Copolymerization

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Direct Synthesis of Functionalized High-Molecular-Weight Polyethylene by Copolymerization of Ethylene with Polar Monomers

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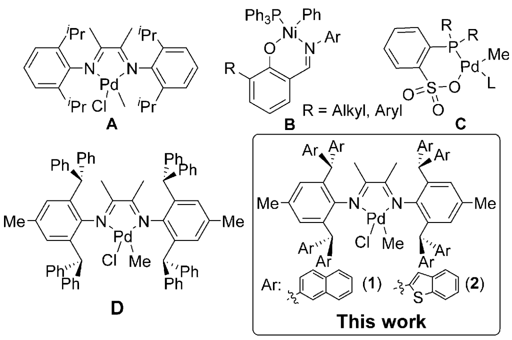
Abstract: *The introduction of even a small amount of polar functional groups into polyolefins could excise great control over important material properties. As the most direct and economic strategy, the transition-metal-catalyzed copolymerization of olefins with polar, functionalized monomers represents one of the biggest challenges in this field. The presence of polar monomers usually dramatically reduces the catalytic activity and copolymer molecular weight (to the level of thousands or even hundreds Da), rendering the copolymerization process and the copolymer materials far from ideal for industrial applications. In this contribution, we demonstrate that these obstacles can be addressed through rational catalyst design. Copolymers with highly linear microstructures, high melting temperatures, and very high molecular weights (close to or above 1 000 000 Da) were generated. The direct synthesis of polar functionalized high-molecular-weight polyethylene was thus achieved.*

Since the Nobel Prize winning discovery made by Ziegler and Natta, transition-metal-catalyzed olefin polymerization has enjoyed great success in both industry and academia. Currently, polyolefin materials constitute almost half of the 300 million tons of the worldwide plastics production.[1] Among the many strategies to modify the properties of polyolefins, the incorporation of functional groups has attracted considerable attention.[2] The introduction of even a small amount of polar functionalities can dramatically improve important properties, such as the surface (e.g., paintability, printability), adhesion, toughness, dyeability, compatibility, and barrier properties, and many others.[2]

Several techniques are available to prepare functionalized polyolefin materials. The post-polymerization functionalization method is widely used because a huge number of non-functionalized polyolefins can be used as starting materials, and no new copolymerization technology is required. However, harsh conditions are usually required owing to the chemical inertness of polyolefins, which could also adversely impact their properties. Ring opening metathesis polymerization (ROMP)[3] and acyclic diene metathesis polycondensation (ADMET)[4] followed by hydrogenation were developed to prepare functionalized linear polyolefins. However, special monomers are required, making these methods not economically viable for large-scale applications. The radical copolymerization of olefins with polar vinyl monomers is widely practiced in industry.[5] However, harsh conditions (high temperatures and pressures) are usually required, affording highly branched copolymers with poor mechanical properties.[5,6] The above-mentioned and some other multistep strategies generally suffer from low cost efficiency, high energy consumption, and, in some cases, poor control over the polymer microstructure. In contrast, transition-metal-mediated catalytic copolymerization holds great potential to overcome these limitations and achieve better control over the polar/nonpolar ratios and the copolymer microstructures.

Despite many years of research, the direct coordination copolymerization of olefins with unprotected polar monomers remains to be a great challenge. This was also recognized as one of the last "holy grails" in this field.[7] The development of novel catalyst systems that can tolerate polar functional groups is the key. A milestone discovery was made by Brookhart and co-workers in the 1990s (Scheme 1, catalyst **A**), who demonstrated the α-diimine–Pd^{II} catalyzed copolymerization of ethylene (E) with methyl acrylate (MA).[8] Subsequently, various functional copolymers with ester and ether functional moieties were prepared.[9] Grubbs and co-workers showed that salicylaldimine–Ni^{II} catalysts can efficiently copolymerize ethylene with polar-substituted norbornene (Scheme 1, catalyst **B**).[10] Recently, Pd^{II} catalysts bearing phosphine-sulfonate ligands or derivatives thereof have emerged as a powerful class of catalysts for olefin–polar monomer copolymerization (Scheme 1, catalysts **C**).[11] Some disadvantages are shared by this limited number of successful



Scheme 1. Representative transition-metal catalysts that can catalyze the copolymerization of olefins with polar monomers.

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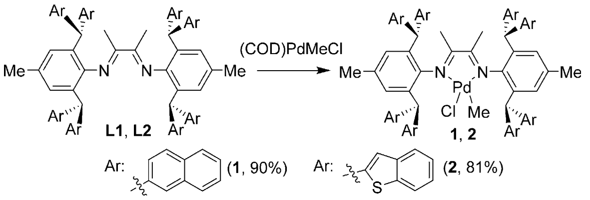
examples, such as greatly reduced activities and copolymer molecular weights.

One of the most distinguishing features of the Brookhart-type α-diimine–Pd$^{\text{II}}$ catalyst (Scheme 1, **A**) is its chain-walking capability, which can migrate the metal center along the polymer chain by β-H elimination and reinsertion with opposite regiochemistry. However, this also represents one of the biggest limitations and a long-standing challenge for this class of catalysts, as highly branched (ca. 100 branches per 1000 C atoms) and totally amorphous polymer and copolymer materials are generated.[9] Recently, we studied the ethylene polymerization and copolymerization properties of a series of α-diimine–Pd$^{\text{II}}$ complexes with dibenzhydryl moieties (Scheme 1, **D**).[12] Very high molecular weight polyethylene (M_n up to 5.4×10^5) and E–MA copolymers (M_n up to 1.9×10^4) could be obtained. Most interestingly, the branching density could be reduced to about 25 per 1000 C atoms, leading to semicrystalline products. Inspired by these promising results, new palladium complexes with further increased ligand steric bulk were designed and prepared by replacing the phenyl groups with naphthalene or benzothiophene units.

The α-diimine ligands **L1** and **L2** were prepared on multigram scale from the reaction of 2,3-butanedione with the corresponding anilines. The palladium complexes **1** and **2** were generated from the reaction of the ligands with (COD)PdMeCl (COD = 1,5-cyclooctadiene; Scheme 2). These palladium complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis. The molecular structure of complex **1** is shown in Figure 1. The Pd center adopts a distorted square-planar geometry, and the effective blockage of the axial positions of the Pd center can be observed from the structure.



Scheme 2. Synthesis of the palladium complexes **1** and **2**.

These palladium complexes are highly active in ethylene polymerization when activated using 1.2 equiv tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF). For both complexes, the catalytic activities reached their maximum at 60 °C in the temperature range of 0 °C to 100 °C (Table 1, entries 1–12). High activities were maintained even at 100 °C whereas the classic Brookhart catalyst **A** (Scheme 1) completely lost its activity at 60 °C. It should be noted that significant loss of catalytic activity was observed after 20–30 min at 80 °C for catalysts **1** and **2** (see the Supporting Information, Figure S3). Further improvements in thermal stability are required for this class of catalysts to become commercially viable.

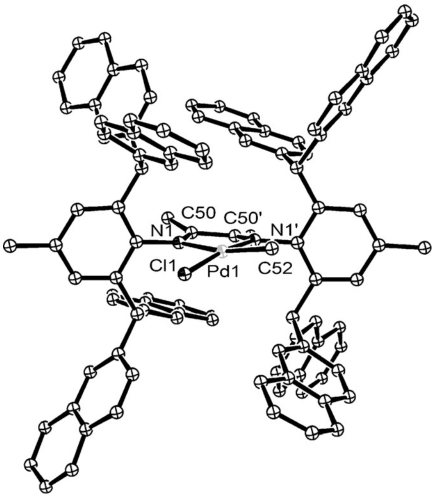


Figure 1. Molecular structure of **1**. Hydrogen atoms omitted for clarity. Ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: Pd1–C52 2.0998(11), Pd1–Cl1 2.192(4), Pd1–N1 2.069(4), Pd1–N1′ 2.069(4); N1-Pd1-N1′ 76.1(3), N1′-Pd1-C52 97.1(3), C52-Pd1-Cl1 86.4-(3), N1-Pd1-Cl1 101.83(18).

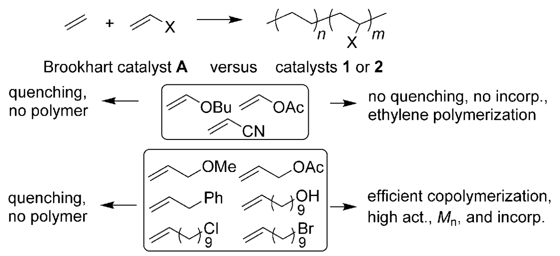
Table 1: Ethylene polymerization with complexes **1** and **2**.[a]

Entry	Cat.	T [°C]	Yield[b] [g]	Act.[b]	M_n[c] [10^4]	PDI	B[d]	T_m[e] [°C]
1	**1**	0	0.38	1.52	3.38	1.07	18	118.2
2	**1**	20	1.63	6.52	16.35	1.06	18	110.1
3	**1**	40	4.23	16.92	53.16	1.09	18	109.2
4	**1**	60	5.56	22.24	51.77	1.05	18	109.5
5	**1**	80	3.64	14.56	33.34	1.25	19	109.4
6	**1**	100	1.45	5.80	8.12	1.49	20	108.5
7	**2**	0	0.44	1.76	11.52	1.36	6	127.2
8	**2**	20	5.12	20.48	78.17	1.21	9	121.1
9	**2**	40	5.50	22.00	90.72	1.26	13	122.5
10	**2**	60	10.24	40.96	42.05	1.23	20	119.0
11	**2**	80	5.98	23.92	32.35	1.23	21	118.3
12	**2**	100	3.20	12.80	12.36	1.53	23	116.5
13[f]	**1**	30	18.24	7.60	393	1.25	18	110.4
14[f]	**2**	30	19.52	8.13	802	1.26	10	120.1

[a] Conditions: precatalyst (10 μmol), NaBAF (1.2 equiv), $CHCl_3$ (5 mL, for **1**) or CH_2Cl_2 (5 mL, for **2**), toluene (45 mL), 8 atm ethylene, 15 min. [b] The yields and activities are averages of at least two runs. Activity (Act.) = 10^5 g mol^{-1} Pd^{-1} h^{-1}. [c] Determined by GPC in trichlorobenzene at 150 °C. [d] B = number of branches per 1000 C atoms, determined by ^{1}H NMR spectroscopy. [e] Determined by differential scanning calorimetry (DSC). [f] Precatalyst (2 μmol), NaBAF (1.2 equiv), $CHCl_3$ (5 mL, for **1**) or CH_2Cl_2 (5 mL, for **2**), toluene (145 mL), 8 atm ethylene, 12 h.

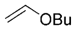
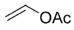
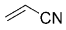
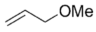
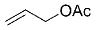
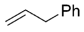
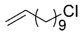
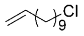
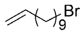
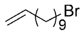
As mentioned above, the classic Brookhart catalyst **A** (Scheme 1) generated highly branched (ca. 100/1000 C), totally amorphous polyethylene. The branching densities of the resulting polyethylene materials were dramatically lower (as low as 6/1000 C) for catalysts **1** and **2**. The ^{13}C NMR spectrum of a polyethylene sample prepared according to Table 1, entry 7 (Figure S21) showed that the polymer is essentially linear, and very similar to commercial polyethylene produced using early-transition-metal catalysts. The branching density of the polyethylene generated by catalyst **1** is independent of the polymerization temperature, and it is similar to that obtained with catalyst **A** and our previously reported catalyst **D** (Scheme 1). Interestingly, the branching density was influenced by the polymerization temperature for catalyst **2**. When the polymerization was carried out for 12 h at 30 °C, polyethylene with an extremely high molecular weight was generated (Table 1, entries 13 and 14; $M_n = 3.9 \times 10^6$ for **1** and $M_n = 8.0 \times 10^6$ for **2**). With catalysts **1** and **2**, high-molecular-weight (M_n up to 4.4×10^5), relatively linear, semicrystalline (T_m close to 120 °C) E–MA copolymers were generated (Table 2, entries 1–4; Table S1).

Brookhart catalyst **A** represents a major breakthrough in the field of coordination copolymerization of ethylene with polar monomers. However, only amorphous copolymers could be generated, and the polar monomer scope is very limited. Many polar monomers (e.g., vinyl halides, vinyl ether, acrylonitrile, vinyl acetate, or styrene) completely shut down the polymerization for various reasons, such as β-halide elimination, formation of stable chelates, or cationic polymerization.[13] When a long spacer is put between the double bond and the polar functional groups (the second group of polar monomers shown in Scheme 3), it becomes easier to incorporate the polar monomers in ethylene polymerization. This strategy has proven to be effective for some early-transition-metal and nickel catalysts.[14] However, this strategy should not work for Brookhart catalyst **A** because of the very fast chain-walking property, which will quickly bring the functional groups close to the metal center.



Scheme 3. Comparison of the ethylene–polar monomer copolymerization properties of classic Brookhart catalyst **A** and catalysts **1** and **2**.

Table 2: Ethylene/polar monomer copolymerization.[a]

Entry	Cat.	Monomer	[M] [mol L^{-1}]	Yield [g][b]	Act.[b]	X_M[c] [%]	M_n[d] [10^4]	PDI[d]	B[e]	T_m[f] [°C]
1[g]	**1**	 COOMe	2.4	1.49	1.24	0.61	44.20	1.68	18	120.0
2[g]	**2**	 COOMe	2.4	3.64	3.03	< 0.1	282	1.57	10	123.8
3[h]	**1**	 COOMe	1.0	0.92	0.77	0.71	5.54	1.89	18	117.0
4[h]	**2**	 COOMe	1.0	0.85	0.71	0.88	7.21	2.35	9	119.0
5	**2**	 OBu	0.5	3.50	35.0	0	15.53	3.04	12	121.3
6	**2**	 OAc	0.5	4.97	49.7	0	61.86	1.89	13	121.5
7	**2**	 CN	0.5	0.38	3.80	0	3.26	2.06	8	125.6
8	**2**	 OMe	0.5	0.22	2.20	0.88	7.54	2.56	16	125.0
9	**2**	 OAc	0.5	2.04	20.4	0.56	39.65	1.76	15	122.6
10	**2**	 Ph	2.0	0.12	1.20	2.04	4.86	2.84	15	124.5
11	**1**	 9 Cl	0.5	0.52	5.20	0.68	9.57	2.62	22	112.9
12	**2**	 9 Cl	0.5	0.99	9.90	0.91	57.14	2.11	19	121.4
13	**1**	 9 Br	0.5	0.59	5.90	0.65	14.10	2.18	22	110.9
14	**2**	 9 Br	0.5	1.10	11.0	0.99	34.18	1.88	13	125.2

[a] Conditions: precatalyst (10 μmol), NaBAF (1.2 equiv), total volume of toluene and polar monomer: 20 mL, 1 h, 8 atm ethylene. [b] The yields and activities are averages of at least two runs. Activity (Act.) = 10^4 g mol^{-1} Pd^{-1} h^{-1}. [c] X_M = Comonomer incorporation (mol %), determined by ^{1}H NMR spectroscopy . [d] Determined by GPC in trichlorobenzene at 150 °C. [e] B = number of branches per 1000 C atoms, determined by ^{1}H NMR spectroscopy. The branches ending with functional groups were added to the total branches. [f] Determined by DSC. [g] $CHCl_3$ (5 mL, for **1**) or CH_2Cl_2 (5 mL, for **2**), total volume of toluene and polar monomer: 95 mL, 8 atm ethylene, 12 h. [h] $CHCl_3$ (5 mL, for **1**) or CH_2Cl_2 (5 mL, for **2**), total volume of toluene and polar monomer: 45 mL, 1 atm, 12 h.

As in previous reports,[13] the first group of polar monomers shown in Scheme 3 (vinyl ether, vinyl acetate, and acrylonitrile) completely shut down the ethylene polymerization process for classic Brookhart catalyst **A**. In contrast, significant polymerization activity was observed for catalyst **2** in the presence of these polar monomers, although no comonomer incorporation was observed (Table 2, entries 5–7). The ligand steric bulk and the high stability of catalyst **2** might be responsible for this phenomenon.

When a spacer was put between the double bond and the polar functional group (the second group of polar monomers shown in Scheme 3), no polymer was generated for classic Brookhart catalyst **A** as expected. In combination with the fast chain-walking feature of catalyst **A**, fast β-halide (for the monomers $CH_2{=}CH(CH_2)_9Cl$ and $CH_2{=}CH(CH_2)_9Br$) or β-OR elimination (for $CH_2{=}CHCH_2OMe$) or the formation of stable π-benzyl intermediates (for $CH_2{=}CHCH_2Ph$) or stable chelate complexes (for $CH_2{=}CHCH_2OAc$) efficiently quenched the catalytic activity.[13] In contrast, high activities (up to 2×10^5 g mol^{-1} h^{-1}), high copolymer molecular weights (M_n up to 5.7×10^5), and good polar monomer incorporation (up to 2.0 %) were observed using catalysts **1** and **2** (Table 2, entries 8–14). The ^{1}H and ^{13}C NMR spectra of these copolymers are shown in the Supporting Information. It should be noted that all of these polar monomers were analytically pure and used without any purification. This also demonstrates the robustness of catalyst **2**.

Clearly, the capability of catalysts **1** and **2** to significantly slow down the chain-walking process enables these copolymerization reactions. This greatly broadens the polar monomer scope for α-diimine–Pd^{II} catalyst systems, leading to the formation of a variety of semicrystalline copolymers. Early-transition-metal catalysts are widely used in industry for the production of semicrystalline polyolefin materials. However, they are easily poisoned by polar functional groups. The classic Brookhart catalyst **A** can copolymerize olefins with some polar monomers, affording amorphous copolymers.[9] The recently described phosphine-sulfonate Pd^{II} catalysts can generate semicrystalline copolymers, while low copolymer molecular weights were usually achieved.[11] Although special polar monomers are required, the current catalyst system holds great potential for future investigations because of its unique properties for the generation of various high-molecular-weight, semicrystalline, polar functionalized polyolefin materials.

Ultrahigh molecular weight polyethylene (UHMWPE) is referred to as a specialty class of polyethylene with M_n values in the range of 10^6–10^7. UHMWPE is of great importance and has wide applications ranging from artificial joints to bullet-proof vests.[15] This material is predominantly prepared using early-transition-metal catalysts, which are easily poisoned by polar monomers.

Very few late-transition-metal catalysts can afford UHMWPE.[16] Owing to the poisoning of such metal centers by polar functional groups, the presence of polar monomers will dramatically reduce the catalytic activity and copolymer molecular weight (to the level of thousands or even hundreds Da). This represents one of the biggest challenges to overcome in this field. With our system, however, very high activities and particularly high copolymer molecular weights (even on the level of millions Da) could be achieved.

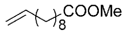
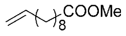
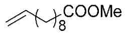
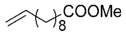
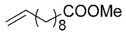
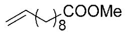
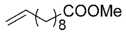
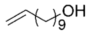
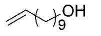
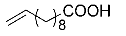
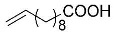
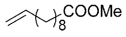
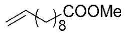
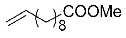
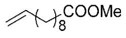
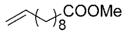
When some specific polar monomers were used, it was possible to achieve the direct synthesis of polar functionalized UHMWPE with this system (Table 3). For entries 1–3, 5, 6, and 8, copolymers with molecular weights close to or above 1000000 Da could be generated. Meanwhile, significant amounts (0.12–1.21 %) of the polar monomers were incorporated. Low branching densities (10–20/1000 C) and high melting temperatures (up to 123.7 °C) were also observed. When the polymerization was carried out at an ethylene pressure of 1 atm, much higher comonomer incorporation (1.41–6.67 %) was realized (Table 3, entries 12–16). This system is highly robust as high activities and molecular weights were still observed even with a carboxylic acid containing polar monomer (Table 3, entries 10 and 11). Because of the livingness of this system, it is also possible to prepare block copolymers with blocks of polyethylene and blocks of polar functionalized polyolefins with molecular weights of > 1000000 Da (Table S2).

As discussed in the introduction, even a small amount of incorporated polar monomer can dramatically alter the copolymer properties. The surface properties of the copolymers were evaluated by determining the water contact angle (WCA) of a copolymer film generated using a solvent process (see the Supporting Information). The WCA for pure polyethylene is 110° (Figure 2, sample from Table 1, entry 2). The WCAs were determined to be 92.3° and 85.7° when the polar monomer incorporation ratio was 0.35 % (Table 3, entry 6) and 2.48 % (Table 3, entry 15). For the acid-functionalized copolymer (Table 3, entry 11), a WCA of 74.1° was measured. The WCAs of these copolymers are even lower than that of polystyrene (92°),[17] which is a paintable polymer.

In conclusion, we have demonstrated that the installation of a naphthalene or benzothiophene substituent in the α-diimine ligand gave palladium catalysts that perform extremely well in ethylene polymerization and copolymerization. In ethylene homopolymerization, these catalysts showed high activity and great thermal stability, generating polyethylene materials with extremely high molecular weights, low branching densities, and high melting temperatures. In ethylene–methyl acrylate copolymerization, high activities and high molecular weights were also achieved.

When a spacer was put between the double bond and the polar functional groups (the second group of polar monomers shown in Scheme 3), classic Brookhart catalyst **A** was completely deactivated owing to its fast chain-walking properties. In contrast, catalysts **1** and **2** enabled the efficient copolymerization of ethylene with these polar monomers with high activity, high copolymer molecular weights, and good comonomer incorporation. In some cases, copolymers with molecular weights close to or even above 1000000 Da were generated. Furthermore, it was demonstrated that the introduction of polar functional groups can dramatically improve the surface properties of these polymeric materials. This is a clear demonstration of the power of ligand design for the control of olefin (co)polymerization processes and polymer properties.

Table 3: Ethylene/polar monomer copolymerization.[a]

Entry	Cat.	Monomer	[M] [mol L^{-1}]	Yield [g][b]	Act.[b]	X_M[c] [%]	M_n[d] [10^4]	PDI[d]	B[e]	T_m[f] [°C]
1	**1**		0.2	10.94	9.12	0.06	242	1.37	22	105.5
2	**1**		0.4	4.32	3.60	0.12	152	1.48	20	105.8
3	**1**		0.6	2.71	2.26	0.21	98.7	1.52	20	105.0
4	**1**		1.2	0.90	0.75	0.32	26.2	1.65	22	105.2
5	**2**		0.6	31.30	26.1	0.12	284	1.21	10	119.2
6	**2**		1.2	17.61	14.7	0.35	105	1.36	11	118.9
7	**2**		2.4	3.97	3.31	0.73	32.9	1.24	11	115.7
8	**2**		1.2	3.20	2.67	1.21	93.3	1.85	14	123.7
9	**2**		2.4	0.88	0.74	2.21	32.3	1.89	14	119.4
10	**2**		1.2	25.10	20.92	1.61	61.9	1.89	12	118.7
11	**2**		2.4	17.36	14.47	1.78	39.6	2.17	15	119.6
12[g]	**1**		0.2	0.07	0.06	3.68	1.6	1.61	25	106.7
13[g]	**1**		0.6	0.03	0.03	6.67	1.1	1.78	38	95.7
14[g]	**2**		0.2	0.44	0.37	1.41	4.4	2.59	15	122.8
15[g]	**2**		0.6	0.16	0.13	2.48	2.1	2.08	16	121.0
16[g]	**2**		1.2	0.06	0.05	4.76	1.7	1.82	24	118.6

[a] Conditions: Precatalyst (10 μmol), NaBAF (1.2 equiv), $CHCl_3$ (5 mL, for **1**) or CH_2Cl_2 (5 mL, for **2**), total volume of toluene and polar monomer: 95 mL, 12 h, 8 atm ethylene. [b] The yields and activities are averages of at least two runs. Activity (Act.) = 10^4 g mol^{-1} Pd^{-1} h^{-1}. [c] X_M = Comonomer incorporation (mol %), determined by ^{1}H NMR spectroscopy. [d] Determined by GPC in trichlorobenzene at 150 °C. [e] B = number of branches per 1000 C atoms, determined by ^{1}H NMR spectroscopy. The branches ending with functional groups were added to the total branches. [f] Determined by DSC. [g] $CHCl_3$ (5 mL, for **1**) or CH_2Cl_2 (5 mL, for **2**), total volume of toluene and polar monomer: 45 mL, 1 atm ethylene, 12 h.

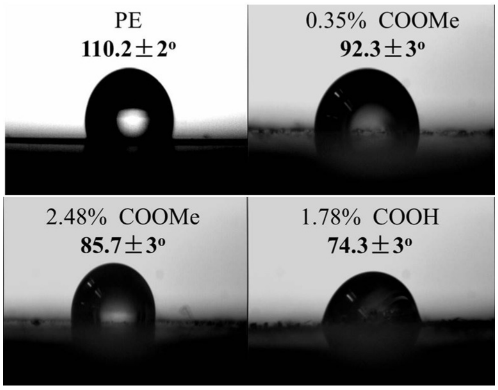


Figure 2. The water contact angles for pure polyethylene and polar functionalized polyethylene.

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