Synthesis of Linear Polyolefin Elastomers Containing Divinylbenzene Units and Applications in Cross-Linking, Functionalization, and Graft Reactions

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ABSTRACT: This paper discusses the synthesis of linear polyolefin elastomers containing divinylbenzene (DVB) units, including poly(ethylene-*ter*-propylene-*ter*-divinylbenzene) (EP-DVB) and poly(ethylene-*ter*-1-octene-*ter*-divinylbenzene) (EO-VDB). Several metallocene catalysts were evaluated to identify a system that can carry out monoenchainment of DVB and produce terpolymer with uniform molecular structure. Some resulting EP-DVB and EO-DVB terpolymers prepared by a *rac*-Et(Ind)$_2$ZrCl$_2$/MAO catalyst show good solubility in common organic solvents, controllable DVB content, high molecular weight, and narrow molecular weight and composition distributions. The uniform terpolymer microstructure also exhibits a DSC curve with a sharp glass transition temperature (T_g) that corresponds to its composition. Some EP-DVB and EO-DVB terpolymers with DVB content <2 mol % show low T_g's, below −45 and −55 °C, respectively. In turn, the pendent styrene moieties in the terpolymers are very versatile and engage in facile thermal and UV cross-linking and functionalization reactions (including maleation and metalation reactions) and in graft reactions. Several interesting thermoplastic elastomers containing a polyolefin elastomer backbone and several PS (amorphous) or s-PS (crystalline) side chains have been prepared by anionic graft-from and metallocene graft-through processes, respectively.

Introduction

Our research on the monoenchainment of DVB monomers in metallocene-mediated olefin polymerization stemmed from our long-standing interest in functional polyolefins,[1] especially the new chemical routes to the functionalization of polyolefins. In our previous communication,[2] we reported the copolymerization of ethylene and 1,4-divinylbenzene (1,4-DVB) by using a *rac*-Et(Ind)$_2$ZrCl$_2$ catalyst. The resulting linear ethylene/1,4-DVB copolymers exhibit good solubility and narrow molecular weight and composition distributions. The pendent styrene moieties in the copolymer resemble styrene monomers that further engage in anionic copolymerization to form PE-*g*-PS graft copolymers under mild reaction conditions.

The extension of this chemistry to prepare new polyolefin elastomers, including poly(ethylene-*ter*-propylene-*ter*-divinylbenzene) (EP-DVB) and poly(ethylene-*ter*-1-octene-*ter*-divinylbenzene) (EO-VDB) terpolymers, is very interesting. Such elastomers containing several very versatile styrene moieties pendent along the polymer chain could provide many distinctive advantages over the traditional EPDM[3] containing 1,4-hexadiene or 5-ethylidne-2-norbornene units, such as high cross-linking efficiency in peroxide, photothermal, and thermal reaction processes and facile functionalization reactions, including metalation and maleation. Subsequently, the metalated styrene[4] can be quantitatively converted to various desirable functional groups, including COOH and OH. On the other hand, styrene can involve thermal [4 + 2] cycloaddition[5] with maleic anhydride (MA). The MA modified polyolefins[6] by far are the most important class of functionalized polyolefins in commercial applications due to their unique combination of low cost, high activity, and good processability. They are the general choice of material for improving reactivity, compatibility, and adhesion of polyolefins. Another advantage over EPDM is that the pendent aromatic residues in polyolefin elastomer can improve much needed interactions[7] with carbon black to further enhance desirable physical and chemical properties, especially for tire applications. In addition, the pendent styrene moieties may also serve as macromonomers for preparing new thermoplastic elastomers, such as EP-*g*-PS and EP-*g*-s-PS graft copolymers.

For commercial applications, elastomers with low $T_g < -45$ °C and "reactive" sites that can effectively form cross-linking networks and produce stable residues are very desirable. In ethylene-based elastomer cases, this means preparing an amorphous random terpolymer containing close to a 60/40 molar ratio[3] of ethylene/propylene or ethylene/1-octene and some monoenchained DVB units. It is also very important to examine the applicability of the commercially available DVB feed source, which contains only about 60 wt % divinylbenzene with a mole ratio between the 1,3- and 1,4-isomer of about 1 to 2.5. The major impurities of ethylstyrene and diethylbenzene may behave like a comonomer and a solvent, respectively, during the polymerization reaction.

Results and Discussion

The chemistry is centered on metallocene cataslysts that can prepare high poly(ethylene-*ter*-propylene-*ter*-

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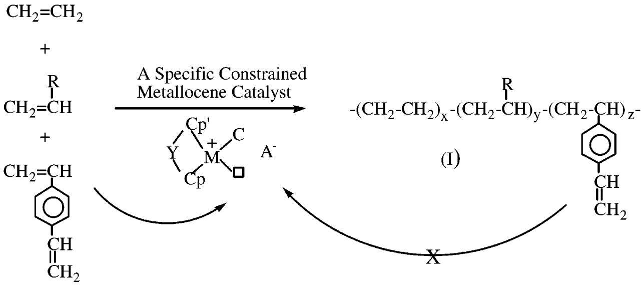
Table 1. A Summary of Terpolymerization[a] of Ethylene, Propylene, and Divinylbenzene Using Various Metallocene Catalysts

	monomer feed			terpolymer composition (mol %)						
catalyst[b]-run	mixed C2/C3[c] (psi)	DVB (mol/L)	polymer yield (g)	C_2	C_3	DVB	VN/PH[c]	M_w (kg/mol)	M_w/M_n	T_g (°C)
I-1	60/40	0.21	5.1	63.8	35.7	0.5	0.78	12	2.3	−48
I-2	60/40	0.71	3.6	74.8	23.8	1.4	0.86	14	2.4	*d*
II-1	60/40	0	2.2	69.5	30.5	0		93	2.1	−53
II-2	60/40	0.30	1.2	67.8	30.6	1.6	0.96	103	2.1	−36
II-3	60/40	0.60	1.1	65.3	30.3	4.4	0.90	128	2.3	−29
II-4	40/60	0.10	1.8	56.4	42.5	1.1	0.94	86	2.1	−51
II-5	40/60	0.30	1.3	59.3	39.0	1.7	0.91	97	2.0	−47
II-6	40/60	0.60	1.1	62.4	32.9	4.7	0.96	98	2.3	−31
II-7	40/60	1.20	0.8	56.0	22.9	21.1	0.96	138	2.1	−22
III-1	60/40	0.07	0.2			most of polymer insoluble				
III-2	60/40	0.35	0.2			most of polymer insoluble				
IV-1	60/40	0.07	4.6			most of polymer insoluble				
IV-2	60/40	0.35	3.8			most of polymer insoluble				

[a] Polymerization conditions: [cat.] = 2.5×10^{-6} mol; [MAO]/[cat.] = 3000; solvent: 100 mL of hexane; temperature: 50 °C; pressure: 30 psi; time: 15 min. [b] I: Cp_2ZrCl_2; II: $Et(Ind)_2ZrCl_2$; III: $Me_2Si(Ind)_2ZrCl_2$; IV: $[(C_5Me_4)SiMe_2N(t\text{-}Bu)]TiCl_2$. [c] C_2: ethylene; C_3: propylene; VN/PH: mole ratio of vinyl group to phenyl group. [d] Partial crystallinity.

Scheme 1



divinylbenzene) (EP-DVB) and poly(ethylene-*ter*-1-octene-*ter*-divinylbenzene) (EO-VDB) terpolymers with linear chain structure and narrow composition and molecular weight distributions. In other words, the ideal metallocene catalyst has an active site with an opening that allows effective incorporation of high α-olefins and styrenic monomers but is also limited to monoenchainment of DVB. After incorporating DVB with only one of the two vinyl groups, the propagating site does not further react the polymeric styrene moieties pendent along the polymer chain, as illustrated in Scheme 1.

Ethylene/Propylene/DVB (EP-DVB) Elastomers. Several metallocene catalysts available in our laboratory, from simple sandwiched Cp structure to high constrained geometry ones, were evaluated in the terpolymerization reaction with ethylene, propylene, and DVB (commercial grade). The polymerization reactions were carried out in a Parr reactor. The desired ratio of ethylene and propylene was mixed in a steel reservoir before piping into the reactor containing a mixed solution of DVB, MAO (methylaluminoxane), and toluene. The polymerization reaction was initiated by charging metallocene catalyst. A constant mixed ethylene/propylene pressure (30 psi) was maintained throughout the polymerization process. To ensure constant comonomer ratios, the polymerization was usually terminated in 15 min by adding dilute HCl/CH_3OH solution. Table 1 summarizes the experimental results of the ethylene/propylene/DVB terpolymers. ^1H NMR, GPC, and DSC were used to determine the terpolymer composition, molecular weight, and thermal transition temperature, respectively. The monoenchainment of DVB can be shown by the combination of polymer solubility and the vinyl group to phenyl group (VN/PH) mole ratio determined by ^1H NMR. In general, the simple sandwiched metallocene catalysts, such as Cp_2ZrCl_2, exhibit very poor incorporation of DVB. On the other hand, the constrained geometry $[C_5Me_4(SiMe_2N\text{-}{}^tBu)]TiCl_2$ catalyst and ansa-metallocene $Me_2Si(Ind)_2ZrCl_2$ catalyst, with open active sites, engage double enchainment of DVB comonomer. The terpolymers 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 DVB units.

The most suitable catalyst is *rac*-$Et(Ind)_2ZrCl_2$ that has a balanced properties, with effective incorporation of comonomers and monoenchainment of DVB. The resulting EP-DVB terpolymers were completely soluble in common organic solvents, such as hexane and toluene at ambient temperature, and had a VN/PH mole ratio >0.9. Up to 21 mol % of DVB units have been incorporated in the terpolymer without any detectable cross-linking reaction. Figure 1 compares the ^1H NMR spectra of an ethylene/1,4-DVB copolymer containing 7.2 mol % pure 1,4-DVB and two DVB containing terpolymers, including an EP-DVB and an EO-DVB containing 3 and 4.4 mol % DVB (commercial grade), respectively. All polymers are prepared by the same *rac*-$Et(Ind)_2ZrCl_2$/MAO catalyst system. The more complicated chemical shifts around the vinyl and aromatic regions in the EP-DVB and EO-DVB terpolymers reflect the incorporation of both 1,3- and 1,4- DVB isomers and ethylstyrene impurity. In addition, Figure 1b shows a chemical shift at 0.8 ppm, corresponding to $C\mathbf{H}_3$ in the propylene units, and a band between 0.9 and 1.7 ppm, corresponding to $C\mathbf{H}_2$ and $C\mathbf{H}$ in the polymer backbone. There are three bands around 5.2 and 5.7 ppm ($CH{=}C\mathbf{H}_2$) and 6.7 ppm ($C\mathbf{H}{=}CH_2$) and an aromatic proton band between 6.9 and 7.4 ppm ($C_6\mathbf{H}_4$). The integrated intensity ratio between all three vinyl protons and the four phenyl protons determines the VN/PH ratio, which is about 0.95. The small shortage of vinyl protons may be related to the incorporated ethylene styrene (no vinyl group). The mole ratio of ethylene/propylene in the terpolymer was determined by an IR technique,[8] by comparing the integrated intensity between the absorption at 1460 cm^{-1}, corresponding to the CH_2 group in the ethylene unit, and the absorption at 1379 cm^{-1}, corresponding to the CH_3 group in the propylene unit. On the other hand, Figure 1b shows sharp chemical shifts with a major peak at 1.3 ppm, corresponding to ethylene units;

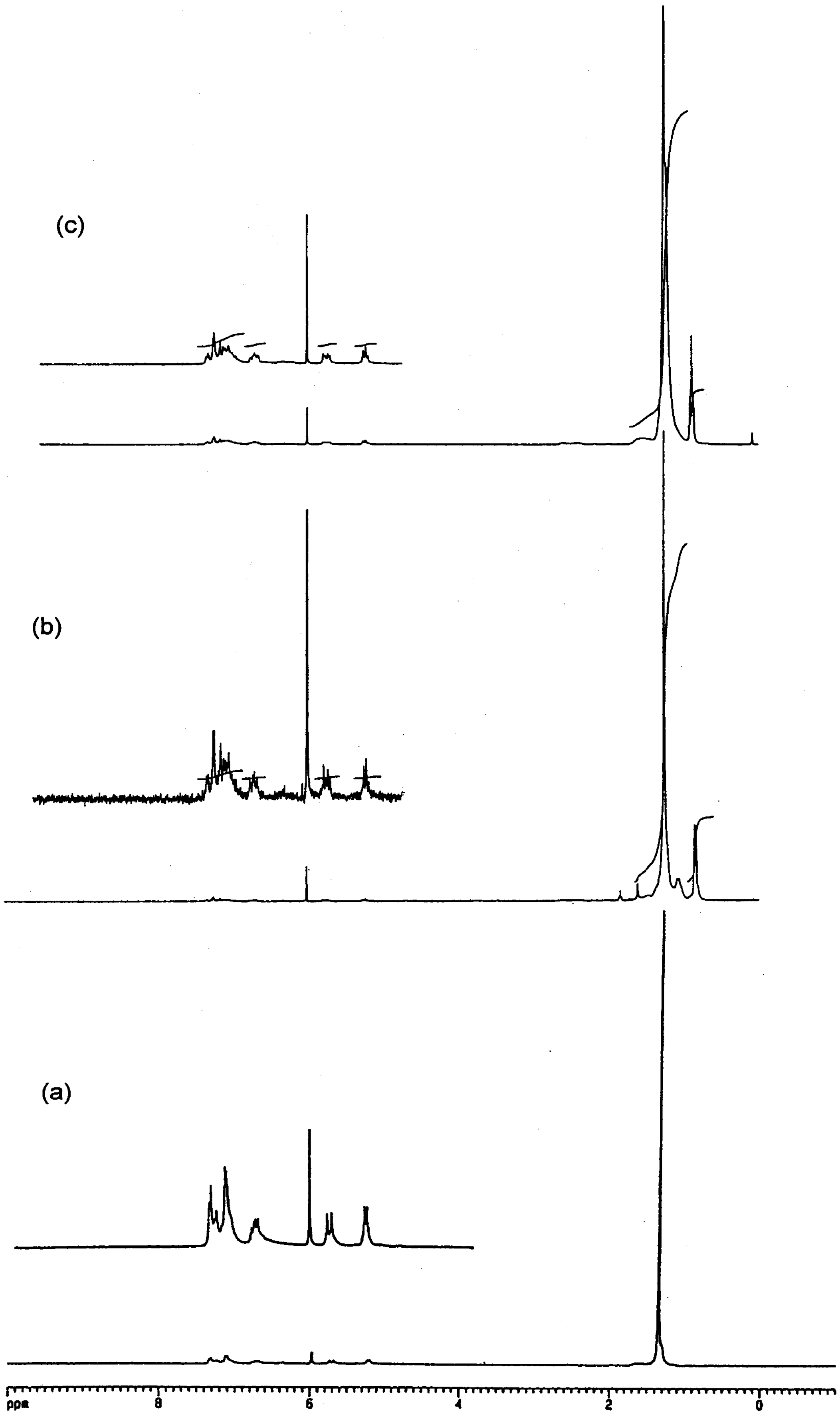


Figure 1. ^{1}H NMR spectrum comparison of (a) an ethylene/1,4-DVB copolymer containing 7.2 mol % pure 1,4-DVB, (b) an EP-DVB terpolymer containing 3 mol % DVB, and (c) an EO-DVB terpolymer containing 4.4 mol % DVB (solvent: $C_2D_2Cl_4$).

several chemical shifts at 5.2 and 5.7 ppm (doublet, $CH{=}C\mathbf{H}_2$) and 6.7 ppm (doublet of doublet, $C\mathbf{H}{=}CH_2$); and aromatic proton peaks at 7.1 and 7.4 ppm ($C_6\mathbf{H}_4$). The peak intensity ratio indicates the VN/PH mole ratio

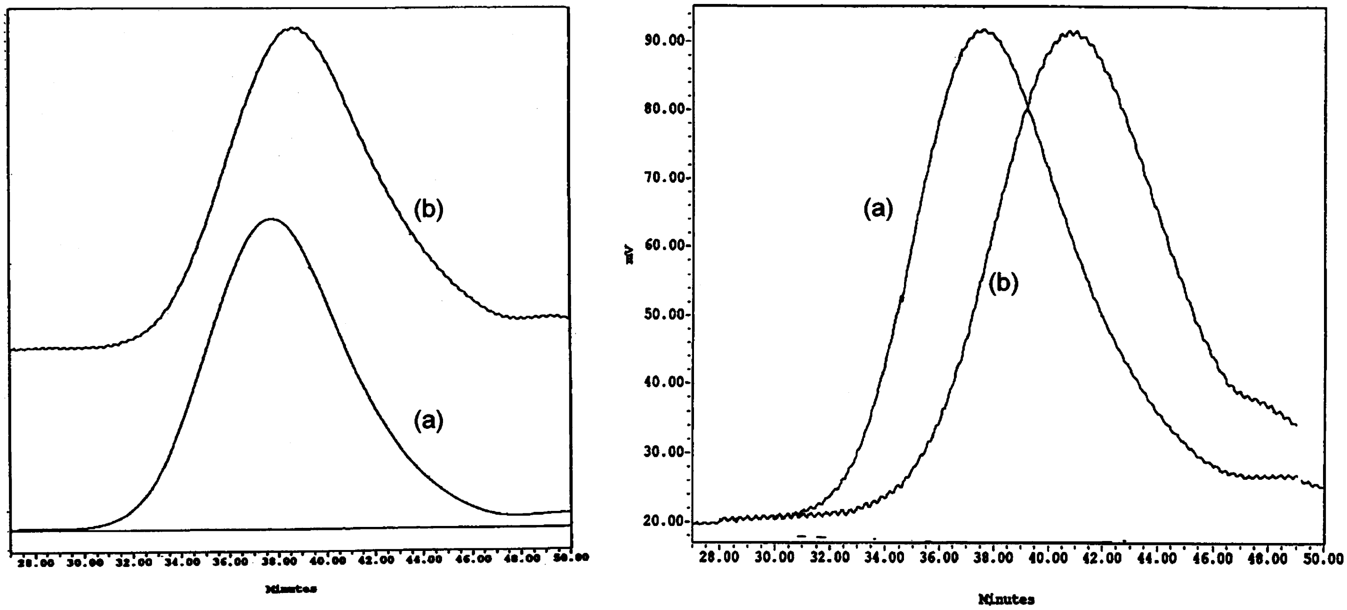


Figure 2. (left) GPC curves of the EP-DVB terpolymer containing 3 mol % DVB using (a) UV and (b) RI detectors. (right) GPC curves of (a) an ethylene/1-octene/DVB terpolymer (run 4 in Table 2) and (b) a corresponding ethylene/1-octene copolymer (run 1).

near unity. GPC equipped with both RI and UV detectors were used to study the molecular weight and composition distributions of the terpolymers. Since DVB has a strong UV absorption at the wavelength of 254 nm, but not ethylene and propylene, the comparison of UV and RI curves of terpolymer provides detailed information on the DVB distribution in all of the terpolymer fractions. Figure 2 (top) shows the GPC UV and RI curves of the EP-DVB terpolymer containing 3 mol % DVB prepared by *rac*-Et(Ind)$_2$ZrCl$_2$/MAO. Both curves show the same shape with relatively narrow molecular weight distribution ($M_w/M_n \sim 2.1$), indicative of an ideal single-site polymerization mechanism, and the addition of DVB did not alter the polymerization process. The small shift in one of the curves, with respect to the other, arises because the eluted fractions pass through the UV detector 15 s before passing through the RI detector, due to the instrument configuration. The almost exact overlap of the UV and RI profiles is a strong indication of the homogeneity of the terpolymer sample. The narrow composition distribution is also exhibited in the DSC curve with a sharp glass transition temperature (T_g) in a flat baseline, which will be discussed later.

As expected, the T_g of the EP-DVB terpolymers is a direct function of the propylene and DVB contents. Comparing the EP-DVB terpolymers (runs III-1 to III-3 and runs III-4 to III-7 in Table 1) with similar ethylene concentration shows that the T_g transition is basically proportional to the DVB content. Overall, EP-DVB material with a low $T_g < -45$ °C is limited to compositions with <2 mol % of DVB content. Despite the random terpolymer structure and the preferred (~60/40) ethylene/propylene ratio, any further increase of DVB raises the T_g of the terpolymer to > -40 °C.

Ethylene/1-Octene/DVB (EO-DVB) Elastomers. In EP elastomers, the primary function of propylene units is to prevent the crystallization of ethylene sequences. In traditional Ziegler–Natta polymerization, propylene is a natural choice because it has the closest reactivity to ethylene. However, in terms of effectiveness of preventing crystallization of ethylene sequences and obtaining low-T_g material, propylene is not the best comonomer, namely due to (i) the small CH$_3$ side group and (ii) the relatively high T_g (~0 °C) of the propylene component. In our quest to prepare polyolefin elastomers with low $T_g < -45$ °C and a wide concentration range of "reactive" DVB units, the EP system clearly shows serious limitations. It is very interesting to replace propylene units with higher α-olefins, such as 1-octene, which can effectively prevent the crystallization of ethylene sequences (as known in LLDPE) and is a low-T_g material[9] with no possibility of self-crystallization. Additionally, it is very interesting to study the metallocene technology in a very complicated termonomer system involving ethylene, 1-octene (high α-olefin), and DVB (aromatic α-olefin). Table 2 summarizes the experimental results of several ethylene/1-octene/DVB terpolymers (EO-DVB) prepared by *rac*-Et(Ind)$_2$ZrCl$_2$/MAO catalyst. All of the terpolymers are completely soluble in hexane or toluene at ambient temperature and show narrow molecular weight and composition distributions. Compared to the corresponding EP-DVB terpolymer, the T_g of the EO-DVB terpolymer is significantly lower. Even with up to 8 mol % of DVB content, the EO-DVB terpolymer still maintains low T_g (~ -50 °C). Compared to runs 1–4 in Table 2, with the same ethylene and 1-octene concentrations, a greater DVB feed increases the DVB incorporation and T_g of the resulting terpolymer. The molecular weight and molecular weight distribution of the terpolymers are slightly increased with higher DVB content. On the other hand, comparing runs 2 and 5 or 4 and 6, with the same 1-octene and DVB concentrations, the molecular weight clearly decreases with less ethylene pressure, which may be due to the significantly higher reactivity of ethylene among the three monomers. Following the monoenchainment of DVB, the subsequent insertion of ethylene is faster than that of 1-octene. The slowdown of the propagating activity after incorporating DVB is also evidenced by the reduction of catalyst activity with increasing DVB concentrations.

Figure 1c shows the ^{1}H NMR spectrum of an EO-DVB terpolymer containing 4.4 mol % DVB units (run 4 in

Table 2. A Summary of Terpolymerization[a] of Ethylene, 1-Octene, and Divinylbenzene Using *rac*-Et(Ind)$_2$ZrCl$_2$/MAO Catalyst

	monomer feed				terpolymer composition (mol %)						
run	C_2 (psi)	C_8[b] (mol/L)	DVB (mol/L)	cat.[c] activity	C_2	C_8	DVB	VN/PH[b]	M_w (kg/mol)	M_w/M_n	T_g (°C)
1	10	0.8	0	7776	61.5	38.5	0		80	2.0	−60
2	10	0.8	0.2	3032	69.4	28.6	2.0	0.99	93	2.1	−57
3	10	0.8	0.4	2016	66.8	29.2	4.0	0.95	93	2.2	−53
4	10	0.8	0.8	1840	74.8	20.8	4.4	0.98	136	2.5	−51
5	5	0.8	0.2	1224	64.4	33.4	2.2	0.92	52	2.2	−60
6	5	0.8	0.8	1128	63.8	29.5	6.7	0.92	59	2.5	−56
7	5	0.8	1.4	1000	69.8	22.2	8.0	0.96	72	2.3	−50
8	5	0.4	0.8	1309	71.8	20.9	7.3	0.92	69	2.0	−55

[a] Polymerization conditions: [cat.] = 2.5×10^{-6} mol; [MAO]/[cat.] = 3000; solvent: 100 mL of hexane; temperature: 50 °C; polymerization time: 30 min. [b] C_2: ethylene; C_8: 1-octene; VN/PH: mole ratio of vinyl group to phenyl group. [c] Catalyst activity: kg/(mol of Zr h).

Table 2). The integrated intensity ratio between all three vinyl proton bands, at around 5.2 and 5.7 ppm (CH═C**H**$_2$) and 6.7 ppm (C**H**═CH$_2$), and the four phenyl protons band, between 6.9 and 7.4 ppm (C$_6$**H**$_4$), determine the VN/PH ratio, which is about 0.95. Figure 2 (bottom) compares the GPC curves this EO-DVB terpolymer with a corresponding poly(ethylene-*co*-1-octene) copolymer (run 1 in Table 2). Despite the terpolymer showing slightly higher molecular weight, the molecular weight distributions are very similar ($M_w/M_n \sim 2.0-2.2$), indicative of an ideal single-site polymerization mechanism.

The thermal transition temperature of the PO-DVB terpolymer was examined by DSC studies. A typical DSC curve (shown in the Supporting Information) has only one sharp T_g transition at ∼−60 °C in a flat baseline, without any detectable melting point. This combination implies a homogeneous terpolymer microstructure with completely amorphous morphology. The same clean DSC curves were observed in all samples, and their T_g's are summarized in Table 2. It is very interesting to note that the EO-p-MS sample with as much as 8 mol % of DVB still shows a $T_g < -45$ °C, which is very different from the corresponding EP-DVB terpolymers discussed earlier.

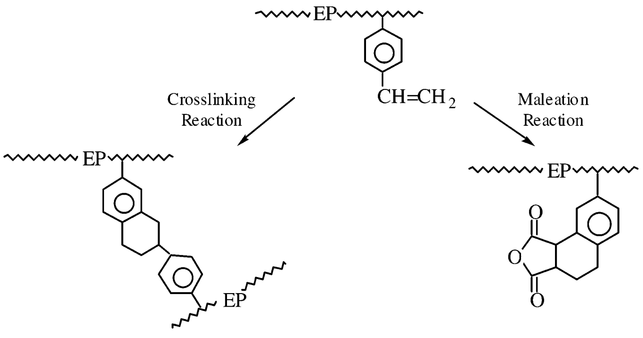
Cross-Linking and Functionalization Reactions. One major advantage of the linear DVB-containing terpolymers is the existence of pendent styrene moieties that are very reactive in many chemical reactions, including free radical, cationic, anionic, and transition metal coordination processes. The pendent styrene moieties can serve as the reactive sites for cross-linking and functionalization reactions or serve as the monomers for subsequent graft reactions that produce polyolefin graft copolymers having a polyolefin backbone and other polymer side chains. There has long been a desire in the industry for developing a facile and controllable method (including chemical, thermal, and radiation processes) to produce cross-linked polyolefin products. The incorporated DVB units in polyolefin elastomers provide an attractive new possibility for all reaction processes. In general, both EP-DVB and EO-DVB elastomers having >1 mol % of DVB units became completely insoluble after heating the sample at 150 °C for 1 h. On the other hand, the UV (source: PC-2, 5−10 mW/cm^2) cross-linking reaction took place at room temperature. The radiated sample was subjected to extraction by boiling toluene to examine the gel content after radiation. Table 3 shows the experimental results of an EP-DVB terpolymer containing 2.3 mol % of DVB units. The same UV-induced cross-linking reaction was also monitored by in situ FTIR spectra (shown in the Supporting Information). The C═C stretching modes between 1720 and 1630 cm^{-1} gradually disappear, with several new peaks appearing between 800 and 1000 cm^{-1}, corresponding to the saturated C−C−H defraction modes. The cross-linking reaction may follow a [2 + 4] cycloaddition reaction,[10] as illustrated in Scheme 2.

Table 3. Gel Content of EP-DVB Terpolymers after UV Radiation[a]

radiation time (min)	gel content[b] (wt %)	radiation time (min)	gel content[b] (wt %)
5	23.4	60	100
15	35.0	120	100
30	76.3	240	100

[a] UV source: PC-2, 5−10 mW/cm^2. [b] After boiling toluene extraction for 12 h.

Scheme 2



The thermal cycloaddition reaction was also extended to the preparation of maleic anhydride (MA)-modified polyolefins (procedures provided in the Supporting Information). This maleation reaction is a selective reaction. All the MA-modified EP-DVB and EO-DVB terpolymers are completely soluble in THF and show no significant change in polymer molecular weight by comparing GPC curves before and after reaction. In the Supporting Information, IR spectra of three maleated EO-DVB terpolymers with 0.86, 1.20, and 11.5 incorporated MA weight percent are compared with that of the starting EO-DVB terpolymer containing 4 mol % DVB units (run 3 in Table 2). The new absorption peaks at 1860 and 1780 cm^{-1} correspond to two $v_{C=O}$ vibrational stretching modes in succinic anhydride. The concentration of incorporated MA units was calculated by a standard industrial method,[11] which is based on the IR carbonyl group absorption intensity and sample thickness.

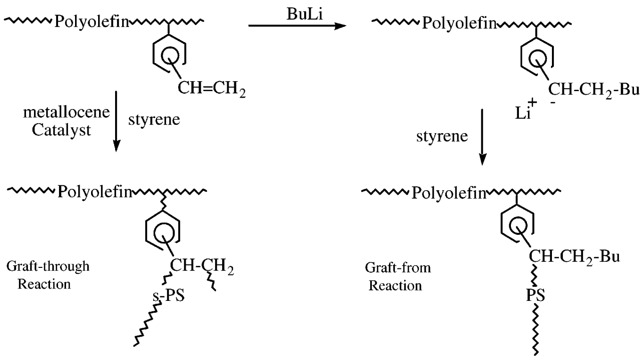
Anionic Graft-from and Metallocene Graft-through Reactions. The pendent styrene moieties in the EP and EO elastomers can serve as macromonomers

Table 4. A Summary of EP-*g*-s-PS and EO-*g*-s-PS Graft Copolymers Prepared by Cp*Ti(OMe)$_3$/MAO Catalyst[a]

	graft conditions					graft copolymer[d]				
run[b]	terpolymer (g)	styrene (g)	isolated yield (g)	hexane soluble (%)	insoluble[c] fraction (%)	EP or EO (wt %)	*s*-PS (wt %)	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)
A-1	EP-DVB/0.28	2.7	2.77	7.1	2.1	10.3	89.7	nd[e]	99	272
A-2	EP-DVB/0.71	2.7	3.23	12.7	2.7	21.9	78.1	nd	92	270
A-3	EP-DVB/1.20	2.7	3.80	15.0	3.0	31.3	68.7	−52	93	267
A-4	EP-DVB/0.57	5.4	4.85	9.0	1.2	11.9	88.1	nd	99	273
B-1	EP-DVB/0.32	2.7	2.74	5.1	4.8	11.6	88.4	−51	99	268
B-2	EP-DVB/0.71	2.7	3.04	10.0	6.2	23.4	76.6	−48	98	262
B-3	EP-DVB/1.20	2.7	3.51	9.9	9.7	34.2	65.8	−44	97	257
C-1	EO-DVB/0.71	4.1	4.64	3.5	2.8	5.3	94.7	nd	99	271
C-2	EO-DVB/0.72	2.7	2.89	5.7	2.7	8.7	91.3	nd	98	271
C-3	EO-DVB/0.72	0.9	1.45	15.3	3.3	24.5	75.5	−57	92	270
C-4	EO-DVB/2.43	2.7	4.65	15.7	3.9	30.8	69.2	−53	93	268

[a] Polymerization conditions: cat.: 5 umol of Cp*Ti(OMe)$_3$; [MAO]/[Cp*Ti(OMe)$_3$] = 1500; solvent: toluene; temp: 50 °C; time: 1 h. [b] Runs A: EP-DVB with ethylene: 52.2 mol %; propylene: 46.5 mol %; DVB: 1.7 mol %; M_w = 86 000; PDI = 2.2; T_g = −56 °C. Runs B: EP-DVB with ethylene: 57.5 mol %; propylene: 39.4 mol %; DVB: 3.1 mol %; M_w = 98 000; PDI = 2.3; T_g = −51 °C. Runs C: EO-DVB with ethylene: 69.4 mol %; propylene: 28.6 mol %; DVB: 2.0 mol %; M_w = 93 000; PDI = 2.1; T_g = −58 °C. [c] Insoluble fraction: the percentage of reaction product insoluble in hexane and *o*-dichlorobenzene. [d] *o*-Dichlorobenzene soluble fraction: composition determined by ^{1}H NMR; thermal properties determined by DSC. [e] nd = not detectable.

Scheme 3



for subsequent graft reactions that produce polyolefin graft copolymers having polyolefin backbone and other polymer side chains. Scheme 3 illustrates two reaction processes, including an anionic graft-from polymerization to prepare polyolefin-*g*-PS graft copolymer having amorphous polystyrene (PS) side chains and a metallocene graft-through polymerization to prepare polyolefin-*g*-s-PS graft copolymer containing syndiotactic polystyrene (s-PS) side chains that exhibit high melting temperature and high crystallinity.[12]

The anionic process begins with a metalation reaction of DVB containing terpolymer with alkyllithium (such as *n*-BuLi/TMEDA) to form a polyolefin containing pendent benzylic anions. By limiting the alkyllithium added to the reaction to the amount required to react with all of the DVB units in the copolymer, the metalation reaction between the pendent styrene unit and the alkyllithium is quantitative. In other words, no purification is needed before adding anion-polymerizable monomers to continue the living anionic graft-from polymerization process. One example is the preparation of EO-*g*-PS graft copolymer. The metalation reaction was carried out by mixing EO-DVB terpolymer in cyclohexane solution with *n*-BuLi/TMEDA at ambient temperature for 1 h. To determine the efficiency, a small portion of metalated polymer solution was reacted with Me$_3$SiCl at room temperature. The silylated polymer was isolated by precipitation in MeOH. Repeated washing with methanol was performed before drying. Figure 3a shows the ^{1}H NMR spectra of the silylated EO-DVB terpolymer. All vinyl peaks have completely disappeared, and the strong peak at 0.05 ppm corresponds to the methyl proton next to Si. Both the metalation and silylation efficiencies were almost 100%.

The major portion of the metalated EO-DVB terpolymer solution was mixed with the styrene monomers. The anionic graft-from reaction was then carried out at ambient temperature for 3 h before adding 2-propanol to terminate the reaction. The resulting EO-*g*-PS graft copolymers were completely soluble in THF. Figure 3b shows the ^{1}H NMR spectrum of an EO-*g*-PS graft copolymer containing ~60 mol % PS. In addition to the chemical shifts for ethylene/1-octene backbone, the new peaks (δ = 6.4−7.3 ppm) are due to aromatic protons in the PS side chains. Overall, the graft-from reactions were very effective—more than 80% styrene monomer conversion within 1 h. The graft content increased proportionally with increasing monomer concentration and reaction time. 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 that each side chain has a similar molecular weight. Therefore, the graft density will be similar to the density of the benzylic anions, and the side chain length is basically proportional to the reaction time and monomer concentration. In other words, this process produces a graft copolymer with relatively well-defined molecular structure.

Preparing EP-*g*-s-PS and EO-*g*-s-PS graft copolymers that have crystalline syndio-specific polystyrene (s-PS) side chains with high melting temperature (T_m ~ 270 °C) is a very interesting process. The graft copolymer with low s-PS content could be useful as a thermoplastic elastomer with high temperature stability, and the ones with high s-PS contents could be a high impact s-PS engineering plastic. As illustrated in Scheme 3, the pendent DVB units in the terpolymer are directly used as macromonomers in the syndio-specific metallocene polymerization of styrene. Usually, the DVB-containing elastomer was first mixed with styrene in homogeneous cyclohexane solution, and then the half-sandwiched metallocene catalysts,[12] such as the Cp*Ti(OMe)$_3$/MAO complex, were then introduced into the solution to initiate graft-through polymerization. The isolated reaction mixture was subjected to a vigorous solvent extraction process by consecutively refluxing it with hexane and *o*-dichlorobenzene in a Soxhlet extractor for 24 h each. Table 4 summarizes the experimental conditions and results of three sets of comparative graft-through reactions, including runs A using EP-DVB with 1.7 mol

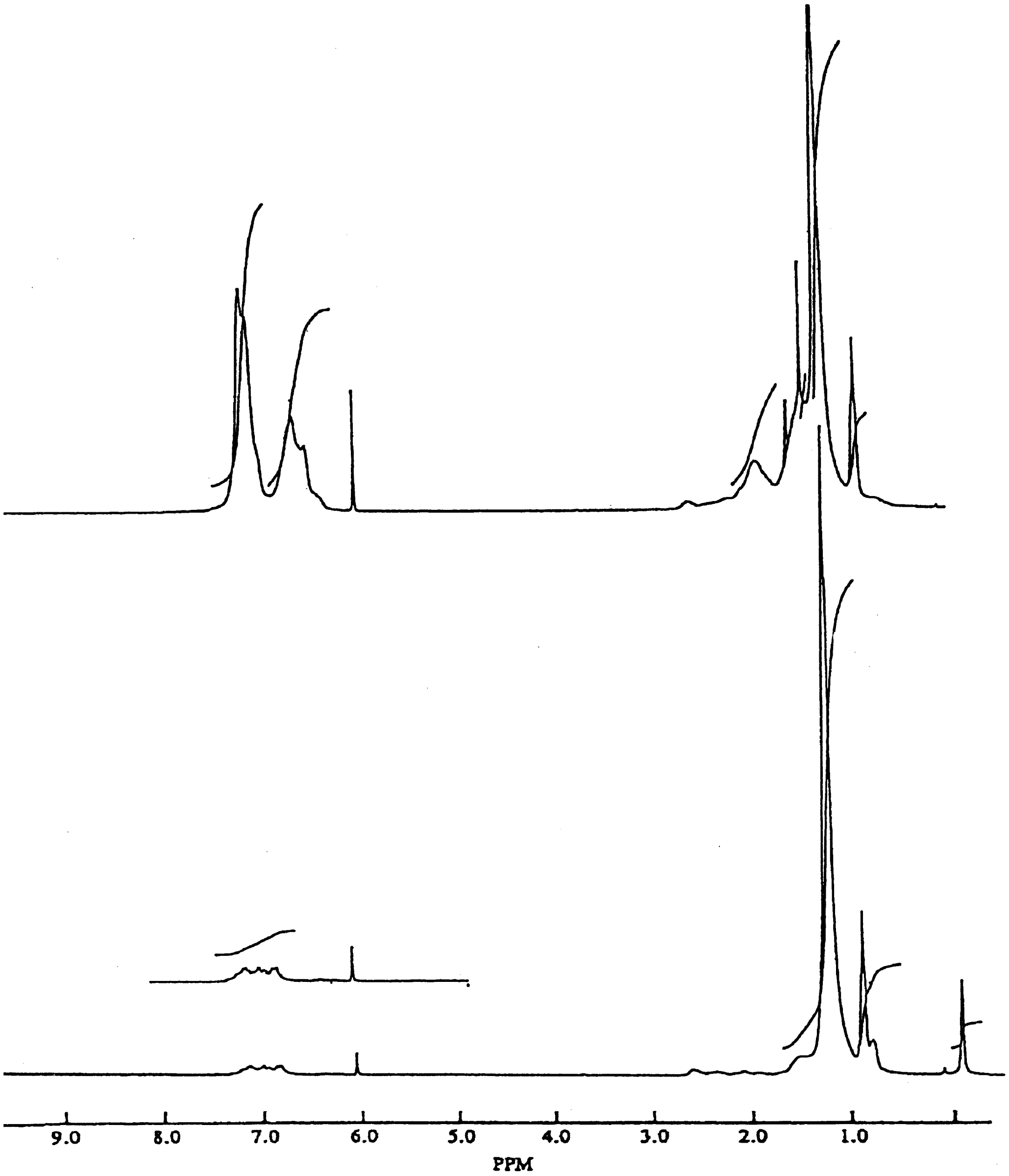


Figure 3. ^{1}H NMR spectra of (a) a silylated ethylene/1-octene/DVB terpolymer with 4 mol % DVB content and (b) a corresponding graft copolymer with ethylene/1-octene/DVB back-bond and polystyrene side chains (solvent: $C_2D_2Cl_4$).

% DVB content, runs B using EP-DVB with 3.1 mol % DVB content, and runs C using EO-DVB with 2.0 mol % DVB content. In general, the conversion of styrene is very high (>80%), and the majority of the resulting polymers (>90%) are soluble in hexane and *o*-dichlorobenzene. Only a small portion of the polymers are insoluble after Soxhlet extraction, some of which may be due to the thermal cross-linking reaction at elevated temperature (as discussed before). By comparing runs A-1 to A-3, runs A-2 and B-2, and runs A-3 and B-3, there is a small but clear correlation between insoluble fraction and reaction condition. The combination of using EP-DVB with low DVB content and high [styrene]/[EP-DVB] feed ratio further reduces the insoluble fraction. It is logical to say that only a very small portion of graft reactions involve two or more macromonomers in most cases. The hexane-soluble fraction was determined to be the unreacted EP-DVB or EO-DVB terpolymer. As seen when runs C-1, C-2, and C-3 are compared in Table 4, a higher concentration of styrene is also needed to minimize the unreacted terpolymer. The major fraction of the reaction product is the graft copolymer, which is completely soluble in *o*-dichlorobenzene at elevated temperature. As shown in Table 4, the composition of the terpolymer can be easily controlled by feed ratio. Figure 4 shows the ^{1}H and ^{13}C NMR spectra of an EO-*g*-s-PS graft copolymer (run C-4) containing 69.2 wt % of s-PS content. In Figure 4a, in addition to the aliphatic proton peaks between 0.8 and 2.0 ppm from both EO and PS chains, there are two sharp aromatic proton peaks at 6.68 and 7.15 ppm, indicating a high syndiotactic arrangement[17] of styrene units in all of the polymers. The EO-DVB involved the graft reaction but did not interfere with the syndiotactic incorporation of styrene in the polymerization reaction. The stereostructure of the polymer was further revealed by ^{13}C NMR. As shown in Figure 4b, all peaks corresponding to s-PS are sharp. According to the literature, the presence of a single resonance[13] for the substituted aromatic carbon in phenyl groups at 145.3 shows that these polymers are highly syndiotactic. The same conclusion can be reached by considering two sharp reso-

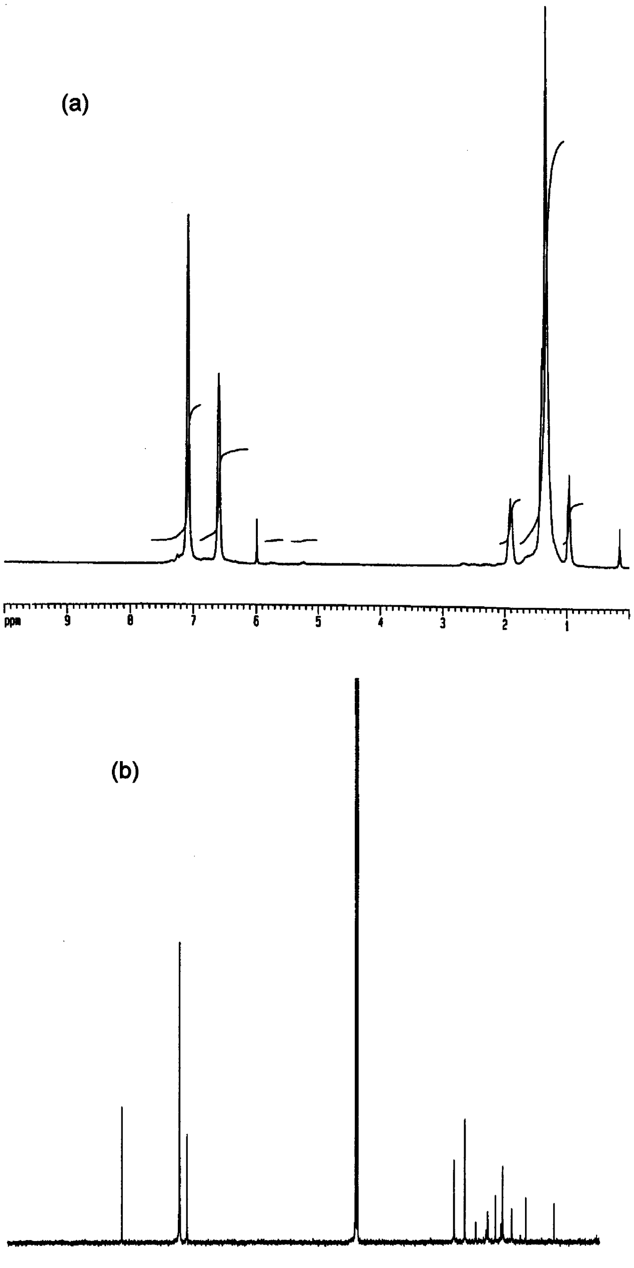


Figure 4. (a) ^1H and (b) ^{13}C NMR spectra of an EO-*g*-s-PS graft copolymer (run C-4) containing 69.2 wt % of s-PS content (solvent: $C_2D_2Cl_4$).

nances at 44.5 and 41.0 ppm, corresponding to the methine and methylene in a highly stereoregular s-PS polymer chain.

DSC curves of three EP-*g*-s-PS graft copolymers (runs A-1, A-2, and A-3) and the corresponding EP-DVB backbone and s-PS side chain are compared in the Supporting Information. All samples were measured with the same weight and were given the same thermal treatment by heating at 20 °C/min. The glass transition temperature ($T_g \sim 95$ °C), melting point ($T_m \sim 270$ °C), and degree of crystallinity (based on $\Delta H_f =$ J/g of s-PS) for the s-PS side chains in the EP-*g*-s-PS graft copolymers are almost the same as those in the s-PS homopolymer, despite the presence of an EP elastic backbone. The T_g of the EP backbone is clearly observed from the EP-*g*-s-PS polymer having 31.3 wt % EP content, which is almost the same (−56 °C) as the starting EP-DVB polymer. Overall, the results indicate that both the EP and s-PS domains are phase-separated. It is interesting to study the compatibility of the graft copolymers in polymer blends. Figure 5 shows a SEM micrograph of a cold fractured film edge from a polymer blend containing s-PS/EP-*g*-s-PS/EPDM (75/10/15 weight ratio). The magnification is 20 000×. The sample was prepared by first melt-blending EP-*g*-s-PS (run A-3 in Table 4) with commercial EPDM (M_n = 150 000 g/mol) containing 2.8 mol % 5-ethylidne-2-norbornene units and then gradually adding s-PS homopolymer ($M_n \sim$ 70 000 g/mol, $M_w/M_n \sim 2.9$) at 300 °C. The polymer mixture was press-molded into a thin film, which was cryro-fractured in liquid N_2 and extracted by hexane at ambient temperature to remove EPDM. The sample was carbon-coated to form a conductive surface. The surface topography exhibits a uniform microphase separation with a continuous s-PS phase and discrete EPDM phases (holes) with a domain size of ~0.1−0.2 μm. The EP-*g*-s-PS is clearly proven to be an effective compatibilizer in the s-PS/EPDM blend.

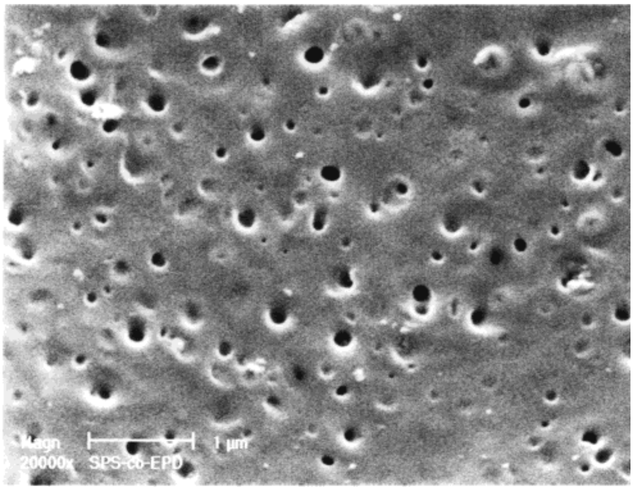


Figure 5. SEM micrograph of a cold fractured film edge from a polymer blend containing s-PS/EP-*g*-s-PS/EPDM (75/10/15 weight ratio). The magnification is 20 000×.

Experimental Details

Instrumentation and Materials. All ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer. Fourier transform infrared spectroscopy was performed on a Digilab FTS-60 instrument on solution-cast films on KBr windows. The molecular weight of the polymer was determined using a Waters GPC. The columns used were Phenomenex Phenogel of 10^5, 10^4, 10^3, and 500 Å. A flow rate of 0.7 mL/min was used, and the mobile phase was THF. Narrow molecular weight polystyrene standards were used to estimate the molecular weight. Differential scanning calorimetry (DSC) was measured (with a heating rate of 20 °C/min) on a Seiko Instrument SSC/5200. Bulk morphology in the polymer films was examined by scanning electron microscopy (SEM), using a Topcon International Scientific Instruments ISI-SX-40 with secondary electron imaging.

All O_2- and moisture-sensitive manipulations were performed inside an argon-filled Vacuum Atmosphere drybox equipped with a MO-40-1 dry train. High-purity grade ethylene, propylene (MG Industries), Cp_2ZrCl_2, *rac*-$Et(Ind)_2ZrCl_2$, *n*-butyllithium (Aldrich), and MAO (Albemarle) were used as received. $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$ and $Me_2Si(Ind)_2ZrCl_2$ were prepared as described in the literature.[14] DVB, styrene, and 1-octene (Aldrich) were dried over CaH_2 before distillation. Hexane and toluene were deoxygenated by argon purge before refluxing for 48 h and then distilled over potassium and CaH_2, respectively.

Terpolymerization Reaction. In a typical terpolymerization reaction (run III-4 in Table 1), the commercial DVB (10 mmol) was added into a Parr 450 mL stainless autoclave reactor with hexane (100 mL) and MAO (3 mL, 2.5 M in toluene). The premixed ethylene (40 psi) and propylene (60 psi) were then connected to the reactor. After saturating both ethylene and propylene gases at 50 °C, the total pressure in the reactor was controlled at 30 psi. The polymerization reaction was initiated by charging a *rac*-Et(Ind)$_2$ZrCl$_2$ (2.5 μmol) toluene solution into the monomer mixture. A constant mixed ethylene/propylene pressure was maintained throughout the polymerization process. The polymerization was terminated within 15 min by adding dilute HCl/CH$_3$OH solution. The polymer was isolated by filtering and washed with MeOH and dried under vacuum for 8 h. About 1.8 g of EP-DVB terpolymer that completely soluble in common organic solvents, such as hexane, toluene, and THF, was obtained. The ^{1}H NMR results showed the terpolymer had a composition of 56.4 mol % ethylene, 42.5 mol % propylene, and 1.1 mol % DVB.

Lithiation and Silylation Reactions. In an argon-filled drybox, 0.86 g of EO-DVB containing 4 mol % of DVB units was dissolved in 100 mL of anhydrous cyclohexane in a 250 mL air-free flask equipped with a magnetic stirrer bar. Next, 0.7 mmol of *n*-butyllithium (*n*-BuLi) solution and 0.7 mmol of tetramethylethylenediamine (TMEDA) were added into the flask, and the resulting solution was stirred at ambient temperature for 3 h before adding 5 mL of trimethylsilane chloride (Me$_3$SiCl). After reacting for 1 h at room temperature, the silylated polymer was isolated by precipitation in methanol. Repeated washing with methanol was performed before drying the resulting polymer under vacuum. The ^{1}H NMR spectrum shows no peak corresponding to a vinyl group and a strong peak at 0.05 ppm, corresponding to the methyl proton next to Si. Both metalation and silylation efficiencies were almost 100%.

Living Anionic Graft-from Polymerization. In a typical example, 3 g of EP-DVB (with ethylene/propylene/DVB = 50.1/47.0/2.9 mole ratio) was dissolved in 100 mL of anhydrous cyclohexane in a 250 mL flask equipped with a stirrer. The metalation reaction was started by adding 1 mL of 2.5 M *n*-BuLi/hexane and 2.5 mmol of TMEDA to the solution. The mixture was stirred at ambient temperature for 3 h before adding a desirable quantity of monomer. The graft reaction was then carried out at ambient temperature for 3 h before adding 10 mL of 2-propanol to terminate the anionic graft reaction.

Metallocene Graft-through Polymerization. In a typical example, 0.71 g of EP-DVB containing 3.1 mol % of DVB units was dissolved in 100 mL of toluene under nitrogen in a 250 mL flask equipped with a stirrer bar. Styrene monomer and MAO were then added into the polymer solution. After stirring the homogeneous solution mixture at 50 °C, the graft-onto polymerization reaction was initiated by charging with a Cp*Ti(OMe)$_3$ ([MAO]/Ti = 1500) catalyst. After 1 h, 10 mL of 2-propanol was added to terminate the graft-onto reaction. The precipitated polymer was filtered and then subjected to a consecutive Soxhlet fractionation using hexane and *o*-dichlorobenzene solvents. There were about 10 wt % of hexane-soluble fraction from the ungrafted EP-DVB terpolymer and a 6.2 wt % insoluble fraction. The major *o*-dichlorobenzene soluble fraction was graft copolymer (EP-DVB-*g*-s-PS), containing EP backbone (23.4 wt %) and s-PS side chains (76.6 wt %). The conversion of styrene was very high (~86%).

Summary

The experimental results clearly show the linear terpolymerization reaction of ethylene, propylene (or 1-octene), and divinylbenzene (commercial source) by the *rac*-Et(Ind)$_2$ZrCl$_2$/MAO catalyst. The formed EP-DVB and EO-DVB terpolymers are completely soluble and exhibit narrow molecular weight and composition distributions. There is no sign of branching or cross-linking reactions, even with high DVB concentrations. The EO-DVB terpolymers show very low T_g's (<-50 °C), even when containing up to 8 mol % of DVB units.

The new DVB-containing polyolefin elastomers benefit from reactive pendent styrene moieties that are very facile in many reactions, including various cross-linking and functionalization reactions. The pendent styrene groups in the polyolefin elastomers can also serve as macromonomers in subsequent graft reactions, via either anionic graft-from or metallocene graft-through polymerization processes, to produce graft copolymers containing a polyolefin elastomer backbone and several pendent polymer side chains, including EP-*g*-PS and EP-*g*-s-PS thermoplastic elastomers.

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Supporting Information Available: Preparation of 1,4-divinylbenzene, maleation reaction of an EO-DVB elastomer, and several figures including (i) DSC curve of an EO-DVB terpolymer (run 5 in Table 2), (ii) FTIR spectra of a starting EP-DVB terpolymer containing 2.3 mol % of DVB units and two UV-radiated samples after 30 min and 1 h irradiation, (iii) FTIR spectra of a starting EO-DVB terpolymer containing 4 mol % DVB units and three maleated EO-DVB terpolymers containing 0.86, 1.20, and 11.5 wt % of incorporated MA units, and (iv) DSC curves the starting EP-DVB terpolymer and three EP-*g*-s-PS copolymers in Table 4, including runs A-3, A-2, and A-1, and s-PS homopolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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and k_1 and k_2 are the absorption constants for anhydride and acid, respectively. Both k_1 and k_2 were determined by calibration of the known commercial compounds (Uniroyal), assuming the absorption constants are independent of the incorporated MA structures.

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