1316 *Macromolecules* **2006,** *39,* 1316−1317

Living Ring-Opening Metathesis Polymerization of Cyclopropenes

Rojendra Singh, Constantin Czekelius, and Richard R. Schrock*

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received November 30, 2005

Revised Manuscript Received January 13, 2006

Living ring-opening metathesis polymerization (ROMP) is a powerful method of synthesizing a variety of polymers and block copolymers with precise molecular weights, low polydispersities, and unique properties.[1−15] In many cases, polymers prepared via living ROMP are derived from bicycloheptenes or bicyclooctenes.[16−20] Interest in ROMP of monocyclic olefins is a consequence of the possibility of preparing block copolymers with elastomeric properties.[20−23] However, lack of diversity of monocyclic substrates suitable for living ROMP has limited the progress in this field.[24,25] To the best of our knowledge, cyclobutenes are the only monocyclic olefins that have been polymerized successfully in a living manner via ROMP,[26−30] despite arguments that 3-, 4-, and 8-membered monocyclic olefins are good prospects for living ROMP.[3] In particular, there is no mention of ROMP of cyclopropenes in the literature. The closest example is a report by Risse and co-workers, who observed ring-opened polymers of cyclopropenes as a side product when cyclopropenes were treated with Pd(II) complexes.[31]

Since some monosubstituted cyclopropenes are reported to be unstable at room temperature,[32] we chose 3,3-disubstituted cyclopropenes as substrates for ROMP. An additional advantage is that when 3,3-disubstituted cyclopropenes are opened to yield a new alkylidene, that alkylidene is similar to the relatively stable neopentylidene or neophylidene initiators of the type Mo(NAr)(CHR)(OR′)$_2$ (Scheme 1).[33] We report here the living ROMP of substituted cyclopropenes using high oxidation state molybdenum Mo(NAr)(CHR′)(OR′)$_2$ initiators.

ROMP of 3-methyl-3-phenylcyclopropene (**A**) in tetrahydrofuran at room temperature using the initiators **1**, **2**, or **3** (Scheme 1) produced ROMP polymers in 94−97% yield. In a typical polymerization, solutions of the monomer were added in one portion to a stirred THF solution of the initiator. After 1 h, the reactions were quenched through addition of excess benzaldehyde, which is known to react in a Wittig-like manner to yield benzylidene-capped polymers. The polymers were precipitated through addition of methanol to the reaction mixture. Proton NMR spectra of the polymers showed that >99% trans double bonds were present, while carbon NMR spectra revealed that the polymers are not highly tactic. All polymers revealed a unimodal peak in gel permeation chromatography (GPC) studies, and the PDI (polydispersity index) was found to be low as one would predict on the basis of a living polymerization, with the exception of polymer obtained using initiator **1** (Table 1); the reasons for the higher PDI when initiator **1** is employed are not yet known. The calculated number-average molecular weights (M_n) (as determined by GPC vs polystyrene standards) for the samples were comparable with the theoretical molecular weights (Table 1). The molecular weights of poly**A** prepared using **2** and **3** as initiators showed a linear dependence vs the number of equivalents of monomer employed (up to 100 equiv), as determined by GPC vs polystyrene standards.

Scheme 1

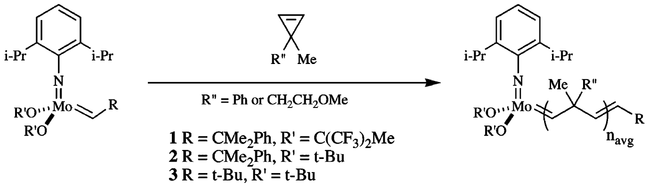

Table 1. Gel Permeation Chromatography Data (vs Polystyrene) in Dichloromethane for Homopolymers of 3-Methyl-3-phenylcyclopropene (A) and 3-(2-Methoxyethyl)-3-methylcyclopropene (C)

initiator (I)[a]	monomer (M)	M/I[b]	M_n(theory)[c]	M_n(found)	PDI	yield (%)
1	**A**	70	9110	8890	1.50	97
2	**A**	76	9900	8210	<1.05	95
3	**A**	100	13000	11900	<1.05	94
1	**C**	100	11200	8990	<1.05	90
4	**C**	100	11200	9930	<1.05	92

[a] See eq 1 for definitions; **4** = [Mo(NAr)(O-*t*-Bu)$_2$CH]$_2$C$_6$H$_4$ (**4**) (Ar = 2,6-diisopropylphenyl). [b] Equivalents of monomer per equivalent of initiator. [c] Number-average molecular weight on the basis of M/I.

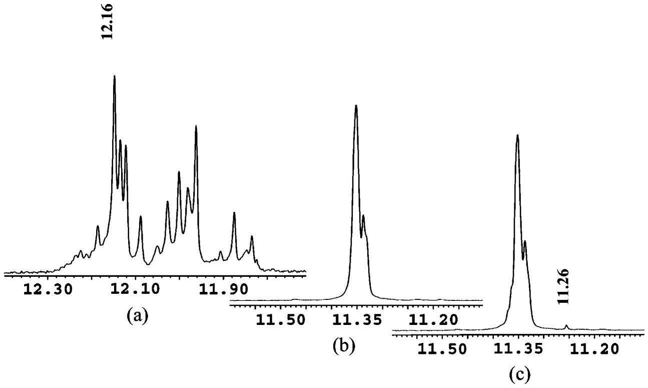

Figure 1. ^{1}H NMR (500 MHz, C$_6$D$_6$, 23 °C) spectra of alkylidene regions showing initiation upon addition of 10 equiv of **A** to initiators **1** (a), **2** (b), and **3** (c). Chemical shifts of initiators in ppm (when visible) are labeled.

A proton NMR experiment in which **A** (8 equiv) was added to **3** (δH$_\alpha$ = 11.26 ppm) showed that initiation was virtually complete (>99%) to yield a propagating species in which the H$_\alpha$ resonance is found at 11.35 ppm (Figure 1). A similar resonance for the propagating alkylidene was detected upon addition of 10 equiv of **A** to **2**, but was not completely resolved in the case of **3**, since the propagating alkylidene resonance (11.35 ppm) and the initiator's H$_\alpha$ resonance (11.41 ppm) overlapped in the proton NMR spectrum. In contrast, addition of 10 equiv of **A** to initiator **1** (δH$_\alpha$ = 12.16 ppm) in C$_6$D$_6$ gave multiple alkylidene resonances (11.96 ppm major) for oligomeric insertion products with incomplete initiation (~50%), as determined by the proton NMR spectrum. Poor initiation may be the reason why poly**A**$_{100}$ prepared using initiator **1** showed a higher PDI (1.50) than that prepared using initiators **2** and **3** (Table 1).

A Grubbs-type Ru initiator, (H$_2$IMes)(PCy$_3$)Cl$_2$RuCHC$_6$H$_5$ (H$_2$IMes = 1,3-dimesitylimidazolidine), also was examined as an initiator for polymerization of **A**. The initial benzylidene species (H$_\alpha$ at 19.09 ppm) was consumed to the extent of 54%

10.1021/ma052560u CCC: $33.50

Table 2. Gel Permeation Chromatography Data (vs Polystyrene) in Dichloromethane for Block Copolymers Consisting of 3-Methyl-3-phenylcyclopropene (A), Dicarbomethoxynorbornadiene (B), 3-(2-Methoxyethyl)-3-methylcyclopropene (C), and Methyltetracyclododecene (D)

initiator	copolymer	first	second	M_n (theory)	M_n (found)	PDI
2	$\mathbf{A}_{75}\mathbf{B}_{205}$	**A**	**B**	52500	32900	1.17
2	$\mathbf{B}_{219}\mathbf{A}_{83}$	**B**	**A**	56300	34300	1.10
3	$\mathbf{A}_{66}\mathbf{B}_{103}$	**A**	**B**	29900	16900	1.04
3	$\mathbf{B}_{100}\mathbf{A}_{66}$	**B**	**A**	28600	15300	1.09
4	$\mathbf{A}_{100}\mathbf{C}_{100}\mathbf{A}_{100}$	**C**	**A**	37200	31900	1.08
4	$\mathbf{D}_{100}\mathbf{C}_{100}\mathbf{D}_{100}$	**C**	**D**	46100	28900	1.05

after 1 h in CD_2Cl_2 at room temperature, and four new resonances (16.70, 16.65, 16.63 (major), and 16.58 ppm) appeared in the alkylidene region. The proton NMR spectra of the same sample revealed the consumption of 83% and 95% of the initiator after 7 and 15 h, respectively. No further change in the NMR spectrum was observed in 24 h. The reaction was slower in C_6D_6; ~25% of the initiator remained after 34 h.

Diblock copolymers of **A** and 2,3-dicarbomethoxynorbornadiene (**B**) were prepared through the sequential addition of monomers to initiators **2** and **3**. The polymerizations were quenched with benzaldehyde and the polymers precipitated from methanol. Two diblock copolymers were prepared for each initiator under identical conditions, the first through addition of **A** followed by **B** and the second through addition of **B** followed by **A**. Both diblock copolymers were isolated in >95% yields and showed unimodal peak distribution with narrow polydispersities as determined by GPC studies (Table 2). This observation is consistent with the polymerization being living under the conditions employed. Similarly, 3-(2-methoxyethyl)-3-methylcyclopropene (**C**) was polymerized by initiator **1** in THF in the same manner as described above for poly**A**. Poly**C** was formed in 90% yield as a light yellow oil, a GPC of which showed a unimodal peak distribution with a polydispersity of <1.05. Finally, the bimetallic ROMP initiator $[Mo(NAr)(O\text{-}t\text{-}Bu)_2CH]_2C_6H_4$ (**4**) (Ar = 2,6-diisopropylphenyl)[34] was employed in order to prepare both a homopolymer of **C** and **ABA**-type triblock copolymers with **C** as the inside block. Poly$\mathbf{C}_{100}$, poly$\mathbf{A}_{100}\mathbf{C}_{100}\mathbf{A}_{100}$, and poly$\mathbf{D}_{100}\mathbf{C}_{100}\mathbf{D}_{100}$ (**D** = methyltetracyclododecene) were prepared successfully in >92% yields; all had narrow polydispersities (Table 2).

Differential scanning calorimetry (DSC) studies on poly$\mathbf{A}_{100}$ revealed a glass transition (T_g) at 50 °C.[35] Poly$\mathbf{C}_{100}$ synthesized using initiator **1** exhibited a T_g at −20 °C, while poly$\mathbf{C}_{100}$ prepared using initiator **4** showed a T_g of −42 °C; this difference might be ascribed to different tacticities and/or blockiness of the polymer backbones, although further characterizations will be required. DSC studies on poly$\mathbf{A}_{100}\mathbf{C}_{100}\mathbf{A}_{100}$ showed homogeneous microphases with a broad transition centered at 0 °C. However, thermal analysis on poly$\mathbf{D}_{100}\mathbf{C}_{100}\mathbf{D}_{100}$ showed two distinct transitions at −42 and 210 °C, which align well with the glass transition temperatures of the individual homopolymers (T_g of poly$\mathbf{C}_{100}$ = −42 °C, T_g of poly$\mathbf{D}_{100}$ = 215 °C). Therefore, there appears to be significant phase segregation in poly$\mathbf{D}_{100}\mathbf{C}_{100}\mathbf{D}_{100}$.

Further studies of ROMP of cyclopropene derivatives are in progress.

Acknowledgment. We are grateful to the U.S. Army (Institute for Soldier Nanotechnology, under Contract DAAD-19-02-D-0002 with the U.S. Army Research Office) for financial support of this work. We also thank the German Academic Exchange Service (DAAD) for a postdoctoral fellowship to C.C.

Supporting Information Available: Experimental details for the synthesis of monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158−165.

(2) Grubbs, R. H., Ed. *Handbook of Metathesis. Applications in Polymer Synthesis*, 1st ed.; Wiley−VCH: Weinheim, 2003; Vol. 3.

(3) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997.

(4) Feast, W. J.; Khosravi, E. *J. Fluorine Chem.* **1999**, *100*, 117−125.

(5) Schrock, R. R. In *Ring-Opening Polymerization*; Brunelle, D. J., Ed.; Hanser: Munich, 1993.

(6) Cho, I. *Macromol. Symp.* **2003**, *195*, 89−94.

(7) Grande, D.; Six, J.-L.; Breunig, S.; Heroguez, V.; Fontanille, M.; Gnanou, Y. *Polym. Adv. Technol.* **1998**, *9*, 601−612.

(8) Trimmel, G.; Riegler, S.; Fuchs, G.; Slugovc, C.; Stelzer, F. *Adv. Polym. Sci.* **2005**, *176*, 43−87.

(9) Albagli, D.; Bazan, G.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 4150−4158.

(10) Mol, J. C. *J. Mol. Catal. A* **2004**, *213*, 39−45.

(11) Saunders, R. S.; Cohen, R. E.; Wong, S. J.; Schrock, R. R. *Macromolecules* **1992**, *25*, 2055−2057.

(12) Boyd, T. J.; Geerts, Y.; Lee, J.-K.; Fogg, D. E.; Lavoie, G. G.; Schrock, R. R.; Rubner, M. F. *Macromolecules* **1997**, *30*, 3553−3559.

(13) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378−8387.

(14) Bazan, G. C.; Oskam, J. H.; Cho, H. N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899−6907.

(15) Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243−253.

(16) Komiya, Z.; Pugh, C.; Schrock, R. R. *Macromolecules* **1992**, *25*, 3609−3616.

(17) Komiya, Z.; Schrock, R. R. *Macromolecules* **1993**, *26*, 1387−1392.

(18) Komiya, Z.; Schrock, R. R. *Macromolecules* **1993**, *26*, 1393−1401.

(19) Pugh, C.; Schrock, R. R. *Macromolecules* **1992**, *25*, 6593−6604.

(20) Lapinte, V.; Fontaine, L.; Montembault, V.; Campistron, I.; Reyx, D. *J. Mol. Catal. A* **2002**, *190*, 117−129.

(21) Panagiotis, D.; Feast, J. M.; Kenwright, A. M. *Polymer* **1994**, *36*, 2787−2796.

(22) Trzaska, S. T.; Lee, L.-B. W.; Register, R. A. *Macromolecules* **2000**, *33*, 9215−9221.

(23) Hejl, A.; Scherman, O. A.; Grubbs, R. H. *Macromolecules* **2005**, *38*, 7214−7218.

(24) Ivin, K. J. M., J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: New York, 1997.

(25) Grubbs, R. H. *Handbook of Metathesis*, 1st ed.; Wiley−VCH: New York, 2003; Vol. 1.

(26) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459−3469.

(27) Perrott, M. G.; Novak, B. M. *Macromolecules* **1996**, *29*, 1817−1823.

(28) Charvet, R.; Novak, B. M. *Macromolecules* **2001**, *34*, 7680−7685.

(29) Wu, Z.; Grubbs, R. H. *Macromolecules* **1994**, *27*, 6700−6703.

(30) Lapinte, V.; De Fremont, P.; Montembault, V.; Fontaine, L. *Macromol. Chem. Phys.* **2004**, *205*, 1238−1245.

(31) Rush, S.; Reinmuth, A.; Risse, W. *Macromolecules* **1997**, *30*, 7375−7385.

(32) Closs, G. L.; Closs, L. E.; Boll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796−3800.

(33) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145−180.

(34) Schrock, R. R.; Gabert, A. J.; Singh, R.; Hock, A. S. *Organometallics* **2005**, *24*, 5058−5066.

(35) DSC scans were performed at a rate of 5 °C/min. The first and subsequent DSC heating and cooling scans were essentially identical, and all heating and cooling scans showed good reversibility for the polymers studied.

MA052560U