5232 *Macromolecules* 1991, *24*, 5232–5233

Poly(di-1-adamantyl fumarate). A Thermally Stable Substituted Polymethylene

1,2-Disubstituted ethylenes polymerize to substituted polymethylenes with difficulty, owing to steric hindrance in the propagation step.[1] Otsu and co-workers[2,3] have studied the free-radical polymerization of dialkyl fumarates and dialkylfumaramides (Scheme I). The increase in the propagation rate and the molecular weight observed with an increase in the steric bulk of the ester groups suggests that inhibition of bimolecular radical termination is responsible for the apparent enhancement of reactivity.

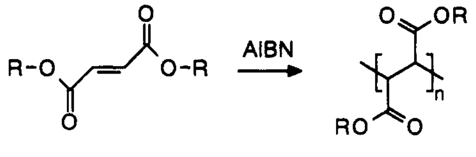
Thermal degradation of the resulting polyfumarates with primary and secondary esters began at 240–250 °C with loss of the alcohol and depolymerization to the monomer.[2] However, those with tertiary alkyl esters (for example *tert*-butyl) decomposed in two steps,[4] with the initial loss of alcohol at 190 °C being followed by residue degradation at 290 °C. During review of our manuscript, Otsu and co-workers described anionic polymerization of various *tert*-alkyl crotonates, including the 1-adamantyl and 3,5-dimethyl-1-adamantyl derivatives.[5] The adamantyl-containing polycrotonates showed an increased resistance to hydrolysis and excellent thermal stability as compared to the *tert*-butyl analogues. To date, the synthesis, polymerization, and thermal characterization of adamantyl fumarates has not been reported. We attempted the synthesis of poly(di-1-adamantyl fumarate) and poly(di-1-adamantylfumaramide) with the expectation of suppressing the thermal elimination of the alkene based on Bredt's rule[6] prohibition of the formation of a double bond at the adamantane bridgehead.

Experimental Procedures. Characterization involved differential scanning calorimetry (DSC; Perkin-Elmer DSC-7), solution NMR (Bruker AC-300), thermal gravimetric analysis (TGA; Du Pont 9900 thermal analyzer), dilute-solution viscosity in chloroform (No. 50 Cannon-Ubbelohde constant-dilution semimicroviscometer), and solid-state NMR (Bruker MSL-200). ^{1}H and ^{13}C NMR spectra were referenced to TMS at 0 ppm while ^{15}N NMR spectra were referenced to glycine at 0 ppm.

Di-1-adamantyl Fumarate. To a stirred solution of 1-adamantanol (12 g, 77 mmol) in 150 mL of dry THF under N_2 was slowly added 52 mL of 1.6 M *n*-BuLi in hexane. The resulting suspension was stirred for 1 h at 25 °C and cooled in an ice–water bath, and a solution of distilled fumaryl chloride (5.73 g, 37 mmol) in 40 mL of dry THF was added dropwise. After being stirred at 25 °C for 6 h, the reaction mixture was poured into 150 mL of deionized water and extracted with three 60-mL portions of CH_2Cl_2. The combined organic fractions were washed with 5% $NaHCO_3$ and then saturated NaCl solution and dried over $MgSO_4$, and the solvent was removed. Washing the resulting light brown solid with hot methanol followed by column chromatography on silica gel (CH_2Cl_2 eluent) afforded 8.4 g (56%) of pure di-1-adamantyl fumarate as a white solid. ^{1}H NMR ($CDCl_3$): δ 6.62 (s, 1 H), 2.16 (br, 9 H), 1.65 (br, 6 H). ^{13}C NMR ($CDCl_3$): δ 164.1, 134.6, 81.7, 41.2, 36.1, 30.8. IR (KBr): 2918, 2853, 1710, 1454, 1324, 1276, 1153, 1055, 979, 877, 814, 773, 735, 692 cm^{-1}. MS: *m/e* 384 (M^+). Mp: 193 °C.

***N,N'*-Di-1-adamantylfumaramide.** 1-Aminoadamantane (8.28 g, 55 mmol), toluene (50 mL), and dimethylacetamide (20 mL) were placed in an ice-cooled flask equipped with an addition funnel, reflux condenser, and nitrogen inlet. Fumaryl chloride (4.0 g, 26 mmol) and toluene (20 mL) were placed in the addition funnel and added dropwise to the rapidly stirring solution. The reaction mixture was allowed to warm to 25 °C and stirred an additional 16 h. The dark gray mixture was poured into acidic water to precipitate a gray solid, which was filtered, washed sequentially with water, dilute base, and water, and then dried in vacuo. Washing with hot ethanol afforded 5.30 g (53%) of the amide as a white powder. Mp: 315 °C dec. ^{1}H NMR ($CDCl_3$): δ 6.65 (s, 2 H), 5.40 (s, 2 H), 2.05, 2.00 (two overlapping br s, 18 H), 1.66 (br d, 12 H). ^{13}C CP/MAS NMR: δ 163.7, 133.9, 52.5, 41.8, 36.9, 30.1. ^{15}N CP/MAS NMR: δ 110.3. IR (KBr): 3295, 2908, 2849, 1719, 1637, 1531, 1454, 1302, 1173 cm^{-1}.

Scheme I



Bulk polymerization of di-1-adamantyl fumarate in the melt was performed at 210 °C in a sealed tube under argon using 1% 2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile (Wako) as the initiator. Solution polymerizations were carried out in a minimum volume of benzene (distilled from CaH_2) deoxygenated by four freeze–thaw cycles, using 1% AIBN (recrystallized from cold methanol) as the initiator at 60 °C for 60 h. The polymer was isolated by precipitation into methanol and purified by reprecipitation from chloroform into methanol, with a final washing by more methanol and drying in vacuo.

Results and Discussion. DSC examination of the fumarate showed an endotherm centered at 80 °C present in the *first* run to 150 °C only (not shown in Figure 1). This transition was followed by a melt at 190 °C and a broad exotherm commencing at 290 °C (Figure 1, lower trace). Once the sample had been heated above 290 °C, it did not melt on subsequent runs. The heat evolved during the exotherm was of the right order of magnitude for a substituted alkene polymerization (40 kJ mol^{-1}), suggesting spontaneous polymer formation. This was confirmed by heating the fumarate in a sealed tube at 300 °C *without* a free-radical initiator to give a polymer (confirmed by IR and NMR spectral analysis) with very low molecular weight ($[\eta] < 0.01$ dL/g).

Melt polymerization of a 0.8-g sample *with added initiator* gave a 36% yield of poly(di-1-adamantyl fumarate) as a white solid. ν(C=O): 1728 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.0 (v br, backbone CH), 2.09 (br), 1.61 (br). The ^{13}C NMR spectra and FT-IR spectra of the monomer and polymer are shown in Figures 2 and 3, respectively. The molecular weight of this material was also low, with $[\eta] = 0.06$ dL/g. The presence of several ^{13}C NMR resonances for both carbonyl and ester carbons suggests that the polymer is atactic.

Solution polymerization resulted in a higher molecular weight material with an $[\eta] = 0.16$ dL/g. DSC analysis (Figure 1, upper 2 traces) of the material revealed no thermal transitions below 300 °C (except for an endotherm at 80 °C on the first run only, broader than that observed for the monomer). The broad 80 °C transition was seen in the di-1-adamantylfumaramide also, and a transition at 97 °C in poly(diisopropyl fumarate) was ascribed to the motion of the ester groups.[7] However, there were no significant changes in the ^{13}C CP/MAS line widths and chemical shifts of the adamantyl peaks over the temperature range 35–80 °C. The disappearance of the endotherm on subsequent runs suggests that it may be associated with some thermodynamically less stable struc-

0024-9297/91/2224-5232$02.50/0

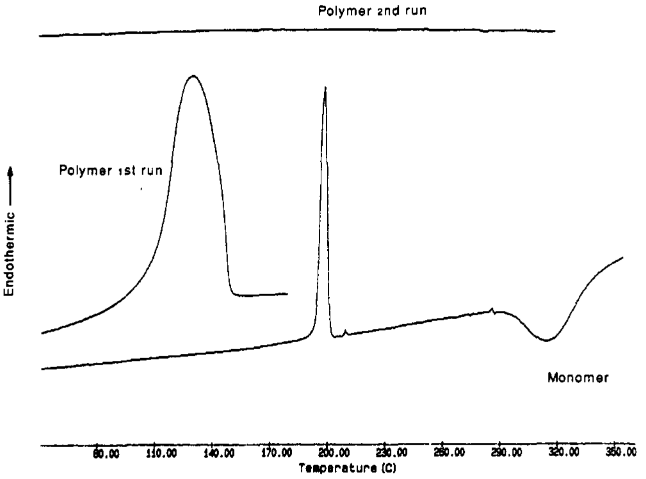


Figure 1. DSC thermograms of di-1-adamantyl fumarate (lower trace) and poly(di-1-adamantyl fumarate) (middle trace of first run up to 180 °C, upper trace of second run on same sample) at a heating rate of 10 °C/min.

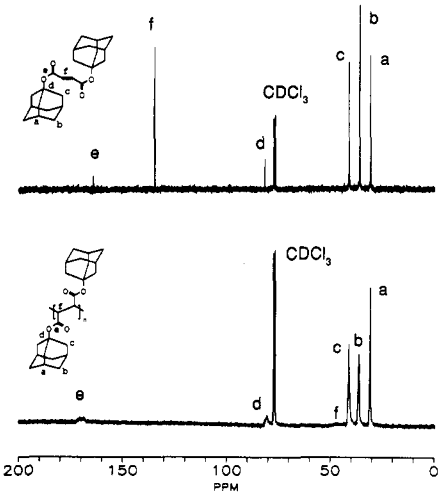


Figure 2. 75-MHz ^{13}C NMR spectra of the di-1-adamantyl fumarate monomer (upper spectrum) and polymer (lower spectrum) dissolved in $CDCl_3$.

ture or loss of excess free volume remaining after the precipitation process.

FT-IR analysis of the sample after heating to 300 °C showed no change in the position of the C=O stretch, implying no acid formation had taken place. TGA showed no mass loss below 290 °C, and less than 5% at 350 °C, beyond which degradation became rapid. Optical microscopy revealed no visible changes **nor sample softening or flow below 290 °C despite the sample remaining soluble**. Above this temperature discoloration became apparent in air. The material formed transparent, brittle films from chloroform. Thus, while poly(di-1-adamantyl fumarate) shows excellent thermal stability, its potential for useful applications is limited by the low molecular weight obtained to date. Otsu et al. similarly noted that the (*tert*-amyloxy)carbonyl substituent was too large to exhibit high polymerization rates.[2] Polymerization of di-1-adamantyl fumarate at higher temperatures (140 °C) using *tert*-butyl peroxide as the initiator also gave a low

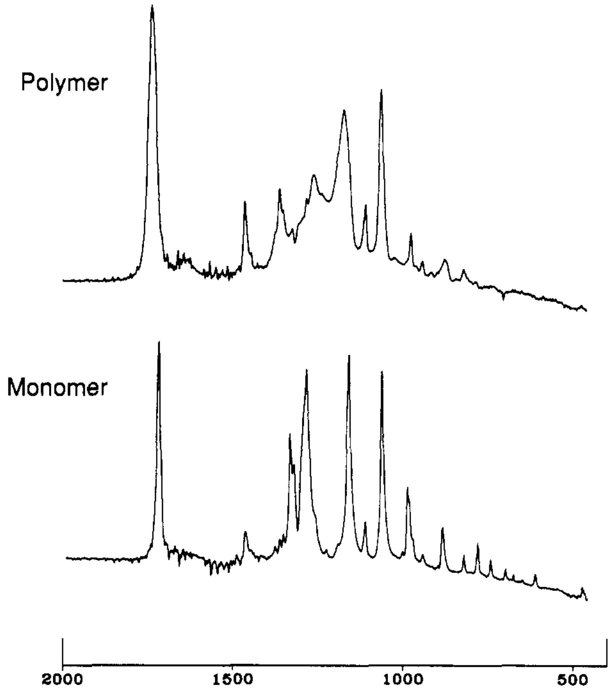


Figure 3. FT-IR spectra (KBr pellets) of the di-1-adamantyl fumarate monomer (lower spectrum) and polymer (upper spectrum).

molecular weight sample. Unfortunately, we have been unable as yet to find a suitable solvent for the radical polymerization of di-1-adamantylfumaramide, and its high melting point makes bulk polymerization unfeasible.

Acknowledgment. This work was supported in part by Imperial Chemical Industries (C & P Ltd.) and in part by the NSF through Grant DMR-8620138. V.R.R. thanks the U.S. Department of Education for a graduate fellowship.

References and Notes

(1) Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Interscience: New York, 1967; Chapter 10, p 332.
(2) Otsu, T.; Yasuhara, T.; Matsumoto, A. *J. Macromol. Sci., Chem.* **1988**, *A25*, 537.
(3) Matsumoto, A.; Tarui, T.; Otsu, T. *Macromolecules* **1990**, *23*, 5102.
(4) Kitano, T.; Ishigaki, A.; Uematsu, G.; Kawaguchi, S.; Ito, K. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 979.
(5) Matsumoto, A.; Horie, A.; Otsu, T. *Polym. J.* **1991**, *23*, 211.
(6) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; Chapter 4, p 138.
(7) Yamada, K.; Takayanagi, M.; Murata, Y. *Rep. Prog. Polymn. Phys. Jpn.* 1984, 27, 321.
(8) Permanent address: ICI (C&P) Ltd., R&T, The Heath, Runcorn, Cheshire, England.

L. J. Mathias,* A. V. G. Muir,[8] and V. R. Reichert

Department of Polymer Science
University of Southern Mississippi
Southern Station 10076
Hattiesburg, Mississippi 39406-0076

Received April 12, 1991
Revised Manuscript Received July 8, 1991