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Synthesis of Linear Ethylene/Divinylbenzene Copolymers by Metallocene Catalysis

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Divinylbenzene (DVB), which contains two reactive vinyl groups, is an excellent cross-linker[1] for the preparation of 3-D polymer networks. In transition-metal-mediated olefin polymerization, some experimental results[2] showed that, even with a very small amount of DVB present, the polyolefin obtained has an ill-defined branched polymer structure. The challenge is to find a way to prepare a linear DVB-containing polymer with a well-defined molecular structure. Our research on the linear copolymerization of α-olefin and 1,4-DVB stemmed from our long-standing interest in functional polyolefins,[3] especially the new chemical routes to the functionalization of polyolefins. The resulting polyolefin (I) containing pendant styrenic moieties could be a versatile intermediate to access a broad range of new functional polyolefins and polyolefin graft copolymers under mild reaction conditions and simple reaction processes.

New metallocene technology[4] provides well-defined catalysts and mechanisms. With a specific metallocene catalyst, it might be possible to control the incorporation process of 1,4-DVB in such a way that it not only effectively incorporates monomers but also selectively reacts with only one of the two vinyl groups. In other words, the catalyst incorporates 1,4-DVB into polymer through single enchainment, but the styrenic moieties already enchained do not react further, as illustrated in Scheme 1.

Table 1 summarizes the experimental results of ethylene/1,4-DVB copolymers prepared using the *rac*-Et(Ind)$_2$ZrCl$_2$/MAO catalyst.[5] Reactions using Cp$_2$ZrCl$_2$/MAO, Ind$_2$ZrCl$_2$/MAO, Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO, and [C$_5$Me$_4$(SiMe$_2$N^{t}Bu)]TiCl$_2$/MAO were also performed. As expected, Cp$_2$ZrCl$_2$/MAO and Ind$_2$ZrCl$_2$/MAO exhibited very poor incorporation[6] of styrenic monomers, including DVB, in the PE chain. Although Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO and [C$_5$Me$_4$(SiMe$_2$N^{t}Bu)]TiCl$_2$/MAO, with open active sites, can incorporate styrene,[7] the copolymers produced are largely insoluble. In the small soluble fraction, the vinyl group to phenyl group (VN/PH) mole ratio is well below unity (<0.6), indicating some double enchainment of the pendant styrene groups.

On the other hand, all poly(ethylene-*co*-1,4-divinylbenzene) copolymers prepared using *rac*-Et(Ind)$_2$ZrCl$_2$/MAO were completely soluble in common organic solvents, such as toluene and xylene, at elevated temperatures. Figure 1 shows ^{1}H NMR spectra of two poly(ethylene-*co*-1,4-divinylbenzene) copolymers containing 1.5 and 7.2 mol % 1,4-DVB units. In addition to the major peak at 1.3 ppm corresponding to ethylene units, several chemical shifts were observed at 5.2 and 5.7 ppm (doublet, CH=C**H**$_2$) and 6.7 ppm (doublet of doublet, C**H**=CH$_2$) and aromatic proton peaks at 7.1 and 7.4 ppm (C$_6$**H**$_4$). The peak intensity ratios indicate the mole ratio of vinyl group to phenyl group is near unity. Generally, the incorporation of DVB comonomers in the copolymer was effective—up to 7.2 mol % of DVB content has been incorporated in the copolymer without showing any detectable branching or cross-linking.

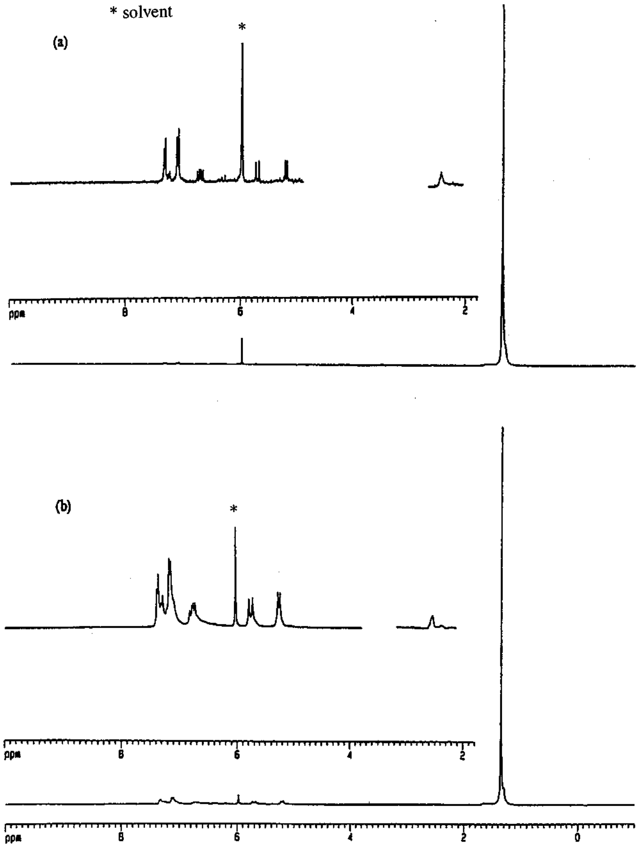

Figure 1. ^{1}H NMR spectra comparison of two linear poly(ethylene-*co*-1,4-divinylbenzene) copolymers, containing (a) 1.5 and (b) 7.2 mol % 1,4-DVB units, respectively (solvent: C$_2$D$_2$Cl$_4$; temperature: 110 °C).

GPC and DSC curves of several poly(ethylene-*co*-1,4-divinylbenzene) copolymers (runs 5−7 and 9 in Table 1) are shown in the Supporting Information. The polymer molecular weight systematically decreases with the increase of 1,4-DVB incorporation, which resembles the ethylene/styrene case[8] due to the lower polymerization reactivity of styrene and the increased rate of chain transfer reaction after 2,1-insertion of styrene unit. All the copolymers exhibit narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ < 2.3), implying a single-site polymerization mechanism. In fact, the $\bar{M}_w/\bar{M}_n$ reduces from 2.6 in PE to 2.1 in poly(ethylene-*co*-1,4-divinylbenzene) containing 7.2 mol % of 1,4-DVB units. The greater diffusibility of monomers in the copolymer structures (due to lower crystallinity) may help provide ideal polymerization conditions. In fact, the catalyst efficiency (in Table 1) also significantly increases with the increase of 1,4-DVB content in the copolymer.

DSC curves show that both the melting point (T_m) and crystallinity (χ_c) of the copolymer are strongly related to the density of the comonomer—the higher the density, the lower the T_m and χ_c. Even a small amount (1.4 mol

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Scheme 1

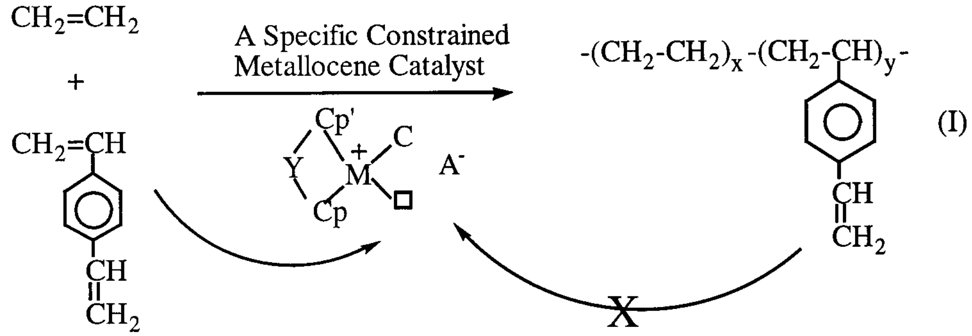

Table 1. Summary of Copolymerization Reactions between Ethylene and 1,4-Divinylbenzene Catalyzed by Several Metallocene Catalysts

	polymerization conditions[a]									
runs	catalyst	1,4-DVB (mol/L)	A[b]	1,4-DVB conv (%)	1,4-DVB in polymer (mol %)	M_w (10^3 g/mol)	M_w/M_n	[vinyl]/[phenyl] (%)	T_m (°C)	solubility
1	Cp_2ZrCl_2	0.492	1880	0.85	0.5			>90		soluble
2	Cp_2ZrCl_2	1.770	424	0.11	1.1			>90		soluble
3	$(Ind)_2ZrCl_2$	0.492	1976	0.87	0.6			>90		soluble
4	$(Ind)_2ZrCl_2$	1.770	408	0.11	1.2			>90		soluble
5	*rac*-$Et(Ind)_2ZrCl_2$	0	1904		0	159	2.6		138.4	soluble
6	*rac*-$Et(Ind)_2ZrCl_2$	0.295	3616	8.21	1.5	135	2.3	95	128.1	soluble
7	*rac*-$Et(Ind)_2ZrCl_2$	0.492	4016	8.38	2.3	79	2.2	96	115.8	soluble
8	*rac*-$Et(Ind)_2ZrCl_2$	0.787	4464	8.36	3.3	52	2.2	95	111.9	soluble
9	*rac*-$Et(Ind)_2ZrCl_2$	1.770	4048	7.35	7.2	34	2.1	97	88.2	soluble
11	$Me_2Si(Ind)_2ZrCl_2$	0.295	3296							insoluble
12	$Me_2Si(Ind)_2ZrCl_2$	0.492	4280							insoluble
13	$[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$	0.0707	1424							insoluble
14	$[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$	0.295	2584							insoluble

[a] Other conditions: 20 psi ethylene pressure, 100 mL toluene solvent, MAO as cocatalyst. [cat] = 2.5×10^{-5} M, [MAO]/[cat] = 1500, 50 °C, 30 min. [b] Catalyst activity: kilograms of polymer per mole of catalyst per hour.

%) of 1,4-DVB comonomer incorporation has a significant effect on the crystallization of polyethylene. Only a single peak is observed throughout the whole composition range, and the melting peak almost disappears at 7.2 mol % of 1,4-DVB content. This general trend was also observed in the of DSC curves of poly(ethylene-*co*-*p*-methylstyrene) copolymers[9] with well-defined copolymer structures. The combination of well-defined melting temperature and systematic reduction of T_m and crystallinity implies the homogeneous reduction of PE consecutive sequences in the copolymers with the increase of 1,4-DVB units and also indicates copolymers with narrow composition distribution.

One major advantage of the poly(ethylene-*co*-1,4-divinylbenzene) copolymers (I) is the existence of several pendant styrenic moieties along the backbone that are reactive in many chemical reactions, including free radical, cationic, anionic, and transition-metal coordination processes. One example is the metalation reaction of poly(ethylene-*co*-1,4-divinylbenzene) copolymer by *sec*-butyllithium in THF to form polymeric anions in the copolymer, which then react with trimethylsilyl chloride, or ethylene oxide, or graft-from polymerization with styrene. The reaction procedures are discussed in the Supporting Information. Figure 2 shows ^{1}H NMR spectra of the silated and hydroxylated copolymers and the resulting PE-*g*-PS graft copolymer. All the peaks corresponding to the vinyl group completely disappear after metalation at ambient temperature. The new peaks at 0.05 ppm in Figure 2a and at 3.65 ppm in Figure 2b correspond to the $-Si(C\mathbf{H}_3)_3$ and $C\mathbf{H}_2-OH$ groups, respectively. The experimental results indicate clean reactions and almost quantitative conversions in each of the metalation, silylation, and hydroxylation reactions.

Some portion of the metalated polymer solution was used in anionic graft-from polymerization with styrene at ambient temperature. The resulting graft copolymer was subjected to Soxhlet extraction by boiling THF to gain no detectable soluble PS homopolymer. The insoluble fraction (soluble in 1,1,2,2-tetrachloroethane at elevated temperatures) is PE-*g*-PS graft copolymer. Figure 2c shows the ^{1}H NMR spectra of a PE-*g*-PS copolymer with ethylene/styrene 45/55 mole ratio. Compared to the ^{1}H NMR spectrum of the starting poly(ethylene-*co*-1,4-divinylbenzene) copolymer shown in Figure 1a, three additional chemical shifts arise at 1.55, 2.0, and 6.4−7.3 ppm, corresponding to $C\mathbf{H}_2$, $C\mathbf{H}$, and aromatic protons in polystyrene. The quantitative analysis of copolymer composition was calculated by the ratio of two integrated intensities between aromatic protons (δ = 6.4−7.3 ppm) in PS side chains and methylene protons (δ = 1.35−1.55 ppm) and the number of protons both chemical shifts represent. Overall, the graft-from reaction was effective—more than 80% monomer conversion within 1 h. Since the graft-from reaction involves a living anionic polymerization, it is reasonable to assume that each benzylic lithium produces one polymer side chain and each side chain has similar molecular weight. In other words, PE-*g*-PS graft copolymers with controlled graft density and graft length can be prepared through this reaction route.

In summary, the experimental results clearly show the linear copolymerization reaction of ethylene and 1,4-divinylbenzene by *rac*-$Et(Ind)_2ZrCl_2$/MAO catalyst. The formed copolymers exhibit narrow molecular weight and

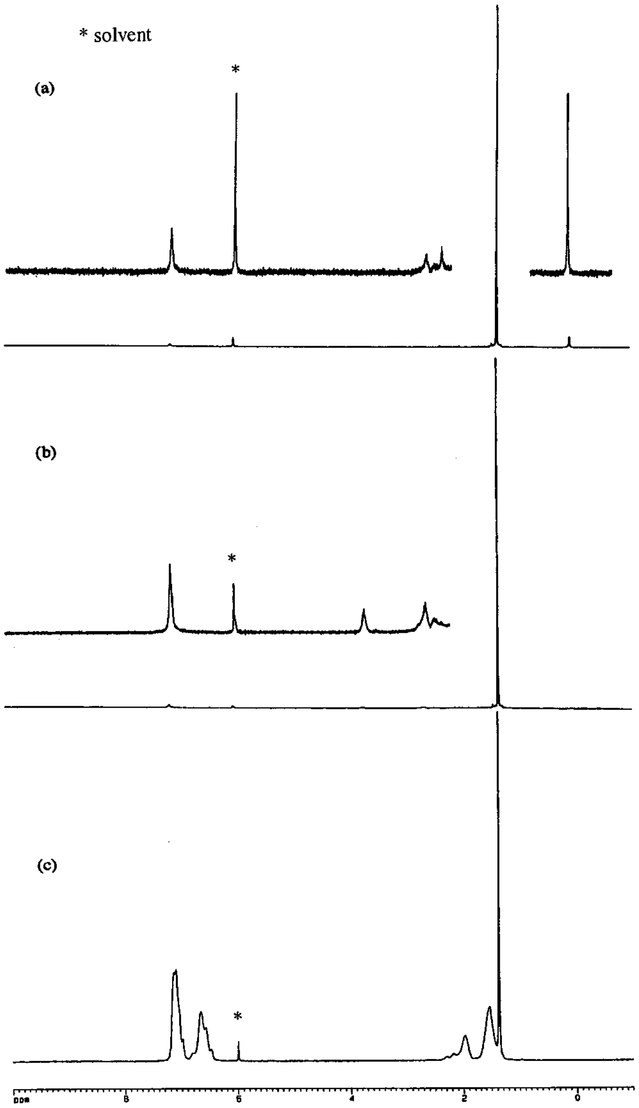

Figure 2. ^{1}H NMR spectra of three modified poly(ethylene-*co*-1,4-divinylbenzene) copolymers, containing (a) trimethylsilyl groups and (b) hydroxy groups, and (c) PE-*g*-PS graft copolymer (solvent: $C_2D_2Cl_4$; temperature: 110 °C).

composition distributions. There is no sign of branching or cross-linking reactions even with high DVB concentrations. The resulting poly(ethylene-*co*-1,4-divinylbenzene) copolymers are very versatile intermediates that can be used for preparing functional polymers and graft copolymers.

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Supporting Information Available: Preparation of 1,4-divinylbenzene, lithiation and silylation reactions of poly(ethylene-*co*-divinylbenzene), anionic graft reaction of poly(ethylene-*co*-divinylbenzene) with styrene, and GPC and DSC curves of poly(ethylene-*co*-1,4-divinylbenzene) copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) George, B.; Mathew, B. *J. Macromol. Sci., Pure Appl. Chem.* **2001**, *38*, 429. (b) Villamena, F. A.; De, L. C. A. A. *J. Appl. Polym. Sci.* **2001**, *82*, 195. (c) Li. Y. H.; Fan, Y. G.; Ma, J. B. *Polym. Degrad. Stab.* **2001**, *73*, 163. (d) Pekcan, O.; Kaya, D. *Polymer* **2001**, *42*, 7865. (e) Zhou, M. H.; Ha, C. S.; Cho, W. J. *J. Appl. Polym. Sci.* **2001**, *81*, 1277.

(2) Machida, S.; Shikuma, H.; Tazaki, T.; Tatsumi, T.; Kurokawa, S. U.S. Patent 5,608,009, 1997.

(3) (a) Chung, T. C.; Rhubright, D. *Macromolecules* **1991**, *24*, 970. (b) Chung, T. C.; Rhubright, D.; Jiang, G. J. *Macromolecules* **1993**, *26*, 3467. (c) Chung, T. C.; Lu, H. L.; Ding, R. D. *Macromolecules* **1997**, *30*, 1272. (d) Xu, G.; Chung, T. C. *J. Am. Chem. Soc.* **1999**, *121*, 6763. (e) Chung, T. C.; Dong, J. Y. *J. Am. Chem. Soc.* **2001**, *123*, 4871.

(4) (a) Kaminsky, W.; Kulper, K.; Brintzinger, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (b) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (c) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85. (d) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(5) In a typical reaction, ethylene was introduced to a 350 mL autoclave that contained 1,4-DVB, MAO, and toluene (100 mL). The copolymerization started upon adding metallocene catalyst to the reactor, and reaction continued at 50 °C under constant ethylene pressure. After 30 min reaction time, the copolymerization reactions were terminated by adding 100 mL of dilute HCl solution in MeOH. The polymers were isolated by filtering, washing with MeOH, and drying under vacuum for 8 h. The resulting ethylene/1,4-DVB copolymers were weighed and subjected to NMR, DSC, and GPC analysis to determine the copolymer composition, thermal transition temperature, molecular weight, and molecular weight distribution.

(6) (a) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Crassi, A. *Makromol. Chem.* **1991**, *192*, 223. (b) Zambelli, A.; Pellecchia, C.; Proto, A. *Macromol. Symp.* **1995**, *89*, 373. (c) Longo, P.; Proto, A. Zambelli, A. *Macromol. Chem. Phys.* **1995**, *196*, 3015.

(7) (a) Pellecchia, C.; Oliva, L. *Rubber Chem. Technol.* **1999**, *72*, 553. (b) Arai, T.; Ohtsu, T.; Suzuki, S. *Macromol. Rapid Commun.* **1998**, *19*, 327. (c) Sernetz, F. G.; Mulhaupt, R. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2549.

(8) (a) Stevens, J. C. *Stud. Surf. Sci. Catal.* **1994**, *89*, 277. (b) Sernetz, F. G.; Mulhaupt, R. *Macromol. Chem. Phys.* **1996**, *197*, 1071.

(9) (a) Chung, T. C.; Lu, H. L. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 575. (b) Chung, T. C.; Lu, H. L. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1017. (c) Chung, T. C.; Hong, S.; Lu, H. L. *Macromolecules* **1998**, *31*, 2028. (d) Chung, T. C.; Lu, H. L. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2795.

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