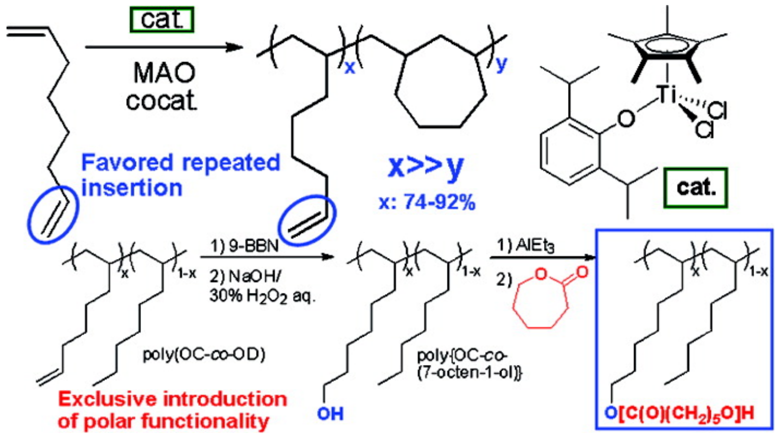
Communication

Facile, Efficient Functionalization of Polyolefins via Controlled Incorporation of Terminal Olefins by Repeated 1,7-Octadiene Insertion

Kotohiro Nomura, Jingyu Liu, Michiya Fujiki, and Arimitsu Takemoto

J. Am. Chem. Soc., **2007**, 129 (46), 14170-14171• DOI: 10.1021/ja076633w • Publication Date (Web): 25 October 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Facile, Efficient Functionalization of Polyolefins via Controlled Incorporation of Terminal Olefins by Repeated 1,7-Octadiene Insertion

Kotohiro Nomura,* Jingyu Liu, Michiya Fujiki, and Arimitsu Takemoto

Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

Received September 3, 2007; E-mail: nomurak@ms.naist.jp

Precise, efficient synthesis of functionalized polyolefins by controlled polymerization attracts considerable attention.[1] Two strategies, (i) direct copolymerization with (protected) polar monomers[1b,2−6] and (ii) post-polymerization modification,[7−9] are commonly employed. However, these approaches often face difficulties owing to the catalyst poisoning, and interaction of the centered metal with the functional groups and/or only limited chemistry like a free radical grafting reaction is available to activate the saturated aliphatic molecular structure,[2,7] although recent progresses in coordination,[1b,3,4] radical[5] polymerization, and others[6,8,9] offer new possibilities. Controlled incorporation of a reactive moiety that introduces functionalities through chemical modification[1a] by incorporation of dienes containing (poorly reactive) internal or strained olefinic double bonds has also been considered as the third approach. We thus focused on this approach especially using nonconjugated diene,[10] although most of previous catalysts favor cyclopolymerization.[11,12] This is because that the promising possibilities of incorporation of terminal olefinic double bond can be expected from the previous results.[10,13] We herein present that a facile introduction of polar functionalities under mild conditions has been achieved via controlled incorporation of terminal olefins by exclusive repeated insertion of 1,7-octadiene (OD) in OD polymerization by a half-titanocene (**1**) (Scheme 1).

$Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**, $Cp^* = C_5Me_5$) was chosen, not only because **1** favored repeated insertion rather than cyclization in 1,5-hexadiene polymerization affording polymers containing terminal olefins with uniform compositions,[10] but also because **1** demonstrated unique characteristics especially for some ethylene copolymerizations.[14,15] $CpTiCl_2(N{=}C^tBu_2)$ (**2**) was also chosen for comparison, because **2** showed notable catalytic activities for 1-hexene polymerization and ethylene/1-hexene copolymerization.[16] The results are summarized in Table 1.[17]

Note that the OD polymerization by **1**-MAO catalyst proceeded with favored repeated insertion (without cross-linking), affording high molecular weight polymers with unimodal molecular weight distributions (runs 1−3). The integration ratio of protons in the terminal olefins (assigned as g,h in Figure 1a) versus those in the aliphatic region (a−e) assumed that the polymerization occurred with an exclusive OD repeated insertion. The selectivity was better estimated by the ^{13}C NMR spectrum (Figure 1b),[17] and all resonances were identified by ^1H-, ^{13}C NMR (dept) spectra and the ^{13}C NMR spectrum after hydrogenation.[17] The selectivity of the repeated insertion (percentage of the double bond, hexenyl group, based on the OD insertion) was affected by the OD concentration employed, but the selectivity was high even under low OD concentration (run 7, OD 2.12 M, 74%); the fact should be a promising contrast to those observed by certain metallocenes which favored cyclization under similar conditions.[12,18] The polymerization by **2** also showed high selectivity of the repeated OD insertion, but the reaction stopped only at the initial stage although the reason is not clear at this moment. The reaction with $Cp^*TiCl_2(N{=}C^tBu_2)$ was also employed, but the resultant polymers were insoluble, suggesting that certain degree of cross-linking accompanied under these conditions.[17] The results suggest that both Cp′ and the anionic ligand affect the selectivity.

Scheme 1

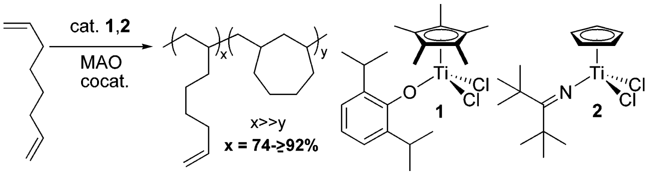


Table 1. 1,7-Octadiene (OD) Polymerization and Copolymerization of OD with 1-Octene (OC) by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**), $CpTiCl_2(N{=}C^tBu_2)$ (**2**) -MAO Catalyst Systems[a]

run	catalyst (μmol)	OD/OC/hexane mL	yield mg	TON[b]	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	double bond (%)[d]
1	**1** (0.3)	15.0/-/-	160	4840	76.3	1.86	92
2	**1** (0.3)	15.0/-/-	160	4840	66.4	1.89	(98)[e]
3	**1** (0.1)	15.0/-/-	120	10900	81.1	1.63	88
4	**1** (0.1)	10.0/-/5.0	104	9400	61.2	1.66	82
5	**1** (1.0)	7.5/-/7.5	227	2060	37.8	2.00	85
6	**1** (0.1)	7.5/-/7.5	66.4	6030	46.5	1.69	82
7	**1** (1.0)	5.0/-/10.0	79	720	17.4	1.89	74
8	**2** (0.1)	15.0/-/-	39.0	3540	65.1	1.7	>95
9	**2** (0.1)	15.0/-/-	39.0	3540	65.6	1.76	>95 (84)[e]
10	**1** (0.3)	0.5/14.5/-	218	6480	42.6	1.63	5.2[f]
11	**1** (0.3)	1.0/14.0/-	256	7620	43.6	1.67	11.7[f]
12	**1** (0.3)	5.0/10.0/-	268	8010	56.0	1.77	37.3[f]
13	**1** (1.2)	0.5/59.5/-	1043	7750	43.4	1.52	1.6[f]

[a] Reaction conditions: catalyst in toluene (1.0 mL), MAO 2.0 (runs 3, 4, 6, 8, 9), 3.0 (runs 1, 2, 10−12), 5.0 (runs 5, 7) or 8.0 (run 13) mmol, 20 min (runs 3, 4 ,6, 8, 30 min) at 25 °C. [b] Monomer consumed (mmol)/mmol-Ti. [c] GPC data in THF vs polystyrene standards. [d] Percentage of hexenyl group based on OD insertion estimated by ^{13}C NMR spectra. [e] Estimated by ^1H NMR spectra. [f] OD content (mol %) estimated by ^1H NMR spectra.

Copolymerizations of OD with 1-octene (OC) by **1**-MAO catalyst afforded high molecular weight copolymers with uniform molecular weight distributions (runs 10−13). The OD contents (degree of hexenyl group) estimated by ^1H NMR spectra could be varied by the OD/OC feed ratio.[17] The resultant copolymers were treated with 9-BBN and then $NaOH/H_2O_2$ (aq) to afford poly{OC-*co*-(7-octen-1-ol)} exclusively (98.9%) without decrease/increase in the M_n values.[17] The OH group in the copolymers were further treated with $AlEt_3$ and were then added ϵ-caprolactone (CL) to afford the graft copolymers, poly{OC-*co*-(7-octan-1-ol}-*graft*-poly(CL), via Al-alkoxide initiated ring-opening polymerization (ROP, Scheme 2). The M_n values increased at longer reaction hours with keeping unimodal distributions, because the ROP occurred in a living manner.[17] The resultant copolymers were identified by ^1H, ^{13}C (dept) NMR spectra, and dsc thermograms.

We have shown that the OD polymerization by **1**-MAO catalyst proceeds with notable selectivity of repeated OD insertion, affording

10.1021/ja076633w CCC: $37.00

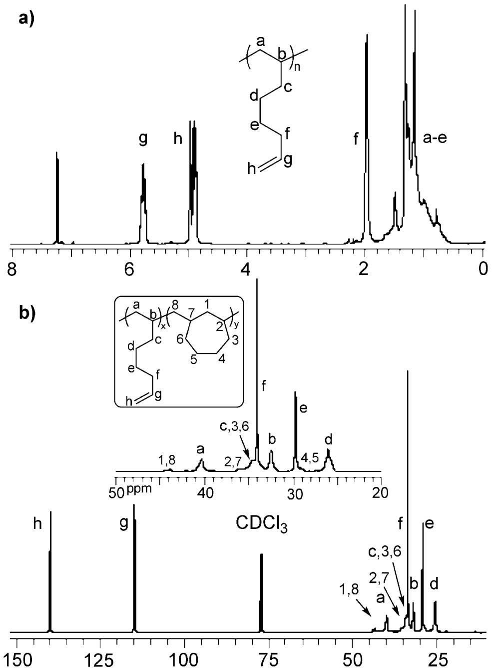
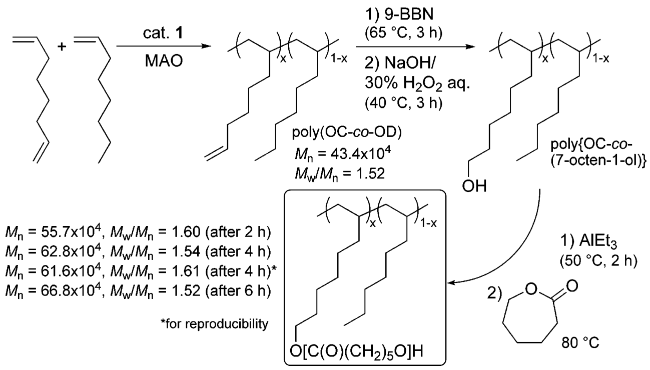


Figure 1. ^{1}H NMR (a, run 2) and ^{13}C NMR (b, run 1) spectra for poly(OD)s prepared by **1**-MAO catalyst (in CDCl$_3$, 25 °C).

Scheme 2



polymers containing terminal olefinic double bonds in the side chain. Introduction of polar functionality under mild conditions has thus been achieved by adopting this approach. The remarkable selectivity in this catalysis would also be applied for introduction of terminal olefins in organic synthesis, which would introduce various functionalities. Since we also succeeded in synthesis of poly(ethylene-*co*-OC-*co*-OD)s,[19] the approach here should present a promising possibility for preparation of functionalized polyolefins under mild conditions.

Acknowledgment. This research was partly supported by Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science (JSPS, No. 18350055). J.L. expresses her thanks to JSPS for a postdoctoral fellowship (P05397). K.N. thanks Tosoh Finechem Co. for MAO.

Supporting Information Available: General experimental procedures, additional polymerization results, ^{1}H, ^{13}C NMR spectra, and dsc thermograms for poly(OD)s, poly(OD-*co*-OC)s, and polymers after functionalization; NMR spectra for poly(ethylene-*co*-OC-*co*-OD)s and their microstructure analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Chung, T. C. *Functionalization of Polyolefins*; Academic Press: San Diego, CA 2002. (b) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479. (c) Chung, T. C, *Prog. Polym. Sci.* **2002**, *27*, 39. (d) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005**, *34*, 267.

(2) Doak, K. W. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Ed.; John Wiley and Sons: New York, 1986; Vol. 6, p 386.

(3) Recent examples (coordination copolymerization): (a) Imuta, J.; Kashiwa, N.; Toda, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1176. (b) Hagihara, H.; Tsuchihara, K.; Sugiyama, J.; Takeuchi, K.; Shiono, T. *Macromolecules* **2004**, *37*, 5145. (c) Wendt, R. A.; Angermund, K.; Jensen, V.; Thiel, W.; Fink, G. *Macromol. Chem. Phys.* **2004**, *205*, 308. (d) Inoue, Y.; Matsugi, T.; Kashiwa, N.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 3651.

(4) Examples for late transition metal catalysts: (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (c) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (d) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Hwang, S.; Grubbs, R. H.; Roberts, W. P.; Litzau, J. J. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 2842.

(5) Selected examples (ATRP, Nitroxide, RAFT etc.): (a) Liu, S.; Elyashiv, S.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 12738. (b) Tian, G.; Boone, H. W.; Novak, B. M. *Macromolecules* **2001**, *34*, 7656. (c) Elyashiv-Barad, S.; Greinert, N.; Sen, A. *Macromolecules* **2002**, *35*, 7521. (d) Venkatesh, R.; Klumperman, B. *Macromolecules* **2004**, *37*, 1226. (e) Venkatesh, R.; Harrison, S.; Haddleton, D. M.; Klumperman, B. *Macromolecules* **2004**, *37*, 4406. (f) Gu, B.; Liu, S.; Leber, J. D.; Sen, A. *Macromolecules* **2004**, *37*, 5142. (g) Liu, S.; Gu, B.; Rowlands, H. A.; Sen, A. *Macromolecules* **2004**, *37*, 7924. (g) Nagel, M.; Poli, D.; Sen, A. *Macromolecules* **2005**, *38*, 7262. (h) Luo, R.; Sen, A. *Macromolecules* **2007**, *40*, 154.

(6) (a) Stibrany, R. T.; Schulz, D. N.; Kacker, S.; Patil, A. O.; Baugh, L. S.; Rucker, S. P.; Zushma, S.; Berluche, E.; Sissano, J. A. *Macromolecules* **2003**, *36*, 8584. (b) Baugh, L. S.; Sissano, J. A.; Kackier, S.; Berluche, E.; Stibrany, R. T.; Schulz, D. N.; Rucker, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1817.

(7) Moad, G. *Prog. Polym. Sci.* **1999**, *24*, 81.

(8) Direct functionalization of polyolefin by Rh catalyzed borylation, (a) Kondo, Y.; Garcia-Cuadrado, D.; Hartwig, J. F.; Boaen, N. K.; Wagner, N. L.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1164. (b) Bae, C.; Hartwig, J. F.; Harris, N. K. B.; Long, R. O.; Anderson, K. S.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 767. (c) Bae, C.; Hartwig, J. F.; Chung, H.; Harris, N. K.; Switek, K. A.; Hillmyer, M. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6410.

(9) Dehydrogeneation of polyolefins by Ir catalyst with pincer ligand, Ray, A.; Zhu, K.; Kissin, Y. V.; Cherian, A. E.; Coates, G. W.; Goldman, A. S. *Chem. Commun.* **2005**, 3388.

(10) (a) Nomura, K.; Hatanaka, Y.; Okumura, H.; Fujiki, M.; Hasegawa, K. *Macromolecules* **2004**, *37*, 1693. (b) Nomura, K.; Takemoto, A.; Hatanaka, Y.; Fujiki, M.; Okumura, H.; Hasegawa, K. *Macromolecules* **2006**, *39*, 4009. References are also cited therein.

(11) Examples for 1,5-hexadiene (HD) polymerization: (a) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953. (b) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270. (c) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (d) Cavallo, L.; Guerra, G.; Corradini, P.; Resconi, L.; Waymouth, R. M. *Macromolecules* **1993**, *26*, 260. (e) Schaverien, C. J. *Organometallics* **1994**, *13*, 69. (f) de Ballessteris, O. R.; Venditto, V.; Auriemma, F.; Guerra, G.; Resconi, L.; Waymouth, R . M.; Mogtad, A. L. *Macromolecules* **1995**, *28*, 2383. (g) Naga, N.; Shiono, T.; Ikeda, T. *Macromolecules* **1999**, *32*, 1348. (h) Jayaratne, K. C.; Keaton, R. J.; Henningsten, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490.

(12) Example for 1,7-octadiene (OD) polymerization, Naga, N.; Shiono, T.; Ikeda, T. *Macromol. Chem. Phys.* **1999**, *200*, 1466.

(13) (a) Synthesis of poly(HD) partially containing 1-vinyl-tetramethylene (VTM) unit, Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 11578. (b) Postpolymerization of VTM fragment in the poly(HD)s and copolymers with ethylene/propylene by cross metathesis, Mathers, R. T.; Coates, G. W. *Chem. Commun.* **2004**, 422.

(14) Review, Nomura, K.; Liu, J.; Padmanabhan, S.; Kitiyanan, B. *J. Mol. Catal. A* **2007**, *267*, 1.

(15) Recent example (copolymerization of ethylene with 2-methyl-1-pentene), Itagaki, K.; Fujiki, M.; Nomura, K. *Macromolecules* **2007**, *40*, 6489.

(16) Nomura, K.; Fujita, K.; Fujiki, M. *J. Mol. Catal. A* **2004**, *220*, 133.

(17) Detailed results are shown in the Supporting Information. Estimation of percentage of terminal olefins in poly(OD)s by ^{13}C NMR spectra (integration of region a, 1,8 and 2,7 carbons) was suitable in terms of reproducibility. All resonances were assigned according to the previous reports, and the ^{13}C NMR (dept) spectra were assigned after hydrogenation. These are also shown in the Supporting Information.

(18) The resultant poly(OD)s were soluble in CDCl$_3$; however, on the basis of the facts in HD polymerization,[10] the polymer may become insoluble upon increasing the catalyst concentration and/or longer reaction time due to the subsequent cross-linking accompanied partially. Low OD conversion seems to be thus important to control the degree of cross-linking.

(19) Activity 29400−102600 kg-polymer/(mol-Ti•h), M_n = (9.7−19.6) × 10^4, M_w/M_n = 1.87−2.12 (**1**, 0.02−0.03 μmol, ethylene 6−8 atm, OD + OC, 10 or 15mL in toluene at 25 °C). More details are shown in the Supporting Information.

JA076633W