4	11.6	1900	1.20
DMAAdCr (9.26)	0.87	THF (56)	-78	1	74.7	11200	1.80

^a Methanol-insoluble polymer.^b Determined by GPC.^c Insoluble in THF.^d TMEDA (0.91 mmol) was added.^e LiCl (2.6 mmol) was added.

polymerization. More detail investigations on anionic polymerization of RCr with several alkylolithiums and on the effects of the additives such as TMEDA or LiCl are now continued.

Structure of Poly(RCr)

All poly(RCr)s obtained were colorless powder, and were soluble in benzene, THF, chloroform and insoluble methanol and *n*-hexane. In Figures 1—3, IR, ¹³C, and ¹H NMR spectra of AdCr and poly(AdCr) are shown, respectively. The absorption due to a carbon-to-carbon double bond did not observed in the spectra of the polymer. Thus it was verified that these polymerization proceeded *via* an opening of the double bond to yield a poly(substituted methylene), *i.e.*, poly(methylmethylene-*alt*-alkoxycarbonylmethylene).

Hydrolysis of Poly(RCr)

Poly(tBCr) and poly(tACr) were readily hydrolyzed by an acidic catalyst; *e.g.*, poly(crotonic acid) (poly(CrA)) was obtained quantitatively by reflux in chloroform in the presence of sulfuric acid. The resulting

Figure 1. IR spectra of (a) AdCr and (b) poly(AdCr).

poly(CrA) was soluble in methanol and alkaline water, and insoluble in many organic solvents. The IR spectrum of poly(CrA) obtained by hydrolysis is shown in Figure 4(a).

On the other hand, the polymers bearing an adamantyl group were found to show resistant

Figure 2. ^{13}C NMR spectra of (a) AdCr and (b) poly(AdCr) in CDCl_3 .

Figure 3. ^1H NMR spectra of (a) AdCr and (b) poly(AdCr) in CDCl_3 .

to hydrolysis; *i.e.*, a partly hydrolyzed polymer was only recovered from poly(AdCr) under the similar conditions (Figure 4(b)). Therefore more severe conditions were required to achieve quantitative hydrolysis of poly(AdCr). Figure 4(c) shows the IR spectrum of poly(CrA) isolated from hydrolysis of poly(AdCr) in concentrated sulfuric acid. It was identical to that of poly(CrA) obtained from poly(tBCr) above.

Figure 4. IR spectra of poly(CrA) obtained by hydrolysis with an acidic catalyst from (a) poly(tBCr), reflux in CHCl_3 , (b) poly(AdCr), reflux in CHCl_3 , (c) poly(AdCr), conc. H_2SO_4 , room temp.

Thermal Properties

Thermal properties of poly(RCr) obtained were investigated. The T_g of poly(AdCr) was not observed under its decomposition temperature, but poly(DMAdCr) showed a small transition at 230°C in the DSC thermogram. Recently, we found that T_g of poly(1-adamantyl methacrylate) was over its decomposition temperature, but its 3,5-dimethyl substituted derivative had T_g of 194°C .¹⁴ The marked increase in T_g by the introducing of an adamantyl moiety into polymers was reported also for other polymers.¹⁵ Moreover, the higher T_g of poly(DMAdCr) rather than the corresponding polymethacrylate may be ascribed to the lessflexible poly(substituted methylene) structure.

Figure 5 shows the results of TGA for poly(RCr) in a nitrogen stream. The initial decomposition temperature (T_{init}) and the maximum decomposition temperature (T_{max}) are summarized in Table II. In the thermograms for poly(tBCr) and poly(tACr), a rapid weight-loss was observed around 200°C , and decomposition proceeded via two or more

steps. The first weight-loss was considered to be due to elimination of olefins from *tert*-alkyl group of the side chain (Scheme 2).¹⁸⁻²⁰

The residual weights of the polymers after

Figure 5. Thermogravimetric analysis of poly(RCr) in a nitrogen stream at a heating rate of $10^{\circ}\text{C min}^{-1}$; (1) poly(tACr), (2) poly(tBCr), (3) poly(MCr), (4) poly(DMAdCr), (5) poly(AdCr).

Table II. Thermogravimetric analysis for poly(RCr)s^a

Polymer	T_{init} °C	T_{max}^b °C
Poly(tBCr)	219	260(279)(318)(378)
Poly(tACr)	206	250(285)(372)
Poly(AdCr)	305	428
Poly(DMAdCr)	308	418
Poly(MCr)	267	400

^a In a nitrogen stream with a heating rate of $10^{\circ}\text{C min}^{-1}$.

^b The values in parentheses indicate the peaks other than the T_{max} in the differential curves.

the first-step decomposition were 58.5% (275°C) and 53.6% (265°C) for poly(tBCr) and poly(tACr), respectively, agreeing with the values calculated with quantitative elimination of isobutene or 2-methyl-1-butene and 2-methyl-2-butene, respectively. The subsequent weight-loss peak due to the formation of an anhydride ring between the resulting carboxylic acids was observed around 300°C , but it seemed that the scission of the main chain also occurred concurrently.

To confirm the formation of poly(CrA), poly(tACr) was heated at 200°C under vacuum. The weight of the residual polymer decreased rapidly within an initial few hours, and then kept almost constant. In the IR spectra of the polymer isolated after heating (Figure 6), the characteristic absorption due to a carboxylic acid was observed. The absorption of anhydride consisting of a 6-membered ring was also observed at 1800 and 1750 cm^{-1} in the spectra when it was heated for a long period.

On the other hand, poly(AdCr) and poly(DMAdCr) were revealed to have an excellent thermal stability, *i.e.*, $T_{\text{init}} > 300^{\circ}\text{C}$ and $T_{\text{max}} \sim 420^{\circ}\text{C}$. These polymers containing adamantyl groups were thermally stable more than the polymer bearing a primary alkyl group, *e.g.*, poly(methyl crotonate) (poly(MCr)) which is derived by esterification of poly(CrA) as mentioned later. The high performance of these polymers may be originated from the stable 1-adamantyl esters which evolve hardly a corresponding olefin because of their rigid

Scheme 2

Figure 6. IR spectra of the polymers recovered after for pyrolysis of poly(tACr) in vacuum at 200°C for (a) 0, (b) 45, (c) 165, (d) 285 min.

Figure 7. ^1H NMR spectrum of poly(MCr) derived from poly(CrA).

and stable skeleton.^{13,21}

Poly(MCr) was obtained by methylation of poly(CrA). In the ^1H NMR spectrum of the resulting poly(MCr) (Figure 7), the methoxy proton was clearly observed as multiplet. This splitting of the methoxy proton signal may be useful for determination of the configuration of poly(RCr),⁸ as well as ^{13}C NMR spectroscopy.²² A study on tacticity of the polymers from β -substituted acrylic esters is important in order to clarify a mechanism and reactivity of the polymerization of 1,2-

disubstituted ethylenes.⁴ The structure and properties of poly(substituted methylene)s are of great interest for us, and further investigations on the tacticity of poly(RCr) are also now in progress.

Acknowledgments. A part of this work was supported by Grant-in-Aids for Scientific Research (No. 01430019) from the Ministry of Education, Science and Culture, Japan, and from Izumi Science and Technology Foundation. The authors are also greatly indebted to Hakusui Chemical Industries Co., Ltd. for supply of 1-hydroxyadamantane and 1,3-dimethyl-5-hydroxyadamantane, and to Mr. Shigeki Mori, Osaka City University, for TGA measurements.

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