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New Polyethylene Macroinitiators and Their Subsequent Grafting by Atom Transfer Radical Polymerization

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There has been a long-standing interest in the synthesis of block or graft copolymers containing ethylene and a suitable functional comonomer that can serve as blend compatibilizers between polyolefins and polar commodity plastics.[1] The ultimate goal is a polymer alloy that combines desirable properties of the individual materials.[2] Early transition metal catalysts are highly oxophilic, making it difficult to copolymerize polar monomers without loss in activity.[3] Late transition metal complexes are more tolerant of functional groups but typically produce branched materials that therefore have low moduli.[4,5] At present, commercial production of functionalized polyolefins is dominated by high-pressure, high-temperature radical processes that offer little control over the polymer architecture.[6]

Efforts in response to these challenges have appeared in the literature.[7] In one example, a metallocene catalyst was used to copolymerize ethylene and 10-undecen-1-ol, protected with tri-ethylaluminum, producing a material with an M_n (number average molecular weight) of 36K and a PDI (polydispersity index) of 3.[8] The alcohol groups were converted into ATRP (atom transfer radical polymerization) initiators, and in a second step, acrylates and methacrylates were polymerized from the polyethylene (PE) backbone. A more recent report demonstrated that a Pd diimine catalyst can incorporate an ATRP initiator directly by chain walking ethylene polymerization, yielding functionalized PE.[9] However, because the resulting material is hyperbranched, it is anticipated to be a poor compatibilizer for linear PE.[10]

Previously, we reported the quasi-living copolymerization of ethylene and functionalized norbornenes using nickel α-iminocar-baxamidato complexes.[11] In this communication, we demonstrate how this catalytic system can be utilized to directly copolymerize ethylene and an ATRP initiator to produce a PE macroinitiator, with excellent control over polymer architecture, via the sequence of steps in Scheme 1. As shown in the first step, [N-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)isobutanamidato]-Ni(η^1-CH$_2$Ph)(PMe$_3$) (**1**) and Ni(COD)$_2$ (bis(1,5-cyclooctadiene)-nickel) (**2**), as the coactivator, are used to copolymerize ethylene with 5-norbornen-2-yl-2′-bromo-2′-methyl propanoate (**3**). The isobutyl variant was chosen because increased bulk adjacent to the imine leads to faster initiation and weaker interactions with polar groups.[12] Compound **3**, which provides the functionality for initiating the ATRP reactions in the second step of Scheme 1, is easily prepared from 5-norbornen-2-ol and bromoisobutyryl bro-mide. Initial efforts showed that, while **1** is inert, **2** immediately yields a metallic precipitate in the presence of **3**. A modified procedure was thus developed, where the **1/2** mixture is exposed to ethylene for a time t_1, after which **3** is added via a prepressurized addition funnel, and the polymerization is allowed to proceed for another period of time, t_2.

A series of polymerization reactions were performed to test the strategy in Scheme 1, at an ethylene pressure ($P_{C_2H_4}$) of 100 psi and 20 °C, using a solution of **1** and **2** (0.24 and 0.6 mM, respectively) in toluene, followed by the addition of **3** (0.06 M) at t_1. The M_n increases linearly with t_2 (from 2 to 22 min) when t_1 is kept constant at 3 min. This dependence, illustrated by the plot in Figure 1, confirms that the polymerization takes place in a controlled manner. Table 1 provides additional information about reaction

Scheme 1. Synthesis of PE Macroinitiator and Its Grafting by ATRP[a]
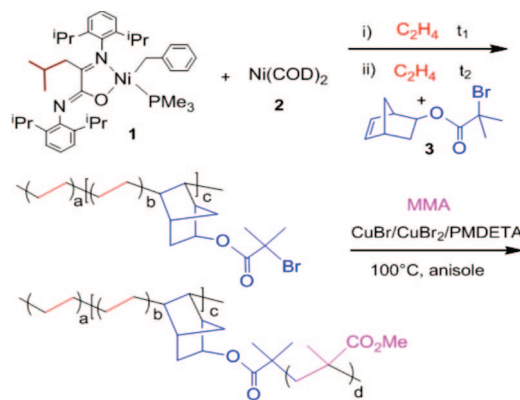
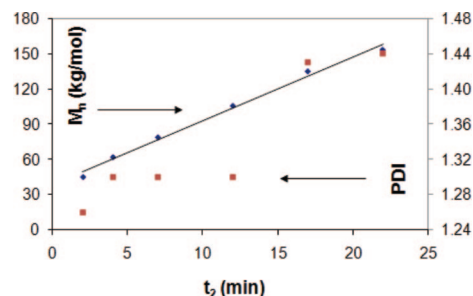[a] PMDETA is *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.

Figure 1. Plot of PE macroinitiator M_n and PDI vs time (t_1 = 3 min).

conditions, along with compositional analysis of the products. As shown in entry 1, when t_2 is 2 min, a polymer with an M_n of 45K and a PDI of 1.3 is produced. This material has a melting point (T_m) of 126 °C, a degree of crystallinity (X_c) of 43%, and ~14 units of **3** per chain (0.9 mol %), as determined by ^{1}H NMR spectroscopy (Supporting Information). Entries 1−3 reveal that there is little variation in the mol % of **3** as a function of t_2. Increasing the reaction temperature from 20 to 29 °C nearly doubles M_n and increases the overall activity 3-fold (entry 1 vs 4). Decreasing the temperature to 16 °C yields a polymer with an M_n of 30K and a substantial decrease in activity. Comparison of entries 1 and 6−8 demonstrates the influence of $P_{C_2H_4}$ on the incorporation of **3**. At $P_{C_2H_4}$ = 400 psi, the inimer content is below the detection limit of ^{1}H NMR spectroscopy, and the T_m is the highest (132 °C). Changing $P_{C_2H_4}$ from 100 to 200 psi yields a decrease in incorporation from 0.9% to 0.4%. At 50 psi (entry 8), the activity decreases by 50% (relative to entry 1) and the **3** content increases to 2.2%. The structure of the final product can also be tailored by changing the concentration of **3** added at t_1, as illustrated by entries 9 and 10. When [**3**] is doubled, the average number of initiators per chain increases from 14 to 27; similarly, when [**3**] is halved, there are

**Table 1.** Polymerization Conditions and Resulting Macroinitiators

entry	t_1	t_2	[3]	T^a	P^b	A^c	mol % 3^d	$M_n{}^e$	$T_m{}^f$
1	3	2	0.06	20	100	360	0.9	45	126
2	3	4	0.06	20	100	370	1.1	62	125
3	3	22	0.06	20	100	330	0.9	154	128
4	3	2	0.06	29	100	960	0.9	80	125
5	3	2	0.06	16	100	200	1.2	30	126
6	3	2	0.06	20	400	390	<0.01	48	132
7	3	2	0.06	20	200	350	0.4	46	127
8	3	2	0.06	20	50	180	2.2	45	123
9	3	2	0.12	20	100	300	1.7	43	125
10	3	2	0.03	20	100	360	0.4	46	127
11	1	4	0.06	20	100	220	2.8	42	115

^{a} Temperature (°C). ^{b} Pressure (psi). ^{c} Activity (kg/mol·h). ^{d} % inimer determined by ^{1}H NMR spectroscopy. ^{e} M_n (kg/mol) determined by GPC. ^{f} Melting point (°C) determined by DSC. All PDIs are between 1.2 and 1.4.

Table 2. Optimization of Grafting Conditions

entry	equiv MMA	volume (mL)	time (h)	M_n	PDI	mol % PMMA^a	$T_m{}^b$	$X_c{}^b$
1	200	5	1	58	1.3	26	126	16
2	200	5	3	62	1.3	40	126	12
3	400	5	3	75	1.7	60	126	7
4	100	5	3	54	1.2	2	127	25
5	200	6	3	58	1.3	25	127	14
6	200	3	3	-	-	-	-	-

^{a} Determined by ^{1}H NMR spectroscopy; ^{b} Melting point (°C) and degree of crystallinity (X_c) determined by DSC. ATRP performed at 100 °C on 50 mg of macroinitiator: [3]/[MMA]/[Cu^{I}Br][Cu^{II}Br$_2$][PMDETA] = 1:200:1:0.05:2.
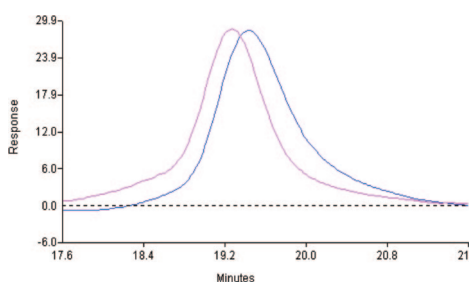
Figure 2. GPC traces of PE macroinitiator (entry 1, Table 1) and PE-*graft*-PMMA (entry 1, Table 2) in *o*-dichlorobenzene at 135 °C.

only 6 initiators per chain. Finally, when t_1 is reduced to 1 min, and the total polymerization time is the same as that in entry 1 (5 min), the inimer content increases from 0.9% to 2.8%. This material has the lowest T_m (115 °C) and X_c (17%). Note that despite variations in pressure, temperature, and [3], one obtains products with low PDIs (between 1.2 and 1.4); this is a remarkable feature considering that **2** is unstable toward **3**.

A series of ATRP reactions were performed as shown in the second step of Scheme 1 by using literature methodologies.[8,13] Typically, 50 mg of macroinitiator (from entry 1, Table 1) were treated with methyl methacrylate (MMA) and a solution of a copper salt in anisole at 100 °C, such that the ratio of reactants was [3]/[MMA]/[Cu^{I}Br]/[Cu^{II}Br$_2$]/[PMDETA] = 1:200:1:0.05:2. The results are summarized in Table 2. After an hour of reaction, M_n increases from 45K to 58K, as illustrated in Figure 2. While the T_m of this material is 126 °C, similar to the starting macroinitiator, the X_c decreases from 43% to 16%. Comparison of entries 1 and 2 reveals that products have low PDIs and increased PMMA content at longer reaction times, indicating a good degree of control over the grafting process. There is also a decrease in X_c, from 16% to 12%, while the T_m remains constant. Although the change in M_n

between 1 and 3 h is small, this has been previously observed in other PE-*graft*-PMMA systems[8] and can be attributed to a propensity to form micellar structures in solution, which alters the hydrodynamic volume and yields inaccurate molecular weight measurements. PMMA side chains were hydrolyzed using sodium methoxide in methanol.[8] GPC analysis confirms that the M_n of the detached chains increases from 8600 (entry 1) to 13,800 (entry 2), while the PDIs remain at ∼1.2.

When [MMA] is doubled, the PMMA content increases from 40% to 60% and the M_n rises to 70K (entry 3), although at the cost of an increase in PDI. Similarly, when [MMA] is halved, the reaction yields only 2 mol % of PMMA after 3 h (entry 4). Comparison of entry 2 to entries 5 and 6 reveals the importance of maintaining a proper volume such that the macroinititator remains in solution and unwanted side reactions do not occur. When the total volume is increased from 5 to 6 mL, the PMMA content shifts from 40% to 25%. However, when the volume is reduced to 3 mL, an insoluble gel is obtained. Successful grafting experiments were also performed using HMTETA in place of PMDETA (Supporting Information).

In conclusion, the method in Scheme 1 provides access to PE-*graft*-PMMA with excellent control over the structural properties of the macroinitiator and the resulting graft copolymers. A key element is the initiation in the absence of **3**, which decomposes Ni(COD)$_2$. Once the active species is generated, the copolymerization of ethylene and **3** proceeds in a controlled fashion. Furthermore, it is noteworthy that the final graft material is semicrystalline, which argues favorably for its use as a blend compatibilizer for linear PE.

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

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