Macromolecules **1995,** *28,* 4347−4349 **4347**

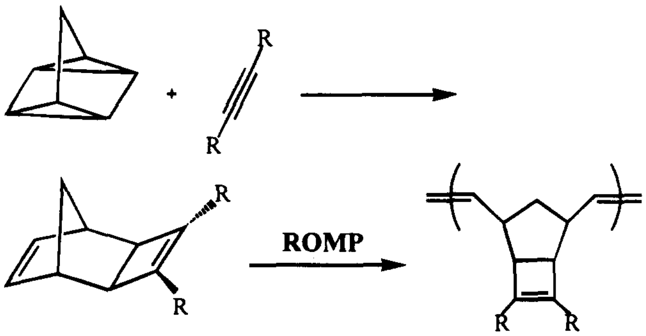
New Polymers from Ring-Opening Metathesis Polymerization of Quadricyclane Adducts

Randall S. Saunders

Sandia National Laboratories, P. O. Box 5800,
Albuquerque, New Mexico 87185-0368

Received December 27, 1994
Revised Manuscript Received April 3, 1995

Introduction. Ring-opening metathesis polymerization (ROMP) has been known for quite some time. With the recent contributions of Grubbs[1] and Schrock,[2] organometallic initiators have been developed that are known to perform ROMP on norbornene-type compounds in a well-behaved and living fashion, resulting in monodisperse homopolymers and block copolymers.[3−7] The polymerization of norbornenes made from cyclopentadiene (Cp) adducts has extensively been studied using these initiators. However, the polymerization of norbornene compounds from quadricyclane adducts (see below)[8−10] has not yet been studied.



It has been observed with certain polymer systems that thermal treatment converts them to electrically conductive carbon.[11,12] Our initial intention was to identify norbornene-type polymers that could similarly be converted to carbon upon thermal treatment. We therefore turned our attention to the polymerization and thermal treatment of quadricacyclane adducts. It has been reported previously that quadricyclane undergoes a $2_\pi + 2_\sigma + 2_\sigma$ cycloaddition with strongly electron-withdrawing dienophiles to give norbornene-type compounds having a fused cyclobutene or cyclobutane ring.[8−10] It was our hope that the fused cyclobutene ring could undergo a thermal ring opening to form a diene, which would undergo further cross-linking through a Diels−Alder mechanism with existing double bonds in the backbone. This highly cross-linked system would hopefully promote the conversion of the polymer in high yield to carbon. This thermal ring opening of cyclobutenes is well-known[13] and is most familiar in the new benzocyclobutene materials currently available from Dow Chemical Co. Apart from our desire to identify high-yield carbon-forming materials, we have observed in some circumstances that adducts with quadricyclane are readily polymerized by ROMP, whereas the analogous Cp adducts cannot be polymerized. These new polymers may therefore also prove useful where certain stereospecific[14] functionalities on the polymer are required, but these functionalities are not tolerated as Cp adducts. Therefore we report in this paper the polymerization of these quadricyclane adducts using a Schrock-type molybdenum based initiator and their comparison to analogous Cp adduct polymerizations.

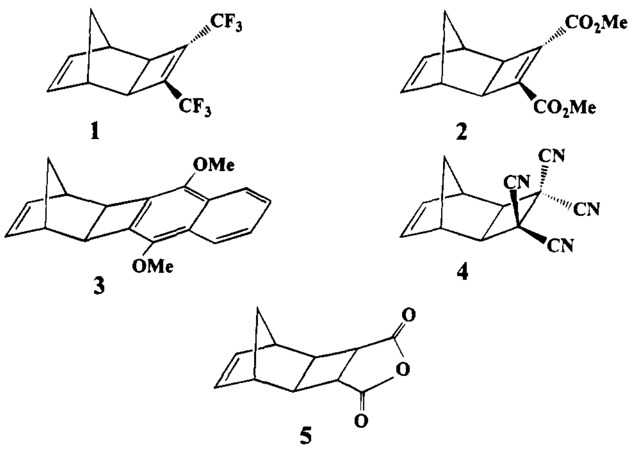


Figure 1. Quadricyclane adducts synthesized and used in this study.

Results and Discussion. All of the monomers in Figure 1 are readily available through reactions with the appropriate dienophiles.[8−10,16] Polymerization of these monomers was carried out in dry tetrahydrofuran (THF) using the Schrock molybdenum based initiator.[15] Each polymer had a target molecular weight of 20 000.

Monomer 1. The polymerization of monomer 1 proceeded smoothly and quantitatively. A proton NMR spectrum was taken of the final product after 1 h (Figure 2a) and showed no remaining peak at 6.2 ppm which would correspond to the strained double bond of the monomer. Instead, a broader bimodal peak from 5.2 to 5.5 ppm was observed and indicated the formation of a polymer having a high trans double bond content[5] (82%) in the backbone. A number of broad peaks appear in the range of 1.0−4.0 ppm, which indicates the existence of a polymer in a multitude of isomeric states. A ^{13}C NMR spectrum was taken of the final polymer and the spectrum is shown in Figure 2b. In comparison to the carbon NMR spectrum of the cyclopentadiene (Cp) adduct,[4] the analogous carbon peaks of poly-**1** are broader, indicating a lack of stereoregularity in the polymer. Polymerization of the Cp adduct with classical ROMP catalysts yields even broader peaks. We therefore conclude that there may be some degree of tacticity in poly-**1**, but not to the extent that it exists in the Cp adduct polymer. This is consistent with a less than quantitative trans content observed in poly-**1**. A closer inspection of the $-CF_3$ carbon signal in the polymer (see inset of Figure 2b) reveals that each signal of the quartet is split into two peaks, which occur in a ratio of 80:20. This is nearly identical to the trans/cis ratio determined from the proton NMR spectrum. We therefore conclude that the splitting of the quartet peaks is associated with the cis/trans configuration of the double bonds in the backbone. The resulting polymer was readily soluble in most organic solvents, indicating a lack of crystallinity (and therefore a lack of tacticity). This is in contrast to the polymerization of the analogous Cp adduct with the same initiator, which shows a crystalline melting point at 200 °C.[4]

Poly-**1** was analyzed by GPC, and the trace is shown in Figure 3. From these results, we conclude that the polymerization of monomer **1** is living and well-behaved. A molecular weight of 22 800 (vs polystyrene standards) and a polydispersity of 1.05 for this polymer were

---

[†] Sandia National Laboratories is supported by the Department of Energy under Contract No. DE-AC04-94AL85000.

0024-9297/95/2228-4347$09.00/0 © 1995 American Chemical Society

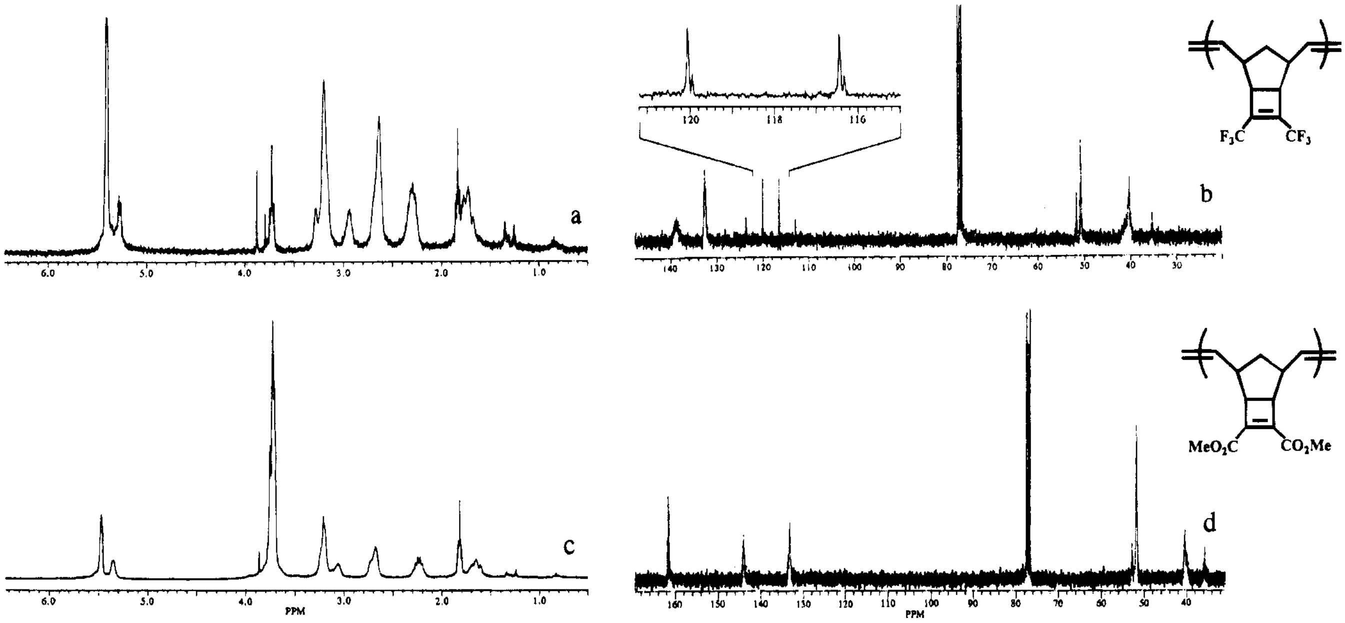


Figure 2. ^{1}H and ^{13}C NMR spectra of poly-**1** (a,b) and poly-**2** (c,d) in $CDCl_3$.

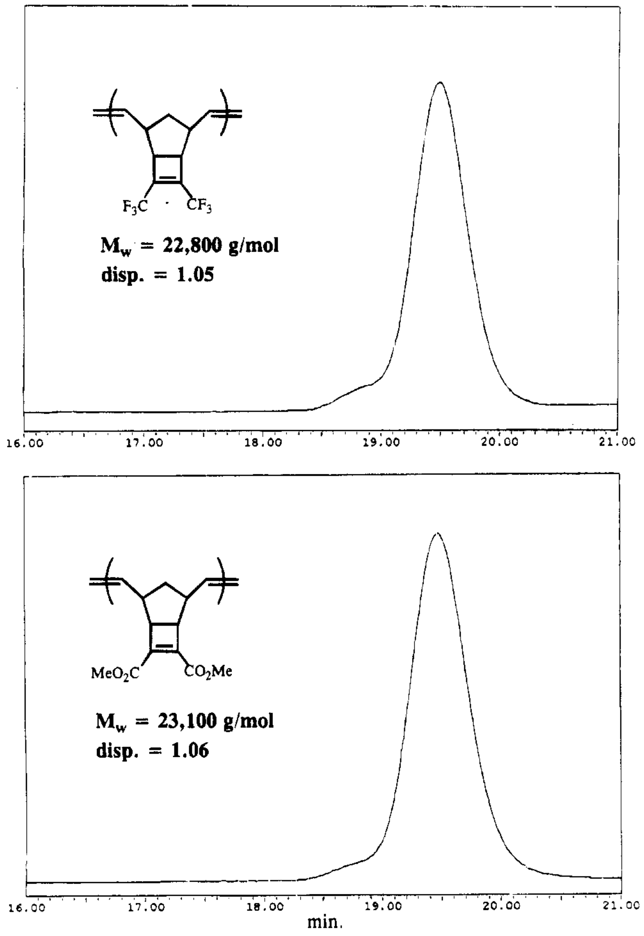


Figure 3. GPC traces of poly-**1** (top) and poly-**2** (bottom). Molecular weights are relative to narrow polystyrene standards.

obtained, indicating that the polymerization is controlled and the resulting polymer is essentially monodisperse. A small shoulder at double the molecular weight can be seen and is associated with minute amounts of impurities terminating two living chains by linking them together. This phenomenon has often been seen in other systems.[5,21] It has been observed previously that the polymerization of the Cp adduct is quite slow, taking up to 5 h under identical conditions.

Monomer 2. Monomer 2 was also polymerized and analyzed by proton NMR (Figure 2c), by ^{13}C NMR (Figure 2d), and by GPC (Figure 3). Again, within the course of 1 h, the NMR spectrum shows the polymerization to be complete: the strained double bond signal at 6.09 ppm has completely disappeared and has been replaced by a broader doublet centered around 5.5 ppm. The double bonds in the backbone are observed to be 75% trans from this spectrum. The ^{13}C NMR spectrum again shows broad peaks, indicating the lack of tacticity in this polymer. The GPC trace shows a molecular weight of 23 100 (vs polystyrene) and a polydispersity of 1.06. This is close to the target weight of 20 000, again indicating that the polymerization of this monomer is well-behaved and the resulting polymer is essentially monodisperse (the small double molecular weight shoulder is also observed for this polymer). Similar reaction times were observed for the analogous Cp adduct with the same initiator.[4]

It is interesting to note here that similar trends are observed when comparing poly-**1** to poly-**2** and when making comparisons between the analogous Cp adduct polymers. Specifically, the trans double bond content in the backbone is decreased when switching from the $-CF_3$ group to the less polar $-CO_2Me$ substituted systems.

Monomer 3. Monomer **3** was swiftly polymerized, forming an insoluble precipitated polymer. Due to the intractibility of this polymer, it was not further characterized.

Monomer 4. The polymerization of monomer **4** is quite interesting. Ten minutes after addition of the initiator a precipitated polymer starts to form, and the amount increases with time. Upon termination of the polymerization after 1 h, the polymer was precipitated in water and dried, and a proton NMR spectrum was taken in DMSO-d_6 (Figure 4, top). The spectrum indicates the presence of a small amount of unreacted monomer (singlet at 6.18 ppm) and of polymer (broad singlet centered around 5.6 ppm). Upon closer examination of the spectrum between 5.0 and 6.0 ppm, a small shoulder is observed upfield from the broad singlet. We

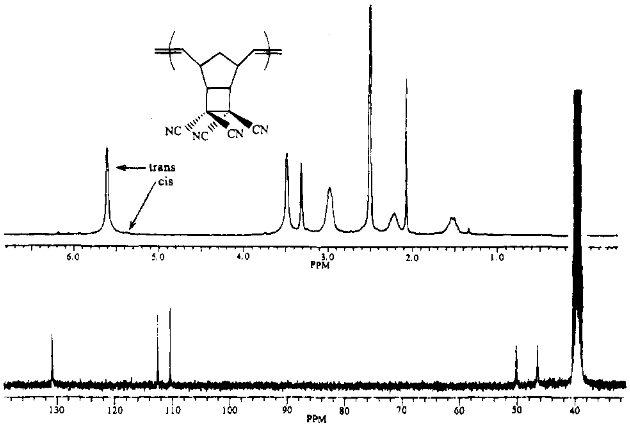


Figure 4. ^{1}H NMR (top) and ^{13}C NMR (bottom) of poly-**4** in DMSO-d_6.

associate the broad singlet with trans double bonds in the backbone,[5] and the small shoulder upfield with cis double bonds. Therefore, this polymer contains a highly trans double bond content in the backbone (>99%). The simpler and slightly more resolved peaks for poly-**4** in the region of 1.5–3.5 ppm (as compared to poly-**2** in DMSO-d_6) would also indicate a more stereoregular polymer. The ^{13}C NMR spectrum (DMSO-d_6; Figure 4, bottom) of poly-**4** shows fairly sharp peaks for the carbon signals, again indicating a high degree of stereoregularity in this polymer. Qualitatively, it is observed that poly-**4** is difficult to dissolve in DMSO and is insoluble in most other solvents. It is therefore possible that this polymer has some degree of crystallinity. Several attempts have been made to polymerize the analogous Cp–tetracyanoethylene (TCNE) adduct without success.[17] It is intriguing, therefore, that the quadricyclane adduct of TCNE can readily be polymerized.

Monomer 5. Attempted polymerizations of monomer **5** and its analogous Cp–maleic anhydride adduct were both unsuccessful. In both cases, a dark brown, gelatinous precipitate forms over time. In this case we assume that there is a competition between ROMP of the monomer and reaction of the catalyst with the anhydride functionality. Difficulty with polymerizing other anhydride functionalized monomers has been observed elsewhere.[18]

Conclusion. This work has demonstrated the first living ROMP of quadricyclane adducts. We have shown that the polymerizations can proceed readily in a well-controlled fashion to yield monodisperse polymers. In several instances, the polymerization of the quadricyclane adducts appears to proceed more quickly and with less stereospecificity. For the TCNE–quadricyclane adduct a polymer could be readily formed, and with stereoregularity, whereas in the Cp adduct polymerization does not occur. This selective polymerization of quadricyclane adducts over CP adducts was also observed for adducts with the diethylazodicarboxylate dienophile.[19,20] ROMP of quadricyclane adducts therefore promises to be a useful tool for the polymerization of stereospecifically[14] functionalized monomers that cannot be tolerated as Cp adducts.

We are currently studying the interesting thermal and photochemical properties associated with these new quadricyclane adduct polymers, as well as synthesis and polymerizaion of other quadricyclane adducts.

Acknowledgment. I thank David Wheeler for his invaluable discussions and his help in interpreting NMR spectra. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

References and Notes

(1) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.
(2) Schrock, R. R. *Acc. Chem. Res.* , **1990**, *23*, 158.
(3) Bazan, G. C.; Schrock, R. R.; Cho, H. N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.
(4) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. V.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
(5) Bazan, G. C.; Oskam, J. H.; Cho, H. N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.
(6) Saunders, R. S.; Cohen, R. E.; Schrock, R. R. *Macromolecules* **1991**, *24*, 5599.
(7) Saunders, R. S.; Cohen, R. E.; Wong, S. J.; Schrock, R. R. *Macromolecules* **1992**, *25*, 2055.
(8) Smith, C. D. *J. Am. Chem. Soc.* **1966**, *88*, 4273.
(9) Tabushi, I.; Yamamura, K.; Yoshida, Z. *J. Am. Chem. Soc.* **1972**, *94* (3), 787.
(10) Kaupp, G.; Prinzbach, H. *Chem. Ber.* **1971**, *104*, 182.
(11) Henrici-Olive, G.; Olive, S. The Chemistry of Carbon Fiber Formation from Polyacrylonitrile. *Industrial Developments*; Springer-Verlag; New York, 1983; p 3.
(12) Wessling, R. A. *Polymer Monographs, Volume 5: Polyvinylidene Chloride*, Gordon and Breach Science Publishers, New York, 1977; pp 158–172.
(13) (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1984; pp 530–538. (b) Criegee, R.; Furrer, H. *Chem. Ber.* **1964**, *97*, 2949.
(14) References 8 and 9 point out that the dienophiles add exclusively in the exo-configuration to quadricyclane.
(15) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
(16) Oliver, A. M.; Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1145.
(17) Private communications with J. Oskam. Both the Feast and Schrock research groups have attempted to polymerize the TCNE–Cp adduct without success.
(18) Novak, B. M. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1989.
(19) Gassman, P. G.; Mansfield, K. T. *Org. Synth.* **1973**, *5*, 96.
(20) Current results to be published later. Both the Cp and quadricyclane adducts with diethylazodicarboxylate were recently made in our lab. The Cp adduct did not undergo ROMP, whereas the quadricyclane adduct did.
(21) (a) Saunders, R. S. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1992. (b) Feast, W. F.; Gibson, V. C.; Khosravi, E.; Marshall, E. L.; Mitchell, J. P. *Polym. Commun.* **1992**, *33*, 872.

MA9465284