Chain Transfer to Aluminum in the Homogeneous Cyclopolymerization of 1,5-Hexadiene

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Recent discoveries of homogeneous stereospecific Ziegler–Natta catalysts[1-4] have created exciting new opportunities for the molecular design of new polymer structures. The molecular design of polymers based on catalytic polymerization reactions requires a detailed understanding of the fundamental organometallic chemistry responsible for catalysis. An understanding of the processes which govern chain transfer is critical for the control of polymer molecular weight. Two major chain-transfer processes prevail in homogeneous Ziegler–Natta polymerization: β-H elimination and chain transfer to aluminum.[4f,g] In general, β-H elimination is the dominant chain-transfer process with homogeneous Ziegler–Natta catalysts.[4d] Herein we report a novel example of a Ziegler–Natta system where chain transfer to aluminum is the predominant chain-tranfer mechanism and demonstrate that aluminum-terminated polymers are readily functionalized.

We have recently reported the stereo-[5] and enantioselective[6] cyclopolymerization[7] of 1,5-hexadiene to give poly(methylene-1,3-cyclopentane) (PMCP). The stereoselectivity of the polymerization for the formation of cis and trans rings is governed by the nature of the metallocene catalyst precursor. The molecular weights of the polymers are also sensitive to the nature of the catalyst precursor. Cyclopolymerization of 1,5-hexadiene with $Cp_2^*ZrCl_2$/MAO (Cp* = pentamethylcyclopentadienyl, MAO = methylaluminoxane) in toluene[8] at room temperature affords oligomeric PMCP with an average molecular weight M_w = 700 where approximately 70% of the carbocyclic rings are cis (Table I). Following acidic workup of the polymer, ^1H and ^{13}C NMR analysis reveals signals due to methylenecyclopentane, cyclopentane, and methylcyclopentane end groups. These results indicate that, under these polymerization conditions, chain transfer occurs both by β-H elimination and chain transfer to aluminum. Integration of the end-group signals[9] indicates that the ratio of β-H elimination to chain transfer to aluminum is approximately 20:80 under these polymerization conditions.

Because β-H elimination is a unimolecular process and chain transfer to aluminum is bimolecular, a temperature dependence on the ratio of these two processes might be expected. In fact, cyclopolymerization of 1,5-hexadiene at −25 °C yields a completely saturated solid polymer (M_w > 4000).[10] The absence of olefin end groups indicates that β-H elimination does not occur under these conditions. Analysis by ^{13}C NMR reveals signals due to methylcyclopentane end groups only, which implies that chain transfer to aluminum is the dominant chain-transfer process under these conditions (Figure 1). Shown in Figure 2a is a ^{13}C NMR spectrum of the methyl end-group region. Based on similarities to model compounds,[11] the resonances at 21.2 and 20.8 ppm are assigned to methyl groups of *trans*- and *cis*-methylcyclopentane end groups, respectively. The ratio of these two resonances is 18:82 and is almost the same as that observed for the trans/cis ratio of cyclopentane rings in the polymer (16:84). Further evidence for chain transfer to aluminum was obtained from deuterium labeling experiments. Deuterolytic workup of

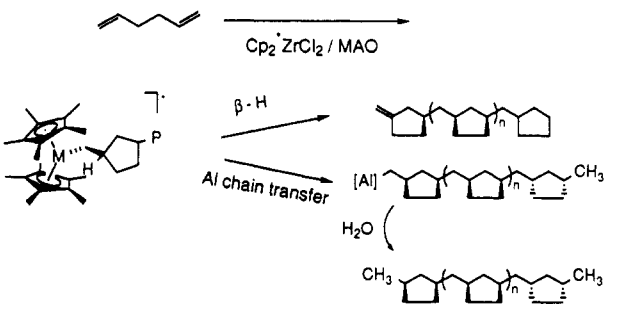

Figure 1. Cyclopolymerization of 1,5-hexadiene.

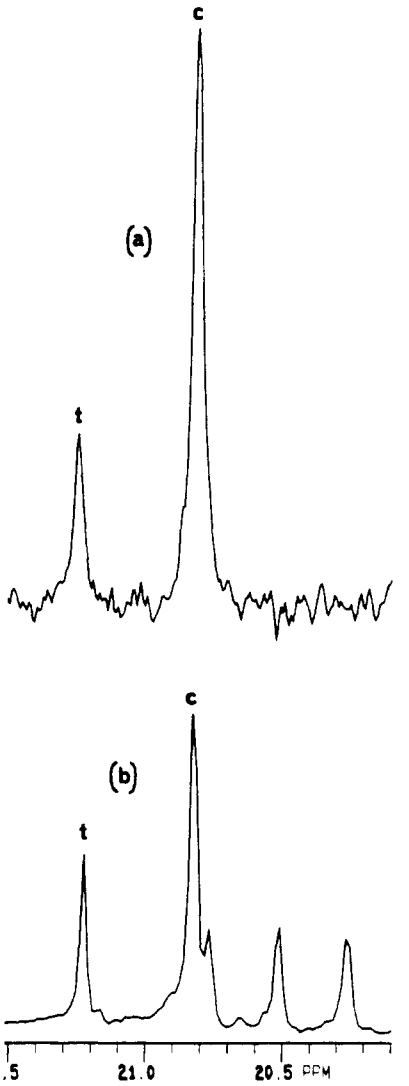

Figure 2. ^{13}C NMR spectra of poly(methylene-1,3-cyclopentane) (400 MHz, 21 °C, $CDCl_3$). (a) Methylcyclopentane end groups after acidic workup. (b) Methylcyclopentane end groups after deuterolytic workup. t = trans; c = cis.

the polymerization reaction mixture affords a polymer whose ^{13}C NMR spectrum is shown in Figure 2b. As seen by comparison of parts a and b of Figure 2, the intensity of the *cis*-methyl end-group resonance at 20.8 ppm is diminished relative to the *trans*-methyl resonance at 21.2 ppm and a 1:1:1 triplet due to a deuteriomethyl end group is clearly visible at 20.5 ppm. An estimation of the degree of deuteriation can be obtained by comparison of the two spectra, using the intensity of the *trans*-methyl resonance as an internal standard. From this analysis, it can be inferred that approximately half of the methyl groups are

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Table I
Cyclopolymerization of 1,5-Hexadiene with $Cp_2^*ZrCl_2$

exp no.	[olefin], M	[cat.], $\times 10^4$ M	T, °C	t, h	conv, %	yield, g	M_w[b]	Al/Zr	cocat	c/t, %
1[a]	2.02	13.0	+21	6.0	99	2.22	700	856	MAO	73/27
2	2.07	4.0	0	5.0	97	3.10	7100	994	MAO	84/16
3	1.68	4.2	−25	5.5	98	25.0	4000	897	MAO	84/16
4	0.64	6.9	−25	5.5	25	0.40	1500	981	TMA/MAO[c]	81/19
5	0.62	6.0	−25	5.5	12	0.40	1000	1000	TMA	83/17
6[d]	1.89	15.0	−25	5.5	81	1.50	1000	1030	TMA/MAO[c]	84/16
7[d]	2.06	5.0	−25	5.5	16	0.45	1480	954	MAO	91/9

[a] Runaway temperature after monomer addition. [b] Determined on a THF-soluble fraction.[10] [c] TMA = trimethylaluminum. TMA/MAO = 50/50 Al mole ratio. [d] Oxidized with dry air, followed by hydrolysis.

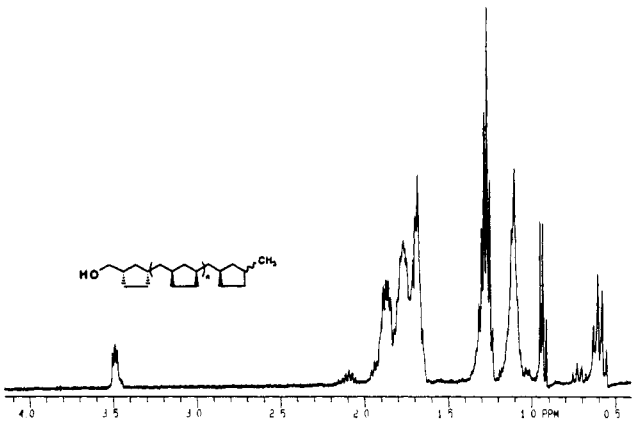

Figure 3. ^1H NMR spectrum of oxidized poly(methylene-1,3-cyclopentane) (400 MHz, 80 °C, $C_2D_2Cl_4$).

deuterated or approximately all of the chain ends are terminated with a deuteriomethyl end group.[12] The ^{13}C NMR data suggest that the deuteriomethyl end groups appear only on cis rings, an observation which is not readily explained by the 16:84 ratio of trans to cis rings in the polymer.[13]

Other workers have reported chain transfer to aluminum as a minor chain-transfer mechanism in homogeneous Ziegler–Natta polymerization.[4f,g] This system represents the first case where transfer to aluminum is the dominant chain-transfer mechanism[5c] and provides a useful synthesis of polymers containing a reactive alkylaluminum end-group functionality.

We have found that oxidation of the aluminum-terminated polymers can be accomplished by careful introduction of air[14] into the polymerization mixture. Oxidation of the aluminum-terminated polymers occurs over a period of 1–2 h, depending on the concentration of MAO in the polymerization medium. Acidic workup affords hydroxy-terminated PMCP. Shown in Figure 3 is the ^1H NMR of a low molecular weight sample of hydroxy-terminated PMCP (M_w = 1000, M_w/M_n = 4.8). The resonances at 3.5 ppm in the ^1H NMR and at 67.8 ppm in the ^{13}C NMR are clear indications of the presence of a (hydroxymethyl)cyclopentane end group. The degree of functionalization of the hydroxy-terminated PMCP can be estimated by integration of the ^1H and ^{13}C NMR spectra. Comparison of hydroxymethyl and methyl end groups shows that approximately 96% of all chain ends are oxidized (no β-H elimination products are detectable).

In summary, we report the cyclopolymerization of 1,5-hexadiene with sterically hindered metallocene catalysts to yield end-functionalized hydrocarbon polymers. These end-functionalized polymers are currently being investigated as macromonomers for the formation of block and graft copolymers.

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Supplementary Material Available: Experimental section and data for poly(methylene-1,3-cyclopentane) and hydroxy-terminated poly(methylene-1,3-cyclopentane) (1 page). Ordering information is given on any current masthead page.

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(8) Polymerizations were carried out using standard Schlenk-tube techniques. $Cp_2^*ZrCl_2$, aluminum cocatalysts, and toluene were placed in a Schlenk tube at the appropriate temperature, and monomer was then added dropwise over 3 min. Polymerizations were terminated by a slow addition of water (or deuterated water) (*Careful*! Exothermic!). Hydroxy-terminated polymers were obtained by bubbling a dry-air/nitrogen mixture into the solution for 30 min from −25 °C to room temperature followed by hydrolysis.

(9) A quantitative ^{13}C NMR spectrum was obtained by utilizing a 9-s pulse delay ($5T_1$) and a pulse width of 57° in an inverse-gated decoupling sequence to minimize NOE. See Shoolery, J. N. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 79.

(10) Molecular weights (M_w) were determined in THF by gel permeation chromatography (GPC) at room temperature. Many of these highly crystalline materials were not completely soluble in THF, and thus the reported M_w's are likely to be lower than the actual values.

(11) *Atlas of Carbon-13 NMR Data*; Breitmaier, E., Haas, G., Voelter, W., Eds.; Heyden & Son Ltd.: London, 1979; Nos. 427 and 428.

(12) Calculated values based upon integration show 49% of the methyl groups to be deuterated; that is, 98% of the chain ends are terminated with a deuteriomethyl end group.

(13) On the basis of the 16:84 trans/cis rings in the polymer, it would be expected that approximately 16% of the deuteriomethyl end groups would be on trans rings. The absence of a trans deuteriomethyl signal might indicate that the cis/trans stereoselectivity improves as the polymerization proceeds and/or chain transfer to aluminum occurs more readily for cis rings. Low molecular weight samples contain a higher percentage of functionalized trans end groups, a result consistent with the former explanation. Further studies are underway to address this issue.

(14) *Careful*! Extremely exothermic. We advise caution when attempting to oxidize alkylaluminum reagents with air.