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Direct Synthesis of Ethylene−Acrylic Acid Copolymers by Insertion Polymerization

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Abstract: Neutral palladium(II) phosphinesulfonato polymerization catalysts were found to be stable toward carboxylic acid moieties and to enable direct linear copolymerization of ethylene with acrylic acid.

While insertion polymerizations of ethylene and propylene are employed industrially on a vast scale, the incorporation of polar vinyl comonomers is challenging. This is due to unfavorable interactions of the free monomer or resulting repeat units with the electrophilic active metal sites, and specific deactivation routes.[1,2] Thus, polyethylenes with incorporated polar units are prepared industrially by high-pressure free radical copolymerization. This is energy consuming and requires costly equipment, and the reaction does not allow for microstructure control. Among the commercial products, acrylic acid copolymers and the corresponding ionomers are unique in that the carboxylate moieties provide enhanced adhesion, toughness, and stiffness.[3]

Wagener et al. reported the synthesis of poly(ethylene-*co*-acrylic acid) in a two-step synthesis by acyclic diene metathesis (ADMET) followed by hydrogenation or by ring-opening polymerization (ROMP) of substituted cyclooctene and subsequent hydrogenation.[4] Especially the ADMET approach is elegant, as it results in polymers with the acid moieties periodically placed on the aliphatic backbone. However, the monomers require multistep synthesis, and the carboxylic acid groups apparently must be protected during polymerization in order to prevent poisoning of the metathesis catalyst.

The aforementioned obstacles concerning the compatibility of vinyl monomers with insertion polymerization catalysts can be met with certain d[8] metal catalysts.[5−7] Today, the state of the art encompasses insertion polymerization of ethylene with a broad scope of functional vinyl monomers,[8−13] including even the very difficult monomers acrylonitrile[14] and vinyl acetate.[15]

Insertion polymerization of free carboxylic acids has remained elusive, however, despite the fact that acrylic acid is a large scale industrial product. The functional groups of the aforementioned vinyl comonomers may reversibly block catalytically active sites by coordination but otherwise can be expected to be inert. By contrast, carboxylic acids may promote additional deactivation pathways by protonation reactions. Also, the carboxylates in equilibrium with the free acid can coordinate to metal centers.

Notwithstanding this general scheme, we studied the effect of propionic acid on ethylene polymerization by the known versatile neutral Pd(II) phosphinesulfonato catalysts. Remarkably, polymerization by **1-dmso** occurred even in 1 M propionic acid solution (Table 1). While polyethylene yields decrease with increasing propionic acid concentration (entries 1-1 to 1-4), a substantial activity of several 10³ turnovers per hour is observed even at the

aforementioned acid concentration. A comparison of polymer yields at different reaction times (entries 1-3, 1-5. and 1-6) reveal that the catalyst retains its activity over the 30 min period studied. The slight decrease in activity found is also observed in comparative polymerizations in the absence of propionic acid (entries 1-1, 1-7, and 1-8). Overall, these data indicate a reversible retardation of polymerization, likely by coordination of the carboxylic moieties, but no detrimental catalyst decomposition by carboxylic acid.

Table 1. Polymerization of Ethylene in Presence of Propionic Acid[a]

entry	concn propionic acid [mol L⁻¹]	time [min]	yield [g]	TOF [mol(C₂H₄) mol(Pd)⁻¹ h⁻¹]
1-1	0.0	30	3.01	61.4×10^3
1-2	0.1	30	0.42	8.5×10^3
1-3	0.3	30	0.33	6.7×10^3
1-4	1.0	30	0.24	5.0×10^3
1-5	0.3	10	0.13	8.2×10^3
1-6	0.3	20	0.25	7.6×10^3
1-7	0.0	10	1.55	94.8×10^3
1-8	0.0	20	2.59	79.4×10^3

[a] Reaction conditions: total volume toluene + propionic acid: 50 mL, 3.5 μmol **1-dmso**, 5 bar ethylene pressure, 95 °C reaction temperature.

For stoichiometric studies of the reactivity of acrylic acid toward the catalyst, the chloride-complex **1-Cl** was employed in conjunction with AgBF₄ as a halide abstraction agent. By comparison to **1-dmso**, this route is advantageous for quantitative studies as it delivers the [(P∧O)PdMe] (**1**) fragment without a relevant preequilibrium of dmso dissociation. Exposure of a CD₂Cl₂ solution formed by the reaction of **1-Cl** with AgBF₄ at room temperature to excess acrylic acid (20 equiv) resulted in the formation of the 2,1-insertion product (Supporting Information (SI)). The pseudo-first-order rate constant of $k_{obs}(25\ °C) = 1.4 \times 10^{-3}\ s^{-1}$ is similar to the insertion rate observed for methyl acrylate under identical conditions ($k_{obs}(25\ °C) = 1.2 \times 10^{-3}\ s^{-1}$). By comparison, the acrylic acid insertion product has a stronger tendency for β-hydride elimination, resulting in the formation of crotonic acid with a first-order rate constant of $2.2 \times 10^{-5}\ s^{-1}$ (see SI).

L: optional coordinated acetone

1-Cl   **1-dmso**
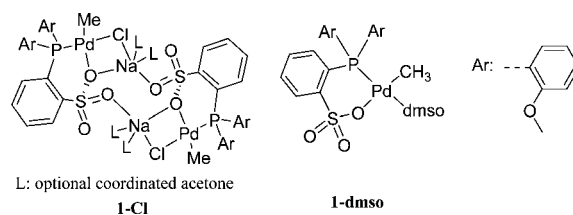
As anticipated from the aforementioned findings, exposure of **1-dmso** to ethylene and acrylic acid under polymerization conditions

Table 2. Copolymerization of Ethylene and Acrylic Acid (AA)[a]

entry	concn AA [M]	1-dmso [μmol]	yield polymer [g]	TOF ethylene[b]	TOF AA[b]	incorp. AA [mol %]	M_n^c [g mol⁻¹]	DP$_n$[c,d]	T_m^e (°C)	χ^e (%)
2-1	0.1	20	1.30	2150	67	3.0	8000	273	112	49
2-2	0.3	20	0.51	770	53	6.4	7400	240	100	43
2-3	0.5	30	0.38	350	38	9.6	6100	189	87	32

[a] Reaction conditions: total volume toluene + acrylic acid: 100 mL, 200 mg of BHT added, 5 bar ethylene pressure, 95 °C reaction temperature, 60 min reaction time, catalyst precursor: **1-dmso**. [b] [mol(monomer consumed) mol(Pd)⁻¹ h⁻¹]. [c] Determined by ¹H NMR spectroscopy. [d] Degree of polymerization. [e] Peak melting point and crystallinity determined by DSC.

results in copolymerization (Table 2). The copolymer nature of the materials obtained was elucidated by ¹H and ¹³C NMR spectroscopy at 130 °C in d_2-tetrachloroethane. Ethylene and acrylic acid based unsaturated end groups result from chain transfer by β-H elimination. For a copolymer with 9.6 mol % incorporated acrylic acid, a ratio of ca. 1:1 was found for acrylic acid and ethylene based end groups. Other than for the aforementioned vinyl acetate and acrylonitrile copolymers, the large majority of acrylic acid derived repeat units is incorporated not in end groups but in the polymer backbone. The methylene units in the α- and β-position give rise to characteristic ¹³C resonances at 32.6 and 27.8 ppm, respectively (Figure 1). The polymers are essentially linear, with ca. 3 methyl branches/1000 carbon atoms.
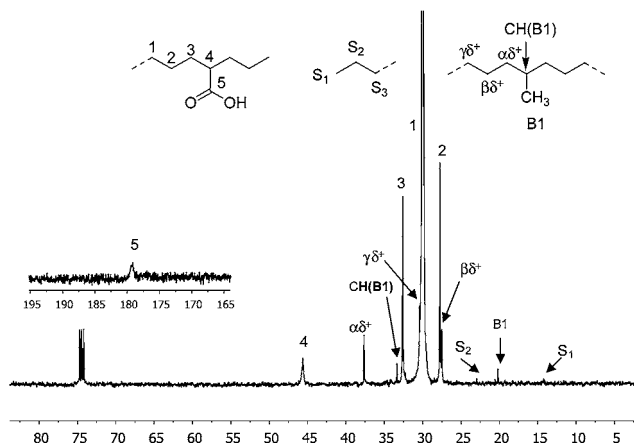

Figure 1. ¹³C NMR spectrum (C₂D₂Cl₄, 130 °C) of copolymer with 3.0 mol % incorporated acrylic acid (4: δ = 45.6; 5: δ = 179.1).

ATR-IR spectra feature a prominent ν(C=O) at 1704 cm⁻¹ (Figure 2). This differs from the ca. 1750 cm⁻¹ expected for free carboxylic acids,[16] as a consequence of hydrogen-bridge cross-links. The distinctive rocking vibration at 720 cm⁻¹ indicates an orthorhombic crystal packing of the polymer.[17] By reaction with NaOH in a toluene/n-butanol solution,[18] the acrylic acid copolymer can be converted to linear ethylene based ionomers, as indicated by ATR-IR spectra which feature the symmetrical and asymmetrical vibration of the carboxylate anion exclusively in the carbonyl region (Figure 2 and SI).[19]

In conclusion, insertion polymerization is possible in the presence of substantial concentrations of free carboxylic acid. Catalytic
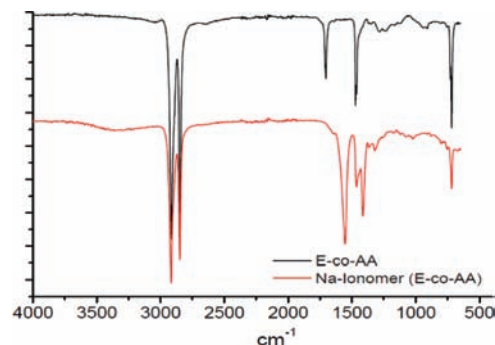

Figure 2. ATR-IR spectra of poly(ethylene-*co*-acrylic acid) (black) and of poly(ethylene-*co*-acrylate) (red), both with 3 mol % incorporation.

copolymerization of ethylene and acrylic acid, both basic industrial monomers, has been demonstrated for the first time. Hereby, carboxylic acid functionalized linear polyethylenes and corresponding ionomers become accessible directly from vinyl monomers.

Supporting Information Available: Experimental procedures and characterization data of compounds; complete ref 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA109194R