4946 *Macromolecules* **2009**, *42*, 4946–4949
DOI: 10.1021/ma9007434

Macromolecules
COMMUNICATION TO THE EDITOR

Tuning Polyethylene Chain Topology via Ring Incorporation in Chain Walking Ethylene Polymerization

Peng Xiang, Zhibin Ye,* Shawn Morgan, Xuewei Xia, and Wei Liu

School of Engineering, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

Received April 6, 2009
Revised Manuscript Received June 2, 2009

The vast developments in transition metal catalysts in the past decades have provided versatile control over chain microstructure of polyolefins. A broad scope of microstructures, including stereoregularity, comonomer incorporation and sequence, molecular weight and molecular weight distribution, can be flexibly controlled by using catalysts of different structures.[1] The discovery of Pd−diimine catalysts by Brookhart et al. in the 1990s represents another further major advance in the area.[2] Featured with their unique chain walking mechanism, this series of late transition metal catalysts enables unprecedented synthesis of novel polyethylenes of controllable chain topology,[3] which is another important structural parameter affecting polymer properties.[4] In ethylene polymerization with Pd−diimine catalysts, chain walking of the catalysts is one basic event competing with chain propagation. The Pd metal center, at the ethylene-dissociated state, can uniquely "walk" along the growing polymer chain by means of β-hydride elimination and subsequent readdition, rendering branching structures.[3] A simple change of ethylene pressure and/or temperature, two parameters that affect the relative rates of the two competitive events, can effectively adjust the catalyst chain walking distance and subsequently tune polymer chain topology from linear to hyperbranched.[3,4]

Thus far ethylene pressure and polymerization temperature are the sole demonstrated parameters which can be changed to tune chain topology of the resulting polymers in Pd−diimine catalyzed ethylene polymerization.[3,4a,4b] We have been searching for alternative polymerization parameters which can be utilized to easily yet effectively tune polymer chain topology in this polymerization. We have recently discovered that incorporation of aliphatic rings, at low contents (0.26−3.6 mol %), into the polymer backbone can effectively linearize polymer chain topology and thus provide another unique strategy for tuning polyethylene topologies from hyperbranched to linear while without changing polymerization temperature and pressure.

To demonstrate this strategy, we carried out chain walking ethylene copolymerizations with diethyl diallylmalonate (DEDAM) as a ring-forming comonomer with a commonly used Pd−diimine catalyst, $[(\mathrm{ArN{=}C(Me){-}(Me)C{=}NAr})\mathrm{Pd}(\mathrm{CH_3})(\mathrm{N{\equiv}CMe})]\mathrm{SbF_6}$ ($\mathrm{Ar} = 2,6\text{-}(\mathrm{iPr})_2\mathrm{C_6H_3}$) (**1**). DEDAM is a substituted 1,6-heptadiene containing two terminal double bonds and a central quaternary carbon bearing two ester substitutes (shown in Scheme 1). This diene and other similar ones have been reported to undergo cyclo-addition in homopolymerization and copolymerization with ethylene using several Pd−diimine catalysts through the consecutive 2,1-insertion of both double bonds on the same monomer by Osakada et al.,[5] giving rise to polymers containing 1,2-disubstituted *trans*-fused five-membered rings. Given its unique ring-forming feature, we used DEDAM herein as the comonomer in the polymerization, attempting to introduce the five-membered ring structure at various low contents into the polyethylene backbone through its cyclo-incorporation (Scheme 1) and to investigate the resulting effect on polymer chain topology.

The polymerizations were performed at three different temperature levels (15, 25, and 35 °C, respectively) under a low but fixed ethylene pressure of 1 atm. The polymerization temperature was varied to investigate its effects on ring incorporation and subsequently polymer chain topology. At each temperature level, DEDAM concentration was varied from 0.08 M up to 0.80 M to adjust the content of ring structure in the resulting copolymers. For the purpose of comparison, ethylene hompolymerizations were also performed at the three respective temperatures as control runs. Table 1 summarizes the polymerization results (polymers **1**−**10**) along with polymer characterization results obtained from nuclear magnetic resonance (NMR) spectroscopy and triple-detection gel permeation chromatography (GPC).

^{1}H and ^{13}C NMR characterizations of the copolymers confirm the complete cyclo-incorporation of DEDAM in all the copolymers with no pendant vinyl groups observed (see Figures S.1 and S.2 in the Supporting Information for representative polymer NMR spectra). All copolymers show signals of the CH and $\mathrm{CH_2}$ carbons of the five-membered rings at 45.4 and 40.4 ppm, respectively, in their ^{13}C NMR spectra. The assignment of these two signals is confirmed on the basis of DEPT (distortionless enhancement by polarization transfer) (135°) spectra of the polymers (see Figure S.2c in Supporting Information for a representative DEPT spectrum). The difference in peak position of the CH and $\mathrm{CH_2}$ carbons (i.e., 5.0 ppm) is similar to that (4.4 ppm) of the model compound with *cis* structure, *cis*-3,4-dimethylcyclopentane-1,1-dicarboxylate (CH, 41.2 ppm; $\mathrm{CH_2}$, 36.8 ppm), while dissimilar to that (1.2 ppm) of the model compound with *trans* structure (CH, 43.2 ppm; $\mathrm{CH_2}$, 42.0 ppm).[5,6] This indicates that the incorporated rings are *cis*-1,2-disubstituted five-membered rings, instead of the *trans*−fused rings found by Osakada et al. in their study of cyclopolymerization of substituted 1,6-heptadienes.[5] In their work, the CH and $\mathrm{CH_2}$ carbons of the incorporated *trans* rings have a NMR peak difference of about 1.0 ppm (CH, 46.6−47.1; $\mathrm{CH_2}$, 45.8 ppm).[5]

The ^{13}C NMR peaks of the carbonyl carbons on the rings also indicate the *cis* structure of the incorporated rings. The carbonyl carbons of the model compound with *trans* structure have been shown to have a single ^{13}C peak at 173.8 ppm while those of the model compound with *cis* structure have two peaks at 173.7 and 173.5 ppm.[5,6] The copolymers synthesized herein generally show multiple peaks for the carbonyl carbons in the region of 172−174 ppm with two primary ones at 172.9 and 172.7 ppm (see the inset of Figure S.2b in Supporting Information for a representative spectrum), which is similar to the model compound of *cis* structure. The carbonyl carbons on *trans*-fused rings have been found by Osakada to have a single peak at 172.0 ppm.[5] This different ring incorporation pattern found here is believed to result from the different diimine backbone structures of the catalysts used in their study (acenaphthyl backbone) and ours herein (methyl substituents on the backbone carbons). The content of DEDAM, i.e., the content of the *cis*-fused five-membered ring, in the copolymers is calculated from their ^{1}H NMR spectra and listed in Table 1. Generally, the ring content is controlled low (0.26−3.6 mol %) in the copolymers to avoid the

---

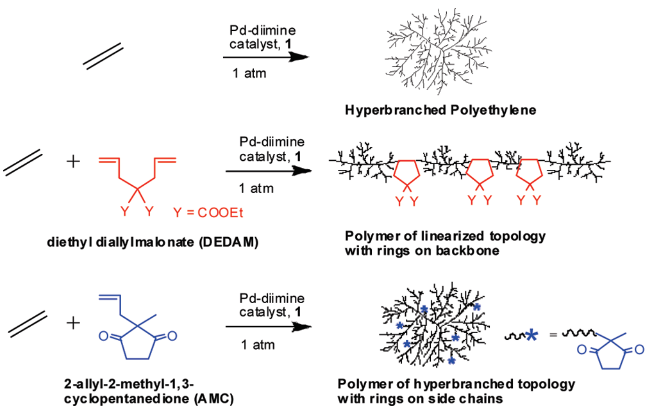
*Corresponding author. E-mail: zye@laurentian.ca. Fax: 1 (705) 675-4862.

Table 1. Polymerization Results and Polymer Characterization Data

polymer	temp (°C)	comonomer[a]	C_2H_4 TOF (1/h)	comonomer content[b] (mol %)	branch density[c] (/1000 C)	GPC−LS−VIS characterization[d]		
						$M_{w,LS}$ (kD)	PDI_{LS}	$[\eta]_w$ (mL/g)
1	15	none	203	0	96	158	1.32	26.5
2	15	DEDAM, 0.16 M	81	0.27	93	111	1.43	25.8
3	15	DEDAM, 0.80 M	44	1.5	88	71.7	1.33	30.2
4	25	none	157	0	96	115	1.29	17.2
5	25	DEDAM, 0.08 M	96	0.26	95	111	1.35	22.5
6	25	DEDAM, 0.40 M	68	1.3	89	64.8	1.24	26.2
7	25	DEDAM, 0.80 M	48	2.7	83	46.4	1.21	27.9
8	35	none	130	0	97	78.4	1.44	11.8
9	35	DEDAM, 0.16 M	35	1.5	90	38.2	1.24	17.7
10	35	DEDAM, 0.40 M	25	3.6	81	25.3	1.22	19.2
11	35	AMC, 0.29 M	25	2.4	86	62.7	1.56	10.8
12	35	AMC, 0.71 M	16	4.9	74	40.1	1.37	9.3

[a] Other polymerization conditions: Pd−diimine catalyst (**1**), 0.1 mmol; solvent, CH_2Cl_2; total volume, 100 mL for polymers 1, 4, and 8, and 50 mL for all the other runs; polymerization time, 22 h for polymers 1, 4, and 8, and 24 h for all the other polymers. [b] The content of comonomer in the polymers was determined using ^{1}H NMR spectroscopy. [c] Total branching density of the ethylene sequences was determined with ^{1}H NMR spectroscopy. [d] The absolute weight-average molecular weight ($M_{w,LS}$) and polydispersity index (PDI_{LS}) were determined with light scattering detector and the weight-average intrinsic viscosity ($[\eta]_w$) was determined with viscosity detector of the triple-detection GPC.

Scheme 1. Schematic Effects of Ring Incorporation on Polymer Chain Topology in Chain Walking Polymerization



formation of ring sequences and it increases with the increase of DEDAM concentration and/or polymerization temperature. On the basis of the low contents and the single CH and CH_2 signals observed in ^{13}C NMR spectra of copolymers, the incorporated rings should be randomly distributed in an isolated manner within the ethylene sequences and the presence of ring sequences should be negligible.

Branching structures of the polymers, resulting from catalyst chain walking, were also analyzed from their ^{13}C NMR spectra. Due to the restriction of ^{13}C NMR technique, only short branches with lengths below six carbons can be distinguished and details on branch-on-branch structures, i.e., chain topology, cannot be obtained.[3a,3b] We thus cannot infer polymer chain topology on the basis of the NMR data. Table S.1 in Supporting Information lists the short chain branch distribution of the polymers. Generally, the polymers show reduced branch densities after the incorporation of DEDAM comonomer and this reduction is more pronounced with the increase of comonomer content (Table 1). This reducing effect of comonomer incorporation on branching density has also been observed in polymers obtained with acrylates as comonomer in our prior studies.[7] All the polymers are highly branched with a total branching density of about 90 branches per 1000 carbons, making them amorphous at room temperature with good solubility in nonpolar or low-polarity solvents, like tetrahydrofuran (THF) and CH_2Cl_2. They all appear as sticky oil-like liquids but with enhanced viscosity at increased ring content. Polymer characterization with differential scanning calorimetry (DSC) indicates the increase of glass-transition temperature with the increase of ring content in the polymers (see Table S.2 in Supporting Information).

Triple-detection GPC incorporating online light scattering (LS), refractive index (RI), and viscosity detectors was used to determine polymer molecular weight and, more importantly, chain topology. The characterizations were carried out with THF as elution phase at 33 °C. In this technique, the light scattering detector allows the direct determination of absolute polymer molecular weight in each GPC elution fraction, and the viscosity detector measures concurrently polymer intrinsic viscosity ($[\eta]$) that is directly related to polymer chain topology with higher values found with polymers of more linear chain topology.[3b] At each polymerization temperature, a consistent reduction in polymer weight-average molecular weight (M_w) is observed with the increase of ring content due to the enhanced chain transfer after the comonomer incorporation. However, the weight-average intrinsic viscosity of the polymers ($[\eta]_w$) tends to increase despite the reduction in M_w (Table 1). This suggests the change, i.e., the linearization, of polymer chain topology and the enlarged coil dimension upon ring incorporation despite the reduced M_w. The molecular weight distribution of the polymers seems to be negligibly affected by ring incorporation on the basis of the marginal change in polydispersity index (PDI) shown in Table 1.

To elucidate the effect of ring incorporation on polymer chain topology, Figure 1a−c show, respectively, the dependence of intrinsic viscosity on molecular weight across the distribution (i.e., the Mark−Houwink plot) for the three sets of polymers synthesized at the three temperature levels. Given the same low ethylene pressure (1 atm) employed herein in the polymerizations, the three homopolyethylene control samples (polymers 1, 4, and 8) synthesized at the respective temperatures should all possess hyperbranched chain topology.[4a,8] Comparing the polymers synthesized at each temperature level, a consistent and significant increase of intrinsic viscosity is observed for polymer fractions of equal molecular weight, across the whole molecular weight distribution, with the increase of ring content in the polymers. A significant change in the intrinsic viscosity curve is even observed with polymers 2 and 5, having a ring content as low as 0.27%, relative to their corresponding control homopolyethylenes. This thus demonstrates the linearization of polymer chain topology upon ring incorporation and, moreover, the level of linearization is enhanced with the increase of ring content.

This unique effect of ring incorporation on linearizing polymer chain topology is compared with those of increasing ethylene pressure and decreasing polymerization temperature, which are

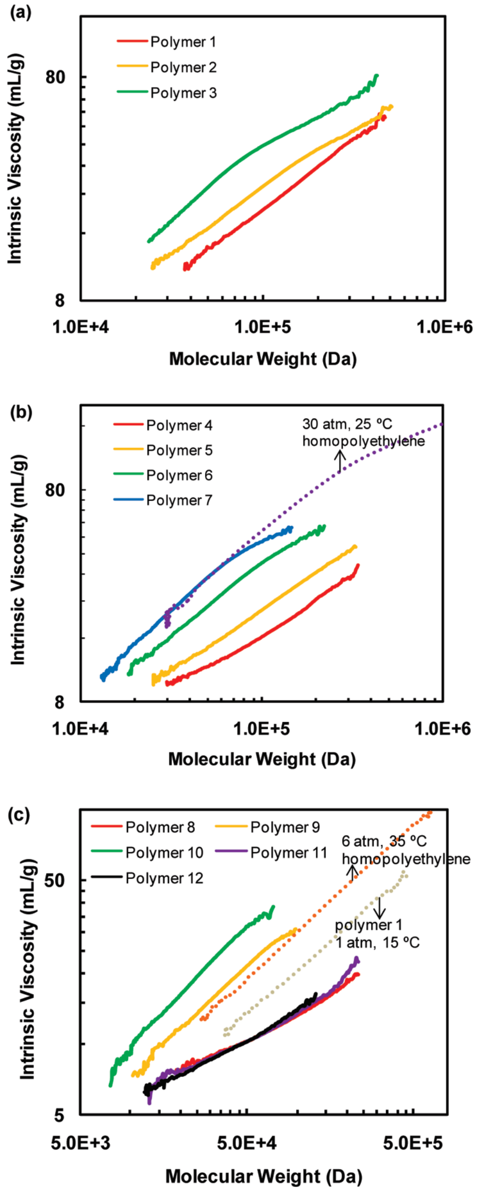


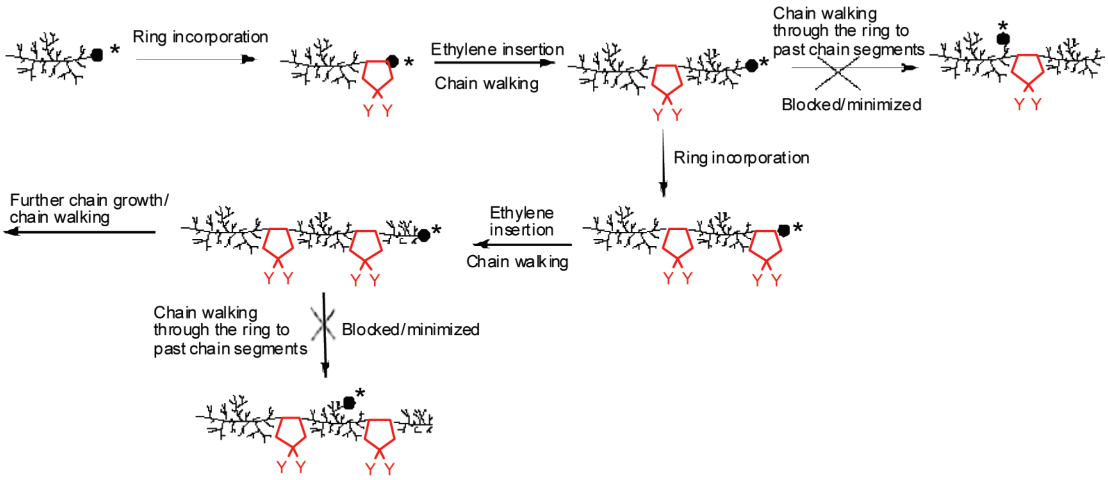
Figure 1. Mark−Houwink plots of polymers synthesized at (a) 15 °C, (b) 25 °C, and (c) 35 °C under 1 atm with various ring contents. The dotted curves in both parts b and c are for control homopolyethylenes synthesized at higher pressure/lower temperature and are included for the purpose of comparison.

well demonstrated methods for obtaining polymers of more linear topology. In Figure 1b (for the set of polymers synthesized at 25 °C), a homopolyethylene of linear topology synthesized at 30 atm and 25 °C is included for comparison. One can see that, within its molecular weight range, polymer 7 containing a low ring content of 2.7% has very similar intrinsic viscosity curves as the homopolymer synthesized at 30 atm. This indicates that the effect of ring incorporation at this content is comparable to that of raising ethylene pressure to 30 atm at this polymerization temperature. In Figure 1c (for the sets of polymers synthesized at 35 °C), a homopolymer synthesized at 6 atm and 35 °C and polymer 1 synthesized at 15 °C are also included. The linearization effect of ring incorporation at a content of 1.5% (polymer 9) on linearizing chain topology has exceeded those achieved through increasing ethylene pressure to 6 atm or reducing temperature down to 15 °C on the basis of its raised intrinsic viscosity curve relative to the other two. These comparisons thus demonstrate that this strategy of ring incorporation for linearizing chain topology is at least as effective as those by increasing ethylene pressure or reducing temperature. A change of ring content in the copolymers can thus tune the polymer chain topology from hyperbranched to linear while without adjusting ethylene pressure and polymerization temperature.

The precise mechanism leading to the above-demonstrated linearized polymer topology upon ring incorporation in polymer backbone is unknown. We hypothesize that it arises from the "blocking" effect of the incorporated rings on catalyst chain walking.[9] The 1,2-disubstituted five-membered rings are incorporated in the backbone (i.e., chain walking passage where the catalyst can walk to) of the polymer chains. After a ring incorporation event, a growing polymer chain is subject to further chain propagation by ethylene insertion and concurrent chain walking. During the chain walking, the Pd metal center can potentially walk back toward the immediate past ring. To walk through the ring to prior chain segments, the metal center, however, has to walk though the two consecutive CH carbons on the ring as the other side of the ring contains a quaternary carbon which disallows the catalyst from walking through. It has been reported that Pd−diimine catalysts can potentially walk through tertiary CH carbons in chain walking, generating branch-on-branch structures, on the basis of the observation of *sec*-butyl branches from ^{13}C NMR spectroscopy.[3b] However, it is envisioned to be thermodynamically more difficult herein for the catalyst to walk past two consecutive CH groups on the 1,2-disubstituted ring as opposed to individual CH groups given its more sterically bulky structure. Each ring can thus act as a "blocking" site on the polymer chain, blocking or minimizing the catalyst metal center from walking through it to the prior chain segments (Scheme 2). In this manner, longer range of chain walking is limited and more linearized chain topology is thus achieved in contrast to the hyperbranched topology in homopolymers resulting from unrestricted longer-range chain walking. Increasing the ring content in the polymer increases the frequency of blocking sites, further restricts chain walking distance, and thus improves the linearity of polymer chain topology.

With the above hypothesis, the rings should be incorporated in the backbone, i.e., the chain walking passage, of the polymers in order to have an effect on catalyst chain walking and polymer chain topology. It is rationalized that polymer chain topology should not be affected if the rings are incorporated as the side groups of the polymers where catalyst cannot walk to and thus no "blocking" effect will result. To verify this, we also carried out ethylene copolymerizations with a commercially available functional olefin having a 5-membered substituted ring, 2-allyl-2-methyl-1,3-cyclopentanedione (AMC in Scheme 1), with the same Pd−diimine catalyst (**1**) at ethylene pressure of 1 atm and 35 °C (polymers 11 and 12 in Table 1). AMC is chosen here as it contains a quaternary carbon separating the ring from the vinyl double bond. On the basis of polymer characterization with NMR spectroscopy, incorporation of AMC though vinyl insertion in the polymer is confirmed with its molar content found to be 2.4% (polymer 11) and 4.9% (polymer 12), respectively (see Figures S.1 and S.2 in Supporting Information for representative polymer NMR spectra). These molar content values are comparable to those of DEDAM in the above copolymers. Due to the presence of the quaternary carbon in AMC, the catalyst cannot walk to the ring atoms of the incorporated AMC units and the rings should be incorporated as the pendant side groups. These two copolymers were also characterized with triple-detection GPC. Their dependencies of intrinsic viscosity on molecular weight are included in Figure 1c for the purpose of comparison. From Figure 1c, these two AMC copolymers have nearly an identical dependency of intrinsic viscosity on molecular weight as the hyperbranched homopolyethylene control sample (polymer 8), indicating no change in polymer chain topology despite the

Scheme 2. Effect of Ring Units on Chain Walking in Chain Walking Ethylene Polymerization



significant ring incorporation as the side groups in these two polymers (Scheme 1). This result supports the above mechanism of the "blocking" effect of the backbone-incorporated 5-membered rings on catalyst chain walking and polymer chain topology. Meanwhile, it also indicates that incorporation of small-sized rings at low contents as the side groups has negligible effect on polymer chain topology.

In summary, we have demonstrated herein the unique linearization effect of ring incorporation on polyethylene chain topology in chain walking polymerization. By controlling the ring content in the polymers via changing the concentration of DEDAM (the ring-forming comonomer) in the polymerization, we can effectively tune polymer chain topology from hyperbranched to linear while without changing ethylene pressure and temperature. Ring incorporation can thus be used as an alternative effective and convenient polymerization strategy for tuning polymer chain topology in chain walking polymerization.

Acknowledgment. This work is financially supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada. Z.Y. also thanks NSERC and the Canadian Foundation for Innovation (CFI) for funding research facilities, and Laurentian University for granting a Research Capacity Development (RCD) faculty award.

Supporting Information Available: Text giving experimental details, polymerization, and polymer purification procedures, polymer characterizations with triple-detection GPC, figures showing polymer NMR spectra, and tables giving polymer short chain branch distribution, and DSC characterization results. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) See some review articles: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1143. (b) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (c) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (d) Resconi, L.; Cavallo, L.; Fait, A.; Piemontes, F. *Chem. Rev.* **2000**, *100*, 1253. (e) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479. (f) Imanishi, Y.; Naga, N. *Prog. Polym. Sci.* **2001**, *26*, 1147. (g) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (h) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30.

(2) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (b) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (c) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(3) (a) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059. (b) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945. (c) Guan, Z. *Chem.—Eur. J.* **2002**, *8*, 3086. (d) Michalak, A.; Ziegler, T. *Macromolecules* **2003**, *36*, 928. (e) Schultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539.

(4) (a) Ye, Z.; Zhu, S. *Macromolecules* **2003**, *36*, 2194. (b) Patil, R.; Colby, R. H.; Read, D. J.; Chen, G.; Guan, Z. *Macromolecules* **2005**, *38*, 10571. (c) Wang, J.; Ye, Z.; Zhu, S. *Ind. Eng. Chem. Res.* **2007**, *46*, 1174. (d) Wang, J.; Kontopoulou, M.; Ye, Z.; Subramanian, R.; Zhu, S. *J. Rheol.* **2008**, *52*, 243.

(5) Park, S.; Takeuchi, D.; Osakada, K. *J. Am. Chem. Soc.* **2006**, *128*, 3510.

(6) (a) Perch, N. S.; Pei, T.; Widenhoefer, R .A. *J. Org. Chem.* **2000**, *65*, 3836. (b) Curran, D. P.; Shen, W. *J. Am. Chem. Soc.* **1993**, *115*, 6051.

(7) (a) Zhang, K.; Wang, J.; Subramanian, R.; Ye, Z.; Lu, J.; Yu, Q. *Macromol. Rapid Commun.* **2007**, *28*, 2185. (b) Wang, J.; Zhang, K.; Ye, Z. *Macromolecules* **2008**, *41*, 2290. (c) Morgan, S.; Ye, Z.; Zhang, K.; Subramanian, R. *Macromol. Chem. Phys.* **2008**, *209*, 2232.

(8) (a) Wang, J.; Ye, Z.; Joly, H. *Macromolecules* **2007**, *40*, 6150. (b) Ye, J.; Ye, Z.; Zhu, S. *Polymer* **2008**, *49*, 3382.

(9) The "blocking" effect has also been observed when cyclopentene is used a ring-forming comonomer in chain walking ethylene polymerization. Cyclopentene is copolymerized into the polymer backbone mainly as 1,3-disubstituted five-membered ring through 1,3-enchainment. These results are to be reported in a subsequent publication.