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Copolymerization of Ethene with Styrene Derivatives, Vinyl Ketone, and Vinylcyclohexane Using a (Phosphine−sulfonate)palladium(II) System: Unusual Functionality and Solvent Tolerance

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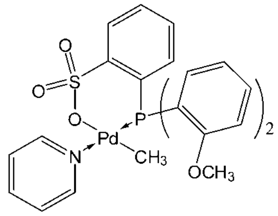
Summary: A (phosphine−sulfonate)palladium(II) system catalyzes the copolymerization of ethene with a variety of styrene derivatives, including those with oxygen functionalities. The copolymerizations also proceed in protic solvents, including water, allowing metal-mediated emulsion copolymerization of ethene and styrene.

The copolymers of ethene with styrene are of great current interest because of their anticipated high viscoelasticity, compatibility with other commodity polymers, and excellent mechanical properties.[1,2] Early transition-metal-based systems are known to catalyze this copolymerization, but these cannot tolerate an oxygen functionality on the styrenic monomer and protic solvents cannot be employed for the reaction.[3,4] Late-transition-metal polymerization systems are known for the polymerization of some monomers with oxygen functionalities.[5,6] However, few[7–9] have been shown to be effective for copolymerization of ethene with styrene; insertion of styrene typically leads to chain termination through β-H elimination. Herein, we describe the first well-defined system for the copolymerization of ethene with a variety of styrene derivatives, including those with oxygen functionalities. Moreover, it is possible to carry out the copolymerizations in protic solvents, including water, allowing for the emulsion copolymerization of ethene and styrene. The same catalyst system can also be employed for the copolymerization of ethene with methyl vinyl ketone, vinylcyclohexane, and other 1-alkenes.

We and others[10–13] have previously reported on the copolymerization of ethene with polar vinyl monomers and norbornene derivatives using the neutral (phosphine−sulfonate)-based system described by Drent and Pugh.[6] Compound **1**[11] was found to catalyze ethene homopolymerization with slightly lower activity compared to the system generated in situ by combining the 2-[bis(2-methoxyphenyl)phosphino]benzenesulfonic acid ($P{\sim}SO_3H$) ligand and bis(dibenzylideneacetone)palladium(0), Pd(DBA)$_2$. However, unlike the system formed in situ, **1** was unreactive toward the copolymerizations of ethene with the polar vinyl monomers studied, presumably because they are too weakly coordinating to displace the coordinated pyridine. The addition of 1 or 2 equiv of the Lewis acid triphenylboron (BPh_3) creates a vacant coordination site on the metal center and allows for easier coordination of the incoming monomer and subsequent insertion into the Pd−CH_3 bond.



Compound **1**

The insertion of styrene into the Pd−CH_3 bond of **1** in dichloromethane-d_2 was followed by in situ NMR spectroscopy. At ambient temperature, **1** readily converts styrene to 1-phenyl-1-propene in the presence of BPh_3, as confirmed by ^{1}H NMR signals at 6.5 ppm (1H, d), 6.3 ppm (1H, m), and 1.9 ppm (3H, d). This is consistent with a 2,1-insertion of styrene into the Pd−CH_3 bond followed by rapid β-H elimination to give a palladium hydride and 1-phenyl-1-propene. Additionally, the conversion of styrene to a second product was shown by ^{1}H NMR signals at 3.2 ppm (1H, q) and 0.7 ppm (3H, dd) along with the replacement of the ^{31}P NMR signal of **1** at 22.7 ppm with a new signal at 11.4 ppm. These observations are consistent with the 2,1-insertion of styrene into the Pd−H bond to give an (η^3-phenylethyl)palladium compound, **2**, as shown in Scheme 1. COSY correlation and ^{1}H NMR splitting in an isolated sample of **2** were used to confirm the structure of the η^3-phenylethyl moiety. The mechanism is supported by the reaction of **1** with styrene-d_8 to produce 1-phenyl-1-propene-d_7 with an unlabeled methyl group and **2**-d_9 with a fully deuterated phenylethyl moiety, as determined by ^{1}H and ^{2}H NMR spectroscopy. The formation of an η^3-phenylethyl species is supported by the absence of pyridine or other ligands in the fourth coordination site of Pd in isolated samples of **2** and the doublet of doublets splitting of the CH_3 group, which is consistent with the complex

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Scheme 1. Conversion of 1 and Styrene to 2 and 1-Phenyl-1-propene through a Palladium Hydride Species

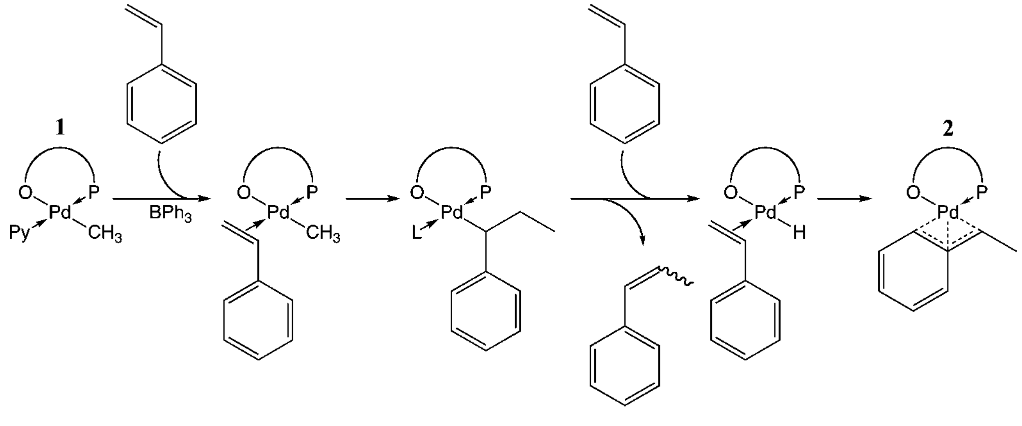
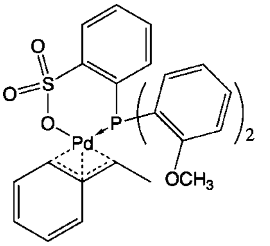


Table 1. Copolymerization using Complex 1 and Triphenylboron[a]

entry	comonomer (amt (g))	ethene pressure (psi)	time (h)	M_w (PDI)[b]	activity (g (mol of Pd)$^{-1}$ h^{-1})	comonomer incorp (mol %)[c]
1	styrene (1)	100	7	7100 (2.3)	9900	4.1
2	styrene (5)	100	7	4700 (1.8)	8260	7.5
3[d]	styrene (5)	100	7	2000 (1.3)[e]	2750	7
4	VCH (1)	100	7	8100 (2.0)	7570	5.2
5	VCH (3)	100	5	3400 (1.4)	9640	11.8
6	propene (3)	100	4	5000 (1.7)	33050	23.4[f]
7	1-hexene (1)	50	15	4000 (3.1)	4850	27[f]
8	1-hexene (2)	50	15	2200 (1.7)[e]	4310	47[f]
9	1-hexene (3)	50	15	1900 (2.0)[e]	5357	53[f]
10	MVK (1)	200	16	15500 (2.4)	1690	4.9
11	MVK (1)	100	16	9600 (2.6)	803	7.7

[a] Conditions: complex **1**, 0.005 g (8.30×10^{-6} mol); BPh_3, 0.004 g (1.66×10^{-5} mol); CH_2Cl_2, 5 mL; 80 °C. [b] By GPC analysis in 1,2-dichlorobenzene at 135 °C using polystyrene standards. [c] By ^1H NMR spectroscopy in 1,1,2,2-tetrachloroethane-d_2 at 110 °C. [d] In the presence of 1 equiv of galvinoxyl. [e] By GPC analysis in THF at 35 °C using polystyrene standards. [f] By ^1H NMR spectroscopy in $CDCl_3$.

splitting observed in the analogous (η^3-crotyl)palladium species previously reported.[10] At ambient temperature, **2** was found to slowly decompose to give styrene and palladium black. Furthermore, addition of 100 psi of ethene to **2**-d_9 in dichloromethane at ambient temperature produced polyethene with a deuterated styrenic end group. The kinetics of styrene insertion into **1** were studied under pseudo-first-order conditions by following the disappearance of the resonance at 22.7 ppm in the ^{31}P NMR spectrum. The reaction is first order in styrene, and the Eyring plot shows a $\Delta H^{\ddagger}$ value of 64.3(6) kJ/mol^{-1} and a $\Delta S^{\ddagger}$ value of −60(20) J/(mol K).



Compound **2**

The results of copolymerization using compound **1** with BPh_3 are summarized in Table 1. Increasing the amount of comonomer in the feed results in its higher incorporation into the copolymer; however, the molecular weight is lowered. The ethene/styrene copolymerization also proceeds in the presence of 1 equiv of the radical trap galvinoxyl, thereby eliminating the role of radicals in the copolymerization. The drop in activity in the presence of the trap can be attributed to the reaction of galvinoxyl with Pd−H species that can attenuate metal-centered nonradical reactions.[14,15]

The solution copolymerizations of ethene with 4-acetoxystyrene, 4-vinylmethylbenzoate, and 4-fluorostyrene were also performed (conditions: complex **1**, 0.005 g (8.30×10^{-6} mol); BPh_3, 0.004 g (1.66×10^{-5} mol); functional styrene, 6.2×10^{-3} mol; ethene, 100 psi; CH_2Cl_2, 10 mL; 80 °C). The catalytic activities for the copolymerizations were 12 800, 16 500, and 16 100 g (mol of Pd)$^{-1}$ h^{-1}, and the comonomer incorporations were 2.8, 6.7, and 4.5 mol %, respectively. The hydrolysis of 4-acetoxystyrene- and 4-vinylmethylbenzoate containing copolymers afforded materials bearing hydroxyl and carboxylic acid functionalities, respectively (see the Supporting Information).

The water contact angles for poly(ethene-*co*-functional styrene) copolymers were measured for thin films coated on glass slides. Poly(ethene-*co*-styrene) containing 4.1 mol % of styrene exhibits an advancing contact angle of 101° and a receding contact angle of 89°. The introduction of 4-acetoxystyrene and 4-vinylmethylbenzoate into the copolymer results in the contact angle dropping to 92° (advancing) and 82° (receding). However, the presence of 4-fluorostyrene results in a slight increase in contact angle with obtained values for poly(ethene-*co*-4-fluorostyrene) of 109° (advancing) and 96° (receding).

The copolymerization of ethene with other vinyl monomers such as vinylcyclohexane (VCH), propene, 1-hexene, and methyl vinyl ketone (MVK) were also performed (Table 1). These

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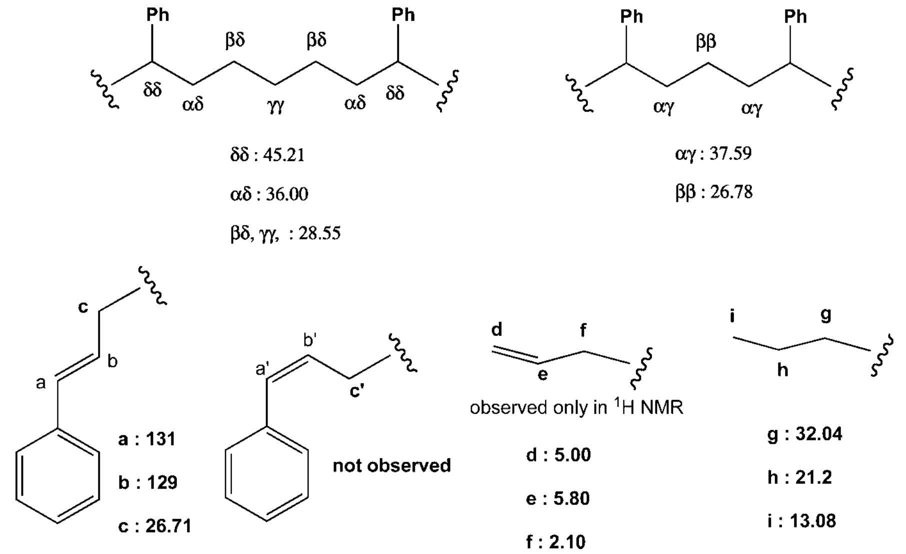

Figure 1. $^{13}C\{^1H\}$ NMR assignment for poly(ethene-*co*-styrene) copolymer in 1,1,2,2-tetrachloroethane-d_2 at 110 °C. The chemical shifts are assigned on the basis of literature values[12,16] and are given in ppm.

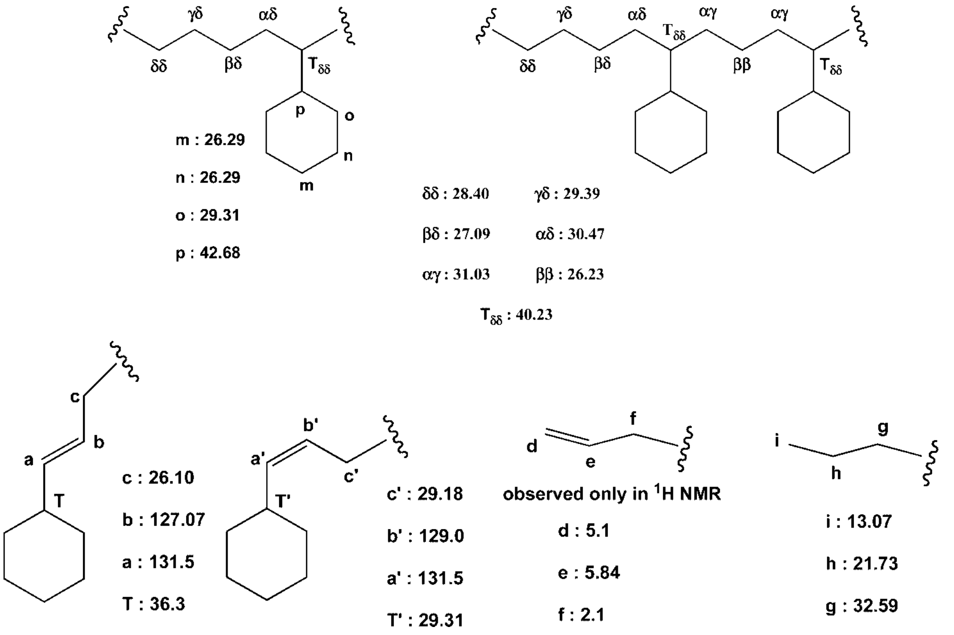

Figure 2. $^{13}C\{^1H\}$ NMR assignment for poly(ethene-*co*-vinylcyclohexane) copolymer in 1,1,2,2-tetrachloroethane-d_2 at 110 °C. The chemical shifts are assigned on the basis of literature values[17] and are given in ppm.

monomers do not readily undergo radical copolymerization. Copolymerization of ethene with 1-hexene results in copolymers with an unusually high incorporation of 1-hexene. Copolymerization with a feed ratio of 3 g of 1-hexene to 50 psi of ethene resulted in material with ~50 mol % of 1-hexene, as determined by ^1H NMR spectroscopy. The structures of all the copolymer materials were confirmed by ^1H and ^{13}C NMR spectroscopy. In the case of poly(ethene-*co*-styrene), the incorporation of the styrene was calculated by comparing the integration of the five aromatic protons of styrene with all the aliphatic protons appearing between 0.9 and 1.9 ppm. The two resonances, a doublet at 6.3 ppm and a multiplet at 6.6 ppm, suggest the presence of $PhCH{=}CHCH_2-$ chain ends formed by styrene insertion and subsequent β-H elimination. The formation of poly(ethene-*co*-styrene) was further confirmed by $^{13}C\{^1H\}$ NMR spectroscopy in 1,1,2,2-tetrachloroethane-d_2 at 110 °C. Both ^1H and ^{13}C NMR analysis revealed the formation of linear copolymers. The ^{13}C resonance at 28.6 ppm suggests the presence of ethene−ethene sequences, whereas resonances at 45, 36, and 28 ppm represent $[-(Ph)CHCH_2CH_2CH_2-]$ carbons (left to right), respectively, and confirm the ethene−styrene linkage.[16] Further, the absence of resonances at 41 and 34−35 ppm demonstrates the absence of a styrene−styrene linkage and also indicates the absence of amorphous polystyrene generated by thermal radical polymerization. The end group analysis performed on low-molecular-weight poly(ethene-*co*-styrene) copolymer (entry 3, Table 1) shows three types of chain ends: styrenic, vinyl, and alkyl (Figure 1). The percentage of the styrenic chain ends is greater than for the other two end groups and is formed by β-H elimination following styrene insertion. The unsaturated carbons next to the aromatic ring show ^{13}C NMR resonances at 129 and 131 ppm and are assigned by high-

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temperature HMQC analysis. The alkyl chain ends are assigned on the basis of literature values.[12] The vinyl chain ends formed by β-H elimination following ethene insertion occur to a much lower extent than the styrenic end groups.

The ^{1}H NMR spectrum of poly(ethene-*co*-vinylcyclohexane) at 110 °C in 1,1,2,2-tetrachloroethane-d_2 shows resonances at 5.1 and 5.5 ppm, suggesting $C_6H_{11}CH{=}CHCH_2-$ chain ends, which were further confirmed by ^{13}C NMR spectroscopy. The incorporation of vinylcyclohexane was determined by comparing cyclic C*H* protons from vinylcyclohexane with all other aliphatic protons. The vinylcyclohexane content values determined by ^{13}C NMR spectroscopy (2 s delay) are close to those calculated by ^{1}H NMR spectroscopy.[17] Furthermore, the ^{13}C NMR resonances observed are in good agreement with literature values and suggest the presence of only isolated vinylcyclohexane units. Similar to the case for poly(ethene-*co*-styrene), poly(ethene-*co*-vinylcyclohexane) also shows unsaturated and alkyl chain ends (Figure 2). The predominant unsaturated end group arises by β-H elimination following vinylcyclohexane insertion, and its percentage increases with an increase in the amount of vinylcyclohexane in the feed (entries 4 and 5, Table 1). The ^{1}H NMR spectra of both poly(ethene-*co*-propene) and poly(ethene-*co*-1-hexene) show vinyl chain ends. The predominant ^{13}C NMR resonances for poly(ethene-*co*-1-hexene) ($\sim$50 mol % 1-hexene) correspond to those reported previously for the alternating copolymer.[18,19]

The copolymerization of ethene with methyl vinyl ketone was also performed (Table 1). The obtained molecular weights and level of methyl vinyl ketone incorporation were similar to those observed for poly(ethene-*co*-styrene).

DSC analysis of poly(ethene-*co*-styrene) (4.3 mol % styrene) showed a T_m value of 106 °C, which is 23 °C lower than for the corresponding linear polyethene. The low T_m value can be attributed to a drop in polyethene crystallinity due to incorporation of styrene units. The T_m values for poly(ethene-*co*-4-acetoxystyrene) and poly(ethene-*co*-4-fluorostyrene) were 114 and 118 °C, respectively. Similarly, the DSC analysis of poly(ethene-*co*-vinylcyclohexane) containing 5.2 mol % of vinylcyclohexane shows a T_m value of 109 °C, whereas the copolymer with 11.8 mol % vinylcyclohexane does not show a T_m value but has a T_g value of -9 °C.

In addition to the copolymerization of ethene with polar styrene derivatives, the unusual functionality tolerance of the catalyst system was demonstrated by performing the aqueous emulsion copolymerization of styrene with ethene. The emulsion copolymerization was performed using 5 g of styrene and 200 psi of ethene (conditions: $P{\sim}SO_3H$ ligand, 0.0065 g (1.61×10^{-5} mol); $Pd(DBA)_2$, 0.0078 g (1.35×10^{-5} mol); galvinoxyl, 0.01 g (2.37×10^{-5} mol); BPh_3, 0.0072 g (2.96×10^{-5} mol); 2,6-di-*tert*-butylpyridine, 0.0056 g (2.96×10^{-5} mol); sodium dodecylbenzenesulfonate, 0.9 g; 30 mL of water and 10 mL of toluene; 90 °C; 4 h), giving 0.3 g of copolymer with 5.8 mol % of styrene incorporation. The high-temperature GPC analysis of the polymer shows a monomodal peak with a M_w value of 2500 and a PDI value of 1.5. Galvinoxyl and 2,6-di-*tert*-butylpyridine were added to suppress radical and cationic polymerizations, respectively, confirming that the obtained copolymer was formed by metal-catalyzed insertion polymerization.

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Supporting Information Available: Text and figures giving experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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