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Linear Polyethylene with Tunable Surface Properties by Catalytic Copolymerization of Ethylene with *N*-Vinyl-2-pyrrolidinone and *N*-Isopropylacrylamide

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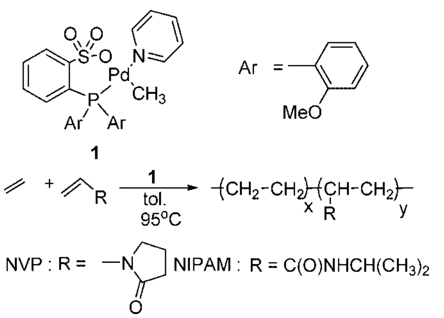
One of the reasons for the ubiquity of high-density polyethylene (PE) is that its physical properties can be drastically altered by careful manipulation of its microstructure and particularly by controlling the length and distribution of alkyl branches along the chain. Instead of alkyl chains, it would be desirable to introduce low amounts of polar groups via postfunctionalization or copolymerization[1] because they are expected to greatly impart the toughness, flexibility, crack resistance, gas permeability, miscibility, adhesion, and paintability of PE. Apart from CO, only a small number of polar monomers such as alkyl acrylates,[2a,b] vinyl ethers,[3] and acrylonitrile[4] have been successfully copolymerized with ethylene (E) by a catalytic process. In a seminal work, Brookhart et al. found that cationic palladium α-diimine complexes can insert a molecule of acrylate predominantly in terminal position of a branched copolymer.[5] In 2002, Drent et al. achieved main-chain acrylate incorporation using Pd-based aryl sulfonated phosphines as in-situ catalysts under mild conditions.[2a] This catalyst[2b,c] has the unique capacity to incorporate polar monomers never copolymerized before, albeit with low incorporations: 5 mol % for vinyl ether,[3] 9 mol % for acrylonitrile (half of it in a terminal position),[4] and less than 1 mol % for vinyl fluoride.[6] The copolymerization of E with a small amount of a truly polar comonomer (i.e., hydrophilic and even water-soluble) would yield novel materials whereby the polar groups would significantly change the surface properties of PE, allowing it to be painted for example.

Copolymers of E with low amounts of polar monomers such as *N*-isopropylacrylamide (NIPAM)[7] and *N*-vinylpyrrolidinone (NVP)[8] can be prepared by free-radical chemistry under high pressure (1300–2400 atm). The resulting copolymers are highly branched, resulting in a drastic loss of crystallinity: polymers containing more than 2–3% NVP are amorphous waxes.[8] Clearly, radical copolymerization of E with these polar monomers does not afford control over the architecture of the polymer. In an elegant work, Wagener et al. have investigated the properties of linear copolymers of E and several polar monomers obtained by either ROMP or ADMET.[9] However, to our knowledge, linear copolymers of E with NIPAM and NVP have never been reported.

We have probed the feasibility of the direct copolymerization of E with NVP or NIPAM using Pd-based well-defined catalyst **1**, which shows activity in copolymerization of E with acrylates,[2,12] norbornene,[10–12] vinyl ethers,[3] and acrylonitrile[4] (Scheme 1). At 95 °C (Table 1) catalyst **1** is able to incorporate NIPAM and NVP, albeit with a decrease of the molecular weight and a significant lowering of the activity. Higher temperature (experiments 6 and 8) generates lower yields due to rapid catalyst decomposition. For all cases, incorporation is low, but exclusively main chain, as demonstrated by ^{1}H NMR and ^{13}C NMR (see Supporting Information). In average, the resulting copolymers contain 1−3 polar groups per chain. These copolymers are essentially linear (∼1 br/1000C by ^{13}C NMR), except when the reaction is carried out at high temperature (115 °C, 5 Me branches/1000C for entry 6). All the polymer chains contain one insaturation, which is consistent with the expected chain transfer mechanism via β-hydride abstraction; however, a high proportion of those are internal, probably due to isomerization by either **1** or a decomposition product of **1**. Indeed, heating **1** in the presence of 250 equiv of octene at 95 °C generates only trace amounts of dimers and trimers and mostly 2-octene and 3-octene. Interestingly, β-hydride abstraction only occurs after an E insertion, and no terminal NVP or NIPAM unit was observed. For acrylate polymerization catalyzed by **1**, β-hydride abstraction can occur after an acrylate insertion, but most acrylates are inserted in the main chain.[2] With Brookhart catalyst, the acrylate ends up in a terminal position via a chain-walking mechanism, unless extreme pressures and an excess of Lewis acid cocatalyst are used.[6]

Scheme 1. Copolymerization Reaction



The introduction of polar units in low amounts along the PE chains results in a lowering of the melting point (T_m, Table 1). The T_m of the linear copolymers containing polar groups obtained by late transition metal catalysis (LTM) varies linearly with the number of polar groups ($r^2 > 0.99$, solid line in Figure 1), irrespectively of the nature of the polar group, as shown by the fact that both the T_m of ethylene−methyl acrylate (E−MA) copolymers prepared with **1**[12] and those of E−NVP polymers are aligned on the same line. This is a legacy of the randomness of these copolymers, which obey a Flory exclusion model whereby T_m is a colligative property (independent of the nature of the branch).[9] Significantly, the T_m of the linear polymers is 10−20 °C above the T_m of the branched ones prepared by free radical polymerization.

The E−NIPAM copolymer exhibits a T_m (111.7 °C) slightly above the predicted value (106.2 °C) for a copolymer with this level of incorporation. This deviation, which maybe is small enough to be considered a statistical fluctuation, may also be explained by the fact that the crystal is reinforced by the presence of H-bonds, as shown by a characteristic N−H stretching band at 3299 cm^{-1}. H-bonds were also found in a 2.1 mol % NIPAM containing PE obtained by radical means.[7]

Thermal properties are consistent with the fact that these copolymers are essentially PE-like: crystalline and with melting points close to 120 °C. However, the presence of a small amount

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Table 1. Copolymerization of Ethylene with NVP and NIPAM in Toluene at 95 °C

expt	monomer	m_{mon}, g/L	catalyst, mg/L	pressure, psi	TON, $\mathrm{mol_{pol}/(mol_{Pd}\ h)}$	mon incorp, mol %	time of reaction, h	T_m, °C	crystallinity,[c] %	M_n,[d] g/mol	contact angle, x/y[b]	mass of polymer, g
1	none	0	25	300	62900	0	2	129.3	72.4	>5000	121.9/118.5	29.3
2	NVP	91	164	350	1930	<0.1	3	128.0	70.5	~5000	109.8/111.7	9.7
3	NVP	213	165	400	1200	0.3	3	127.7	68.1	3770	109.1/108.0	5.2
4	NVP	525	150	300	64	1.2	72	119.8	48.8	3410	105.7/103.5	6.5
5	NVP	924	194	350	27	2.0	50	115.1	43.4	4190	101.3/95.2	2.0
6[a]	NVP	260	75	150	34	2.6	3.5	107.5	35.8	3021	nd	0.081
7	NIPAM	85	150	420	193	3.2	6	111.7	35.0	1230	112.3/107.2	1.6
8[a]	NIPAM	167	100	200	23	4.1	4	nd	nd	1290	109.7/100.9	0.080

[a] $T_{\mathrm{reaction}} = 115$ °C. [b] Before and after vapor treatment. [c] $\Delta H_{100\%\ \mathrm{cryst\ PE\ melt}} = 294$ J/g.[13] [d] Determined by NMR; nd: not determined.

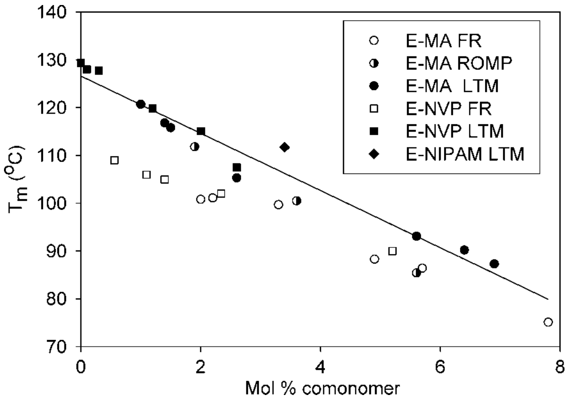

Figure 1. Comparison of linear (LTM, late transition metal catalyzed and ROMP) and branched (FR, free radical) copolymers vs mol % comonomer (LTM E−MA: prepared by our group,[12] LTM E−NVP: Table 1, LTM E−NIPAM: Table 1, E−MA ROMP: prepared in ref 9, E−MA FR: commercial samples,[9] E−NVP FR: prepared in ref 8).

of highly polar functionalities is sufficient to drastically alter their surface properties. Solvent-borne films were prepared by applying a solution of polymer in refluxing chlorobenzene on a glass substrate. Once dried, the water contact angle (CA) of these polymer films was evaluated (Table 1) and found to decrease with monomer incorporation. It is well-established that CA is dependent not only on the PE microstructure but also on the roughness of the surface and therefore on its preparation method.[14] For example, for pure PE, literature CA values vary from 90 to 170°.[15,16] In our case, for pure PE, a CA of 121° was found, which is consistent with the high values of CAs obtained for solvent-cast films. The introduction of a small amount of polar groups is sufficient to reduce the CA by as much as 22°. Aging the films with a hot atmosphere saturated with water provokes the segregation of the most polar groups at the interface polymer−air, resulting in a CAs as low as 95°, which is now close to the CA of water on polystyrene (92°),[17] a paintable polymer. This significant drop in CA is also comparable to the typical reduction of CA generated by corona discharge[18] on a solvent-cleaned PE. This plasma treatment is widely used in industry to improve bondability, wettability, and paintability of PE by the introduction of surface oxygen or nitrogen-containing groups.

To conclude, linear copolymers of E and NVP or NIPAM were prepared and shown to combine the main characteristics of HDPE with a significantly higher surface energy. We envision that such an approach could enable PE to be painted in the future without specific surface treatment. Importantly, the synthesis of catalysts which allow higher comonomer incorporations is currently under scrutiny. These catalysts would permit the preparation of novel amphiphilic copolymers based on E, NVP, and NIPAM and of easily functionalized PE.

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Supporting Information Available: Experimental part of the polymerization reactions and polymer characterization (NMR, DSC, IR data). This material is available free of charge via Internet at http://pubs.acs.org.

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