Macromolecules

Volume 36, Number 15 July 29, 2003

Communications to the Editor

Synthesis of Novel, Cubane-Containing Norbornene-Based Polymers

Ronny Priefer, Sophie Nguyen, Patrick G. Farrell, and David N. Harpp*

Department of Chemistry, McGill University, Montreal, Canada H3A 2K6

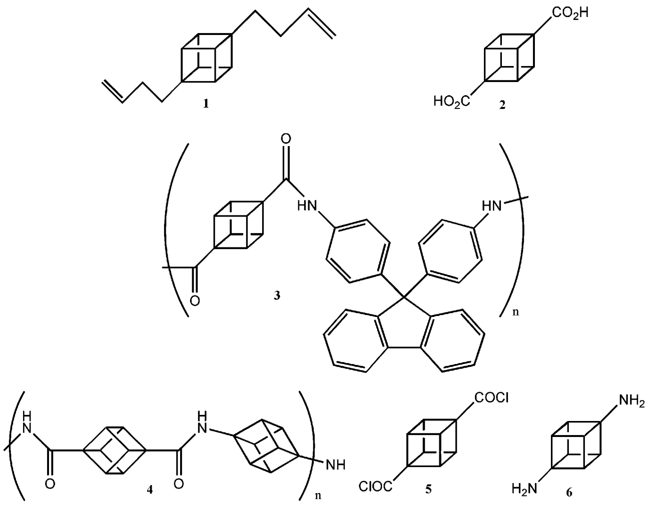
Received December 3, 2002
Revised Manuscript Received April 24, 2003

Since its initial synthesis by Eaton in 1964,[1] cubane and its derivatives have been extensively studied, and various syntheses have afforded a wide array of functionalities.[2] However, the preparation of cubane-containing polymers has only begun to receive attention since 1996.[3−5]

The first example of the formation of a cubane-containing polymer was published by Chauvin,[3] in which a metathesis polymerization of 1,4-bis(homoallyl)-cubane (**1**) was reported. This technique afforded an oligomer with 6−7 repeat units, and the authors attributed the lack of elongation of the chain to lack of solubility.[3] Soon after, Kakuchi performed polycondensation reactions of cubane-1,4-dicarboxylic acid (**2**) with a range of aromatic diamines.[4] With 9,9′-bis(4-aminophenyl)fluorene (**3**), they successfully obtained a polymer of ∼25 repeat units, with a PDI of 2.41. However, this polymer was only soluble in very polar solvents (i.e., DMF, DMSO).[4] Recently, Mahkam and Sanjani reported the synthesis of poly(cubyl cubanamide) (P-CCA, **4**) via a polycondensation of cubane-1,4-dicarbonyl chloride (**5**) with 1,4-diaminocubane (**6**).[5] P-CCA contained ∼43 repeat units, but as with the previous examples, insolubility in nonpolar solvents was exhibited. These workers were able to obtain a polymer of ∼68 repeat units by the polycondensation of 1,4-diaminocubane with adipoyl chloride.[5]

Here, we report the first examples of cubane-containing polymers where solubility in low-polarity solvents is not a problem. This was accomplished by tethering a cubane derivative to the polymer backbone via an ester linkage. In addition, the thermodynamic behavior of the polymers is remarkably similar to that of the simple cubane functionality.

Chart 1



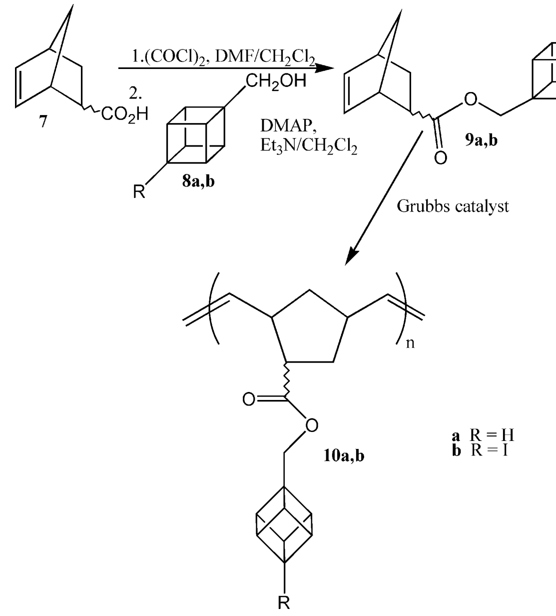
Commercially available 5-norbornene-2-carboxylic acid (**7**: mixture of *endo* and *exo*) was reacted via a Vilsmeier reaction [$(COCl)_2$, DMF] to form the acid chloride. This was subsequently reacted with either cubylcarbinol (**8a**)[6] or 1-iodo-4-(hydroxymethyl)cubane (**8b**)[6] to form the corresponding norbornene esters **9a**[7] and 9**b**.[8] The products exist as mixtures of *endo* and *exo* adducts, which could be separated via column chromatography. However, for the purpose of polymerization, the separation was not performed, and the purified mixture of diastereomers was used. Reacting norbornene **9a** with Grubbs catalyst in a ROMP reaction[10] in THF under N_2 for 24 h at room temperature afforded polymer **10a** upon precipitation with pentane. This reaction was repeated using norbornene **9b** and polymer **10b** was obtained. In the synthesis of **10b**, a ratio of ∼65:1 of **9b** to catalyst was used, and ultimately the polymer exhibited a molecular weight (GPC using polystyrene standards) of $M_n = 2.7 \times 10^4$ (calculated $M_n = 23\,989$) and PDI = 1.11. This corresponds to ∼71 units. In the formation of polymer **10a**, a ratio of ∼88:1 of **9a** to catalyst was used. This produced a polymer of $M_n = 3.6 \times 10^4$ (calculated $M_n = 21\,479$), PDI = 1.26, and ∼143 units. Neither polymer exhibited a glass transition or melting temperature. TGA revealed that **10a** and **10b**

---

* Corresponding author: e-mail david.harpp@mcgill.ca.

10.1021/ma025906z CCC: $25.00

Scheme 1. Synthesis of Cubane-Containing Norbornene Polymers[9]



undergo a 10% weight loss at 383 and 250 °C, respectively (Figure 1).

The weight losses from the TGA curves correspond to the loss of the carboxyl group as well as the cubane functionality. The loss of tethering groups from polynorbornenes has been reported in the past, and their TGA resembles the decomposition of polymer **10a**.[11] However, the rapid decomposition of polymer **10b** was rather startling. Examples of the greater stability of non-iodo-functionalized cubane derivatives have been reported in the past;[12] however, the route of decomposition has never been ascertained.

Upon heating neat **8b**, the solid melts and then gradually darkens until vigorous decomposition occurs at ~250 °C. This appears to correspond with the exotherm detected in the DSC at 253 °C and the rapid loss of mass in the TGA. The presence of I_2 and HI was detected in the resulting decomposed product.[13] With **8a**, the solid melts and, upon further heating, evaporates. This suggests that the thermodynamic behavior of cubane-containing polymers is similar to that of the simple cubane precursor and that they might ultimately be useful for the synthesis of a variety of potentially explosive cubane polymers.

To determine whether reactions could be performed on polymer **10b** so that other functionalities eventually could be attached to the cube, **10b** was reacted with lithium di-*tert*-butyl dibenzylide and quenched with MeOH to give polymer **10a**.[14] Thus, we believe that the replacement of iodine by alternative electrophiles could ultimately deliver a range of cubane-containing norbornene-derived polymers.

In conclusion, two cubane-containing norbornene polymers have been synthesized. These represent the first examples of high molecular weight cubane-containing polymers where the products have significant solvent solubility. The polymers have been shown to behave thermally like simple cubane derivatives. The conversion to a range of functionalized cubane moieties by lithiation of **10b** and subsequent addition of a variety of electrophiles is in progress.

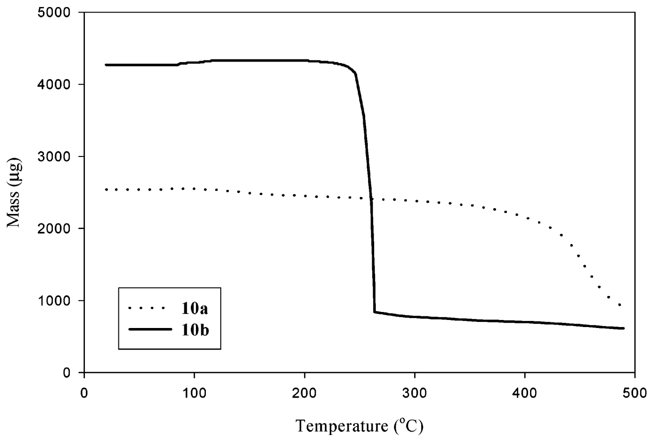


Figure 1. TGAs of polymers **10a** and **10b**.

Acknowledgment. The authors are grateful to Professor Allan Hay for special insights and thank Professor H. Sleiman and Dr. Z. Giaolodoia for helpful discussions, Mr. O. Terreau for performing GPC analysis, and Dr. A. Hlil for performing TGA and DSC experiments. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.

References and Notes

(1) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962, 3157.
(2) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421.
(3) Chauvin, Y.; Saussine, L. *Macromolecules* **1996**, *29*, 1163.
(4) Kakuchi, T.; Hirahata, W.; Yano, S.; Kaga, H. *Polym. Bull. (Berlin)* **1997**, *38*, 651.
(5) Mahkam, M.; Sanjani, N. S. *Polym. Int.* **2000**, *49*, 260.
(6) Priefer, R.; Farrell, P. G.; Harpp, D. N. *Synthesis* **2002**, 2761.
(7) ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.21-1.55$ (m), 1.86−2.01 (m), 2.24 (dd, 4.40, 10.40 Hz), 2.90 (br s), 2.94−2.99 (m), 3.04−3.11 (m), 3.19 (br s), 3.24 (br s), 3.85−3.93 (m), 3.99−4.03 (m), 4.11 (d, 12.40 Hz), 4.19−4.32 (m), 5.89 (dd, 3.20, 6.00 Hz), 6.09−6.12 (m), 6.16 (dd, 2.80, 5.20 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 29.4$, 30.5, 38.5, 41.7, 42.6, 43.3, 43.4, 44.6, 45.8, 45.9, 46.4, 46.9, 47.4, 48.6, 49.6, 55.2, 56.0, 64.6, 64.9, 67.3, 131.8, 135.2, 137.5, 138.1, 174.8, 176.0; viscous oil. HRMS: calcd for $C_{17}H_{18}O_2$ H^+ 255.1385; found: 255.1394.
(8) ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.24$ (d, $J = 8.40$ Hz), 1.28−1.44 (m), 1.48 (d, 8.00 Hz), 1.90 (m), 2.23 (dd, 4.40, 10.00 Hz), 2.90 (br s), 2.94 (t, 3.20 Hz), 2.96 (t, 4.00 Hz), 2.98 (br s), 3.16 (br s), 3.99−4.06 (m), 4.13−4.34 (m), 5.84 (dd, 2.80, 5.80 Hz), 6.10 (ddd, 2.80, 6.00, 12.8 Hz), 6.16 (dd, 3.20, 5.20 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 29.4$, 30.5, 38.5, 41.7, 42.5, 43.2, 43.4, 45.8, 46.3, 46.9, 48.4, 49.7, 54.5, 54.6, 54.7, 56.8, 63.7, 63.8, 64.0, 66.6, 132.1, 135.5, 137.7, 137.9, 174.6, 176.2; mp 38−45 °C. HRMS: calcd for $C_{17}H_{17}O_2I$ H^+ 381.0351; found: 381.0359.
(9) Polymers **10a** and **10b** in Scheme 1 are not meant to indicate pure isotactic or syndiotatic stereochemistry.
(10) Grubbs, R. H.; Pine, S. H. *Comprehensive Organic Synthesis;* Pergamon: New York, 1991; Vol. 5, Chapter 9.3.
(11) Biagini, S. C. G.; Coles, M. P.; Gibson, V. C.; Gilles, M. R.; Marshall, E. L.; North, M. *Polymer* **1998**, *39*, 1007.
(12) Priefer, R.; Farrell, P. G.; Harpp, D. N. *Tetrahedron Lett.* **2002**, *43*, 8781.
(13) The residue was partially dissolved in H_2O to afford a brown liquid with pH ~ 4, which was active to starch paper. A precipitate formed upon addition of aqueous $AgNO_3$ which could be dissolved with saturated $Na_2S_2O_3$. The initial color faded upon addition of saturated Na_2SO_3. Mass spectrometry revealed signals that correspond to I_2 (254) and HI (128).
(14) ^{1}H and ^{13}C NMR as well as FTIR of **10a,** prepared from **10b**, were identical to that prepared from the ROMP reaction of **9a.** $M_n = 1.9 \times 10^4$ (calculated $M_n = 17\,942$).

MA025906Z