Thermally Stable Cyclopolymer from the Ether Dimer of Adamantyl α-Hydroxymethylacrylate

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Introduction. Much attention has been given to the synthesis of polymers that have adamantyl moieties in or pendent to the polymer chain because of improved thermal properties over analogous aliphatic derivatives. For example, radial polymerization of adamantyl methacrylate gives a polymer with a high decomposition onset temperature (254 °C) and with no apparent thermal transitions below this temperature.[1] Adamantyl acrylate gives a polymer with a higher decomposition onset temperature (292 °C) but with an observable glass transition (153 °C).[1] Anionic polymerization of adamantly crotonate leads to a polymer with a decomposition onset temperature of 305 °C owing to its less flexible main-chain structure.[2] The even less flexible polymer derived from diadamantyl fumarate also shows a high decomposition onset temperature (ca. 290 °C) and no lower temperature transitions.[3] Excellent thermal stability of cyclopolymers has previously been described for materials obtained through cyclopolymerization of dialkyl α,α′-dimethylenepimelates.[4]

We have been investigating the cyclopolymerization of ether dimers of several α-hydroxmethylacrylates.[5-8] Especially interesting is the enhanced cyclization observed in the polymerization of the ether dimer containing bulky *tert*-butyl ester groups. This material affords high molecular weight (>500 000) cyclopolymer without cross-linking.[6,7] This phenomenon was ascribed to steric interactions inhibiting intermolecular addition much more than intramolecular cyclization.[7]

During study of the cyclopolymerization efficiency of various ether dimers,[9] it occurred to us that the adamantyl ester derivative should undergo facile conversion to soluble, high molecular weight cyclopolymer with excellent thermal properties. We describe here the diadamantyl monomer and polymer.

Results and Discussion. Initial attempts to synthesize the ether dimer of adamantyl α-hydroxymethylacrylate were carried out at 95 °C based on the successful synthesis of various other ether dimers at this temperature. However, polymerization was found to occur during the final stages of dimerization (indicating an excellent propensity for cyclopolymerization of this monomer), and the temperature was lowered to 80 °C. The product crystallized from methyl alcohol was determined to be a pure ether dimer by ^{1}H and ^{13}C NMR.[10]

Polymerizations were carried out by adding various amounts of toluene to 2.0 g of the ether dimer in a small round-bottomed flask, purging with nitrogen, and heating in an oil bath at the temperatures listed in Table I. In some cases, a trace of AIBN was added to accelerate polymerization, although spontaneous polymerization was reproducible and reliable. The resulting polymers were purified by reprecipitation into acetone twice. Polymerization conversions (as determined from the weight after the first precipitation) were kept to less than 15% except for the sample prepared for measurement of physical properties (run no. 4 in Table I).

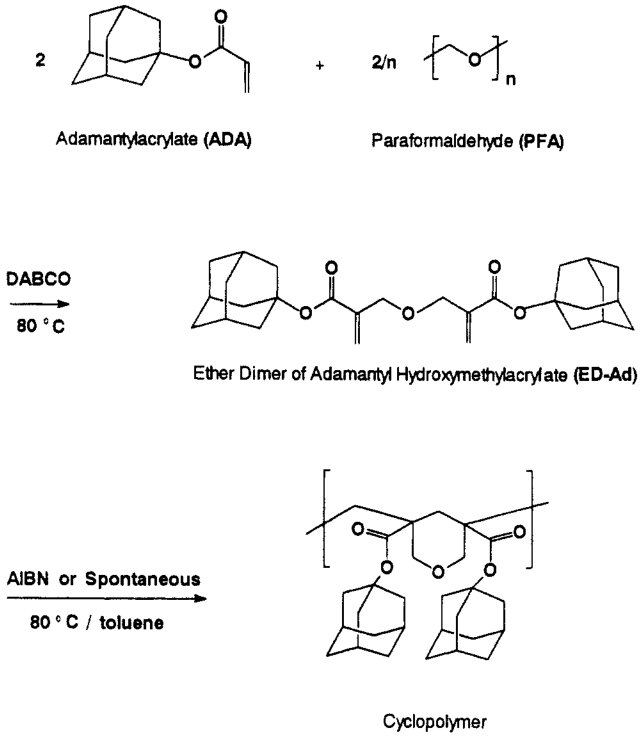

Figure 1. Overall synthesis of the monomer and polymer of the ether dimer of the adamantyl ester.

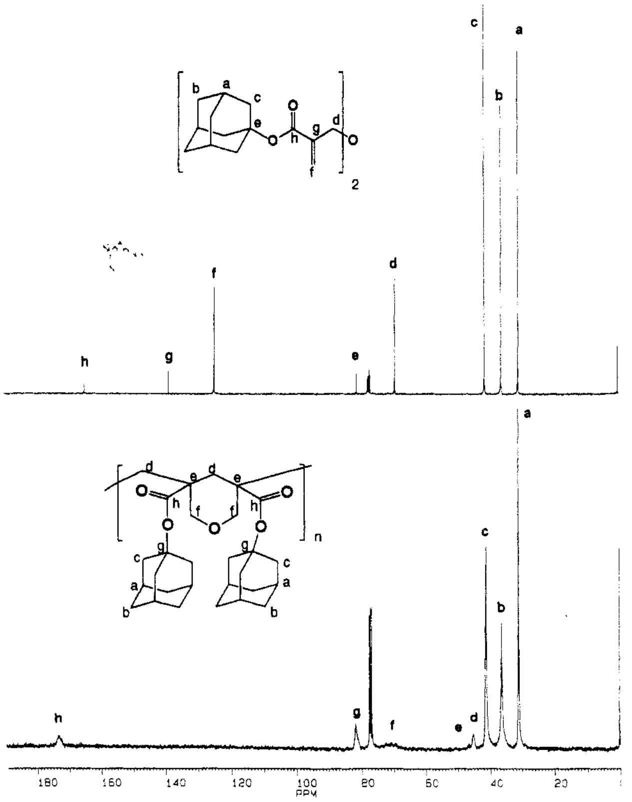

Figure 2. ^{13}C NMR spectra (CDCl$_3$) of the monomer (upper spectrum) and the polymer obtained from high-conversion cyclopolymerization.

Polymer characterization involved both ^{1}H and ^{13}C solution NMR (Bruker AC-300), differential scanning calorimetry (DSC; Du Pont 9900 thermal analyzer), thermal gravimetric analysis (TGA; Du Pont 9900 thermal analyzer), gel permeation chromatography (GPC; Tosoh HLC-8020), and dilute solution viscosity in chloroform (Cannon-Ubbelohde microviscometer). The fraction of cyclized units (f_c) in the polymers was calculated from the ratio of intensity of one of the double bond protons (6.05-6.4 ppm) to the total intensity of the methylene plus

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Table I. Feed Contents and Polymerization Results for Various Conditions with the Ether Dimer of the Adamantyl Ester of α-Hydroxymethacrylic Acid

run	feed (g)			temp	time	conv	[M]	
no.	dimer	toluene	AIBN	(°C)	(min)	(%)	(mol/L)	f_c[a]
1	2.0	7.51	0.001	80	10	11.8	0.42	0.987
2	2.0	1.44		80	50	2.5	1.27	0.974
3	2.0	1.44	0.002	65	17	2.9	1.27	0.963
4	2.0	3.03		80	1110	87.2	0.83	ca.1.0

[a] The standard deviation in f_c values was 0.002.

methine protons (0.4–5.0 ppm) in the ^{1}H NMR spectra of purified polymers. Reviewers have pointed out that this requires a very high accuracy and precision. We have repeatedly evaluated several samples under different conditions of concentration and spectrometer settings and obtained a standard deviation of 0.2% which leads to an estimated error of 0.5% in the determined f_c values discussed below. While this may marginally change the calculated values of the rate constant ratios, activation energy differences, and frequency factors, their *relative* values with respect to related derivatives, and the overall conclusions drawn, are not affected.

As shown in Table I, the values of cyclized fraction f_c are very high. The ratio of rate constant k_c/k_i (subscripts "c" and "i" indicate intramolecular reaction with cyclization and intermolecular propagation, respectively) at 80 °C was estimated to be 99 mol/L from the plot of $1/f_c$-1 versus [M] using equation $1/f_c\text{-}1 = 2[M]k_i/k_c$.[10] This value is close to that of the *tert*-butyl ester (83.0 mol/L) but much higher than that of the ethyl ester (19.0 mol/L)[8] which means that the steric effect of the adamantyl ester groups on cyclization efficiency is close to that of the *tert*-butyl ester groups. The difference in activation energy (E_c-E_i) and the ratio of the collision frequency factor (A_c/A_i) at a concentration of 1.27 mol/L were estimated to be 5.7 kcal/mol and 340 000 mol/L, respectively, from the plot of $\ln(1/f_c\text{-}1)$ versus $1/T$ using equation $\ln(1/f_c\text{-}1) = \ln(2[M]A_i/A_c) + (E_c\text{-}E_i)/RT$. These values are comparable to those calculated for the *tert*-butyl ester dimer (5.0 kcal/mol and 110 000 mol/L) but much different from those of the ethyl ester analog (3.1 kcal/mol and 1600 mol/L). The major difference in cyclization efficiency between the adamantyl and ethyl esters arises from the difference in the values of A_c/A_i. This implies that the effect of the ester substituent in inhibiting intermolecular addition more than intramolecular cyclization is increased with the bulkiness of the substituent. In other words, the entropic disadvantage for intermolecular addition is enhanced by bulky substituents.

The highly efficient cyclopolymerizability observed for low conversion samples explains the successful synthesis of soluble, high molecular weight (M_n = 40 000, M_w = 290 000, estimated from GPC with polystyrene standards) cyclopolymer obtained at high conversion (87%; run no. 4 in Table I), although difficulty in filtration of a THF solution suggests a highly branched structure. The viscosity of this sample also indicated high molecular weight ($[\eta]$ = 0.77 dL/g). Transparent brittle films were obtained from a methylene chloride solution, which suggests an amorphous cyclopolymer with a rigid polymer backbone. The ^{1}H NMR spectrum of this sample showed no residual double bonds. Peak assignments for the ^{13}C NMR spectrum were made by reference to the *tert*-butyl ester analog. The disappearance of one of the backbone carbon peaks is attributed to peak "d" appearing under peaks "c" and "b". Sharp peak "e" at ca. 42 ppm is similar to quaternary backbone carbon peaks of related cyclopolymers.

DSC analysis of the sample showed a glass transition temperature of 260 °C, with degradation becoming rapid beyond 375 °C. TGA analysis of the sample showed excellent thermal stability with a decomposition onset temperature of 335 °C and a 5% weight loss temperature of 375 °C. The maximum in the decomposition process occurred at ca. 420 °C. These values indicate that this cyclopolymer has comparble or better thermal stability than the adamantane-containing vinyl polymers described in the literature. The decomposition pattern in the TGA thermogram is similar to that of adamantyl acrylate in which most decomposition takes place over the temperature range of 350–450 °C, with the higher onset temperature perhaps being related to the higher activation energy for cyclization. In addition to advantages of high thermal stability, the availability of soluble, high molecular weight cyclopolymer by radical polymerization should allow the development of improved physical properties necessary for specific applications.

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(10) Adamantyl acrylate (manufactured by Hakusui Chemical Industry, Ltd.; 30.9 g, 0.15 mol), paraformaldehyde (4.5 g, 0.15 mol), 1,4-diazabicyclo[2.2.2]octane (DABCO, 2.25 g), and *tert*-butyl alcohol (9.0 g) were stirred and heated in a round-bottomed flask at 80 °C for 6 days. The resulting mixture was poured into 450 mL of methyl alcohol and stirred for 6 h at room temperature. The crystalline ether dimer gradually precipitated during stirring. The precipitant was filtered and dried in vacuo: yield 15.8 g (46.4%); mp 93 °C; ^{1}H NMR ($CDCl_3$) δ 6.20 (s, 1H), 5.81 (s, 1H), 4.20 (s, 2H), 2.15 (s, 9H), 1.67 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 164.7, 138.8, 124.5, 81.0, 69.0, 41.3, 36.2, 30.8.
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