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# Preliminary evaluation of polyesters with pendent adamantyl groups synthesized from 5-adamantylisophthalic acid and 1,4-butanediol

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## Summary

Adamantane-containing polyesters were prepared from dimethyl 5-adamantylisophthalate and 1,4-butanediol using melt polymerization catalyzed by titanium isopropoxide. The adamantyl group caused a large increase in $T_g$ (of 80 to 142 °C) by inhibiting chain segmental motion in these flexible chain polymers. Surprisingly, the copolymer with 25 mol% dimethyl 5-adamantylisophthalate displayed semi-crystalline behavior as confirmed by DSC and X-ray diffraction results. The amorphous copolymers were soluble in chloroform and methylene chloride while the semicrystalline material was not.

## Introduction

Aromatic diacid/aliphatic diol polyesters are tough, semi-crystalline materials. Poly(ethylene terephthalate), PET, and poly(butylene terephthalate), PBT, and their copolymers are examples of these industrially important thermoplastics used as engineering polymers, fibers, and container plastics. An extensive number of derivatives have been prepared from a variety of aliphatic diols.[1] These polymers can be synthesized by the direct melt esterification of terephthalic acid or dimethyl terephthalate with the appropriate diol using a basic metal catalyst such as titanium (IV) isopropoxide. Properties can be manipulated by comonomer incorporation to control thermal behavior such as melting point and crystallization kinetics, glass transition temperature, and mechanical properties. A limitation of these polymers, however, is their relatively low glass transition temperatures ($T_g$).

Incorporating adamantyl groups into a variety of polymers has been shown to increase the $T_g$ significantly over the parent polymers. Adamantyl groups have been placed in polymers as part of the main chain,[2,3,4] and as side groups.[5,6,7,8,9,10] Pendent adamantyl groups have been shown by us[7-10] and others[5,6] to markedly increase $T_g$ of the parent polymer (> 100 °C). Adamantane has already been incorporated into polyesters using 1,3-adamantanediols or 1,3-adamantanedicarboxylic acids.[11] Unfortunately, the polymers were of low molecular weight due to the steric hindrance of groups attached to the adamantane.

The results reported here are a preliminary study of the synthesis and characterization of polyesters derived from 1,4-butanediol with 5-adamantyl isophthalic acid and copolymers with terephthalic acid.

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## Experimental

All chemicals were purchased from the Aldrich Chemical Company except where noted. Dimethyl 5-adamantylisophthalate was prepared as previously described.[12]

Intrinsic viscosities were determined in $CHCl_3$ at 30 °C. $^1H$ and $^{13}C$ NMR spectra were obtained in $CDCl_3$ or DMSO using a Bruker AC-300 spectrometer operating at 300.019 MHz for hydrogen and 75.469 MHz for carbon. IR spectra were recorded on an ATI-Mattson Galaxy 5020 FTIR spectrometer. Differential scanning calorimetry (DSC) was performed using a TA DSC 2920 module (TA 2100 controller) at a heating rate of 10 °C/min in a nitrogen atmosphere. Thermogravimetric analysis was conducted on a TA SDT 2960 module (TA 2100 controller) at a heating rate of 20 °C/min in nitrogen and air environments.

*Polymerization.*[13]

Dimethyl 5-adamantylisophthalate (**1**, 1 g, 3.05 mmol) and 1,4-butanediol (**2**, 0.4835 g, 5.37 mmol ) were charged to a 25 mL round bottom flask fitted with a Dean-Stark trap and a mechanical stirrer. The mixture was heated to 170 °C under a nitrogen blanket and titanium (IV) isopropoxide (**3**, 5μL) was added by syringe. The temperature was maintained at 140 °C for 2 h and methanol distilled from the reaction flask. After 2 h, the reactor was placed under vacuum, the temperature was gradually increased to 230-240°C and maintained there for 8 h. The reaction mixture was cooled to 23 °C and then dissolved in $CH_2Cl_2$. The polymer was isolated by precipitation into methanol to remove the catalyst and collected by filtration; yd ca 100%; intrinsic viscosity 0.26 dL/g; $^{13}C$ NMR ($CDCl_3$): $\delta$ 166.073, 152.18, 130.56, 130.34, 127.85, 64.61, 42.78, 36.40, 28.63, 25.41.

## Results and Discussion

New polyesters were prepared from 5-adamantyl dimethyl isophthalate (**1**) by melt transesterification with butanediol (Figure 1). Polymerizations were carried out using a typical two stage method.[13] Agitation was by a magnetic stir bar due to the limited scale of the reaction. The initial reaction temperature was increased from 140 to 170 °C to facilitate dissolution of the dimethyl ester and give a homogeneous reaction mixture. The initial stages of the reaction were monitored qualitatively by the evolution of methanol. After two hours, there was no additional distillate collecting in the trap. A vacuum connector was added, vacuum applied and the polyesterification continued at 240 °C for 2-6 h to give homopolymer samples (**4**) with intrinsic viscosities of 0.12-0.28 dL/g.

The low molecular weights obtained are apparently due to a reduced rate of reaction. $^{13}C$ NMR spectra showed resonances consistent with the proposed polyester structure and did not indicate side reactions that would limit polymer molecular weight (Figure 2). We suggest two factors contributed to the low rates. First, after 2 h, the reaction mixture was no longer stirring and the lack of agitation inhibited effective removal of the butanediol byproduct which retarded the rate of reaction. Second, the presence of the large hydrophobic adamantyl group changed the polarity of the reaction medium, slowing ester formation.

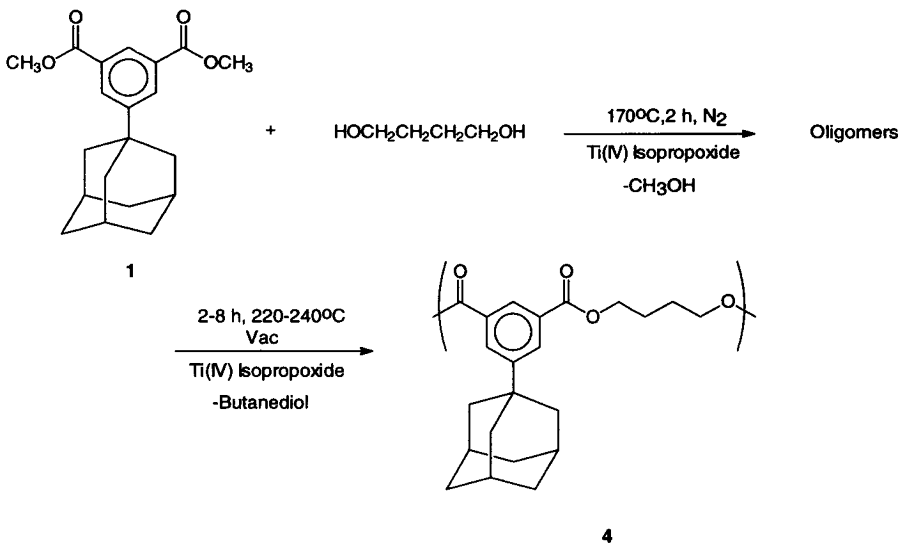

**Figure 1** Synthesis scheme for adamantyl-substituted polyesters.

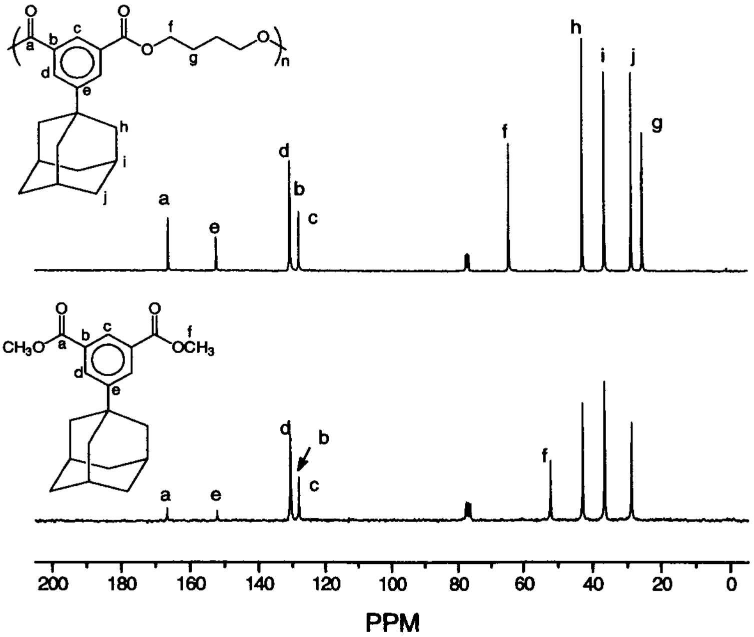

**Figure 2** $^{13}$C NMR spectra of **1** and the homopolymer **4**.

The fact that polymer intrinsic viscosities increased from 0.12 to 0.26 on increasing the reaction time from 2 to 6 h is consistent with a slow reaction.

Copolymers with dimethyl terephthalate were also prepared using the same general method and with a reaction time of 6 h. These polymers were prepared at 50:50 (**5**)and 25:75 (**6**) mole-ratios of **1** and the terephthalate ester, respectively. These copolymers had intrinsic viscosities of 0.31 and 0.38 dL/g, respectively. Their $^{13}$C NMR spectra showed two resonances, 166.1 and 165.6, of intensity equal to the feed ratios, suggesting that both monomers were incorporating into the copolymer in a random fashion (Figure 3).

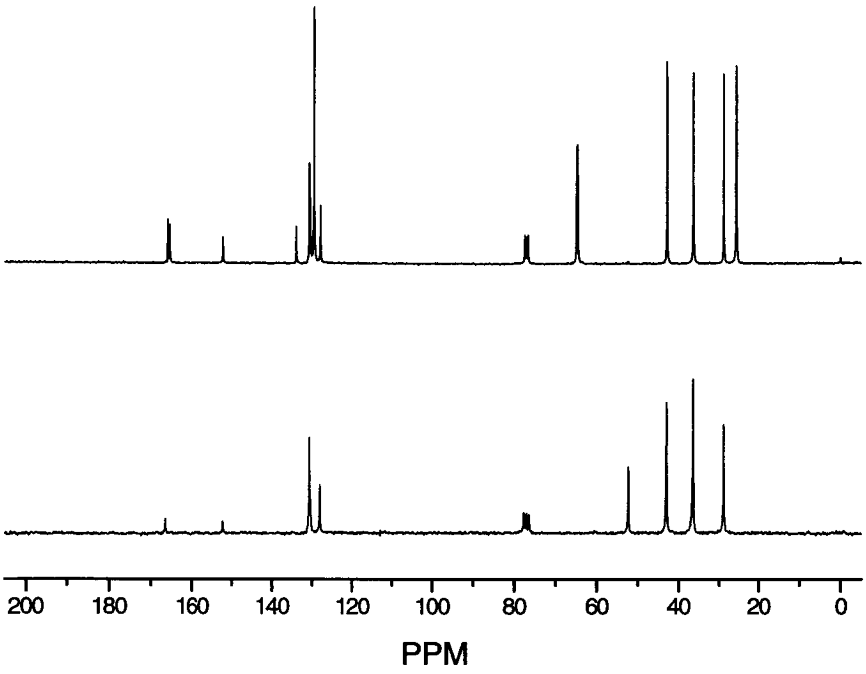

**Figure 3** $^{13}$C NMR spectra of **1** (lower) and copolymer **5**

The effect of the adamantyl group on $T_g$ was investigated by using DSC. The homopolymer **4** had a $T_g$ of 117 °C and showed no indication of melting or crystallization. This is an increase of 142 °C over the value of -25 °C reported by Wunderlich for totally amorphous poly(butylene terephthalate), PBT, and approximately 80 °C higher than that reported for the semi-crystalline material.[14] The copolymer **6** showed a broad endotherm with a peak at 157 °C on the first scan after annealing the sample at 120 °C in a vacuum oven. The melting transition appeared to be composed of overlapping events as shown in Figure 4. The enthalpy for the entire transition was approximately 22.4 J/g. Rapidly quenching the sample and reheating it resulted in a distinct, but small endothermic transition of 4.7 J/g at 171.9 °C. In comparison, the $T_m$ for poly(1,4-butylene terephthalate) was reported to be 234 °C.[14] The lower melting point suggests a new crystal form or, more likely, a poorly formed crystal structure due to the large number of defects in the polymer backbone.

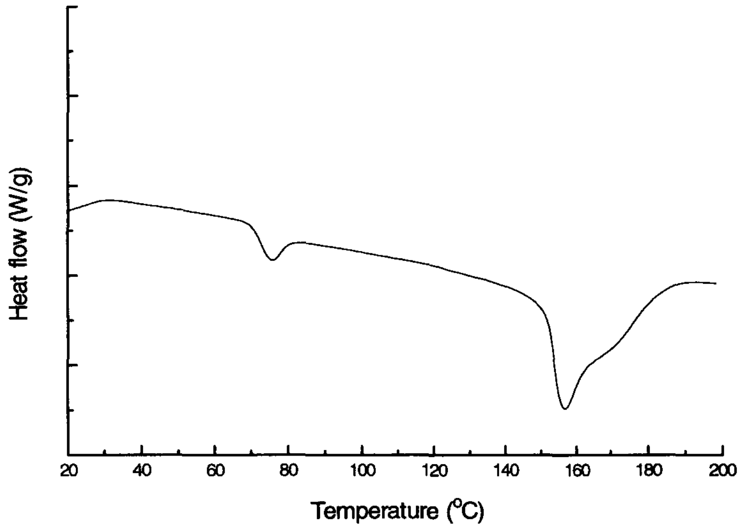

**Figure 4** DSC trace for Polymer **6** after annealing at 150°C for 8 h.

Considering the structure of copolymer **6**, the DSC results were surprising; at 25 mol% of 5-adamantylisophthalate units in the polymer, there is one defect in 4 repeat units on average ,made up of a large, bulky pendent adamantane. Wide angle X-ray diffraction patterns for polymers **4** and **6** are shown in Figure 5. The homopolymer showed only a broad peak indicative of an amorphous glass. In contrast, the copolymer **6** showed three additional broad reflections at 20, 23, and 25 degrees 2 θ suggesting crystalline order and supporting the DSC results. The breadth of the reflections indicated a high dispersity in the ordered phase and suggested poorly developed crystallites.

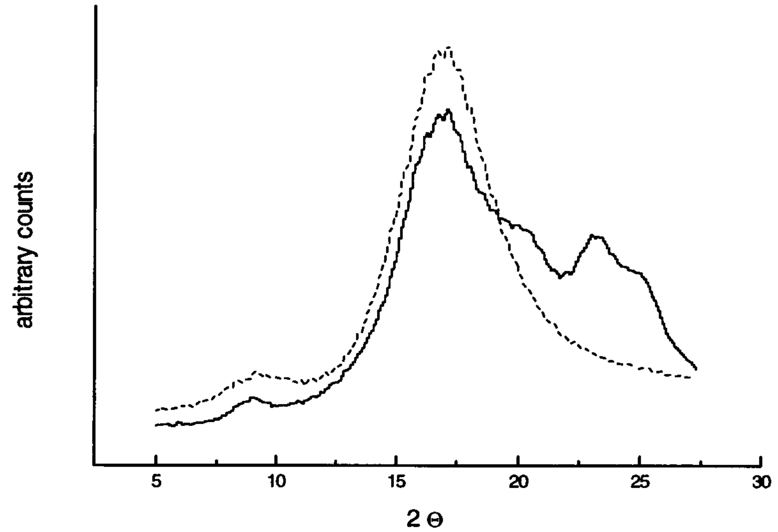

**Figure 5** WAXD pattern for polymer **4** (····) and copolymer **6** (—).

## References

1. Encyclopedia of Polymer Science and Engineering, Vol. 12; John Wiley & Sons: New York, 1988.
2. Chern, Y. T.; Wang, W. L. *Macromolecules*, **1995**, *28*, 5554.
3. Chern, Y. T.; Chung, W. H. *J. Polym. Sci., Polym. Chem. Ed.*, **1996**, *34*, 117.
4. Pixton, M. R.; Paul, D. R. *Polymer*, **1995**, *36*, 3165.
5. Wang, J. J.; Chern, Y. T.; Chung, M. A. *J. Polym. Sci., Polym. Chem. Ed.*, **1996**, *34*, 3345.
6. Chern, Y. T. *Polym. Bull.*, **1996**, *36*, 59.
7. Mathias, L. J.; Reichert, V. R.; Muir, A. V. G. *Chem. Mat.*, **1993**, *5*, 4.
8. Matsumoto, A.; Tanaka, S.; Otsu, T. *Macromolecules*, **1991**, *24*, 4017.
9. Avci, D.; Kusefoglu, S. H.; Thompson, R. D.; Mathias, L. J. *Macromolecules*, **1994**, *32*, 2937.
10. Tsuda, T.; Mathias, L. J. *Macromolecules*, **1993**, *26*, 4734.
11. Khardin, A. P.; Radchenko, S. S. *Russ. Chem. Rev.*, **1982**, *51*, 272.
12. Lewis, C. M.; Mathias, L. J., manuscript in preparation.
13. Kollodge, J. S.; Porter, R. S. Macromolecules, **1995**, 28, 4089.
14. Wunderlich, B.; Thermal Analysis, Academic Press: Boston, 1990, p 426.