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Binuclear Initiators for the Telechelic Synthesis of Elastomeric Polyolefins

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Abstract: Novel binuclear complexes, 4,4′-bis{[*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-propanamidato-κ^2-*N*,*O*-(trimethylphosphine)nickel(II)]methyl}-1,1′-biphenyl (**2a**) and 4,4′-bis{[*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-4-methylpentamidato-κ^2-*N*,*O*-(trimethylphosphine)nickel(II)]methyl}-1,1′-biphenyl (**2b**), were synthesized by linking two nickel centers through a bis(benzyl) fragment. When activated with nickel bis(1,5-cyclooctadiene) ($Ni(COD)_2$), **2a** and **2b** are capable of polymerizing ethylene in a quasi-living fashion, producing polymers with approximately twice the molecular weights relative to those obtained by using a structurally related mononuclear system. In addition, **2b/**$Ni(COD)_2$ was utilized to synthesize a series of pseudo-triblock polyethylene (PE) macroinitiating copolymers, bearing atom-transfer radical polymerization (ATRP) initiators. Pseudo-pentablock copolymers were also prepared by taking advantage of a pressure-pulsing technique, wherein the ethylene pressure was increased from 100 to 500 psi in order to produce semicrystalline ethylene-rich end-blocks. Copolymers with elastomeric properties were synthesized by grafting *n*-butyl acrylate from the PE macroinitiators via ATRP. Examination using monotonic and step-cyclic stress−strain tests demonstrates that the materials exhibit large strains at break (1600−2000%) and excellent elastic recoveries at large strains (~80%). That materials with such desirable properties could not be attained using a mononuclear initiator demonstrates the clear advantage of growing the polymer via a telechelic mechanism.

Introduction

Metal-mediated olefin polymerizations have attracted a great deal of academic and industrial interest because they allow large-scale syntheses of commodity materials.[1,2] If the reaction conditions give rise to a living polymerization, the products have more predictable molecular weights and narrower polydispersity indices (PDIs).[3] In addition, higher-order architectures such as block, graft, and end-functionalized materials can be prepared by using this methodology.[4] While several catalysts are capable of polymerizing olefins in a living manner, few can *copolymerize* olefins and polar comonomers with the same degree of control.[5] This difference is largely attributed to the oxophilicity of traditional olefin polymerization catalysts, which are composed of early transition metals that may be readily poisoned by functional groups. Less electrophilic metals, like Ni and Pd, must be used to prepare functionalized polyolefin copolymers. Brookhart's cationic Ni and Pd diimine catalysts, Grubbs's Ni salicylaldimine catalysts, and more recently Pd phosphine sulfonate systems have been successful in producing random copolymers of ethylene and functionalized comonomers.[6−8]

In this regard, α-iminocarboxamidato nickel precatalysts **1a**,**b**, shown in Figure 1a, offer unique opportunities to generate materials with tailored, higher-order architectures.[9−11] When these initiators are activated with bis(1,5-cyclooctadiene)nickel ($Ni(COD)_2$), they can be used to generate a variety of materials, ranging from random copolymers of ethylene and norbornene acetate[10] to more complex tapered diblock and tetrablock structures.[11,12] More recently, a methodology has been developed for preparing polyolefins grafted with polar chains by copolymerizing an initiating monomer, or *inimer*, that is capable

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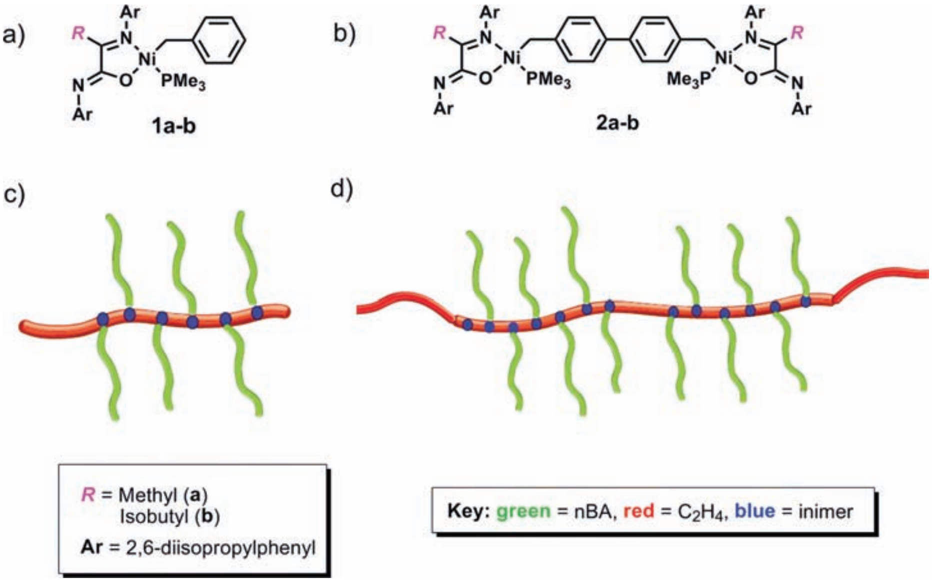

Figure 1. Structures of **1a**,**b** (a) and **2a**,**b** (b), and cartoon representations of graft copolymers prepared using initiators **1b** (c) and **2b** (d).

of undergoing atom transfer radical polymerization (ATRP).[13,14] Commodity monomers such as methyl methacrylate, *n*-butyl acrylate (nBA), and *tert*-butyl acrylate have been grafted from the resulting macroinitiators using ATRP. A cartoon representation of these structures is shown in Figure 1c.

One area of polymer science that takes advantage of precisely engineered materials is the field of thermoplastic elastomers (TPEs). For example, while polyolefin elastomers show superior mechanical properties relative to conventional rubber materials,[15−20] they are nonpolar and, as such, suffer from poor adhesion and low compatibility with polar plastics. Further, their tendency to absorb significant quantities of oil is problematic because it has been associated with reduced mechanical performance.[21] On the other hand, TPEs prepared from acrylic monomers have enhanced compatibility and oil resistance in comparison to polyolefin elastomers but suffer from low elongation at break.[22,23] In a recent report, we demonstrated how these two problems can be addressed by covalently linking polyacrylates and polyolefins in the form of a graft copolymer (see Figure 1c).[4,14] This class of materials was prepared by grafting nBA from polyethylene (PE) macroinitiators with varying inimer content, prepared using **1b**/Ni(COD)$_2$. Graft copolymers generated from macroinitiators with the highest inimer content exhibited the greatest elongation at break and elastic recoveries. However, these grafts also suffered from insufficient crystallinity, which resulted in nonuniform deformation behavior.

It seemed reasonable that a superior elastomer could be prepared by placing the amorphous inimer-rich segment in the center of the molecule, similar to conventional TPEs (as shown in Figure 1d). In addition, crystallinity could be increased by using a pressure-pulsing technique, wherein inimer incorporation at the chain ends is drastically reduced by rapidly increasing the ethylene pressure. Achieving this target structure requires that both chain ends are capable of incorporating additional monomer after the inimer copolymerization has taken place. Such a requirement is nicely addressed with a telechelic initiator, in which two chain ends propagate independently.

Despite being widely reported for other living methodologies such as anionic[24] and free-radical,[25,26] “inside-out” or telechelic polymerization of olefins by binuclear organometallic catalysts remains a relatively unexplored synthetic strategy.[4,27,28] The majority of bimetallic olefin polymerization catalysts[29−36] feature a multidentate ligand capable of coordinating two metal

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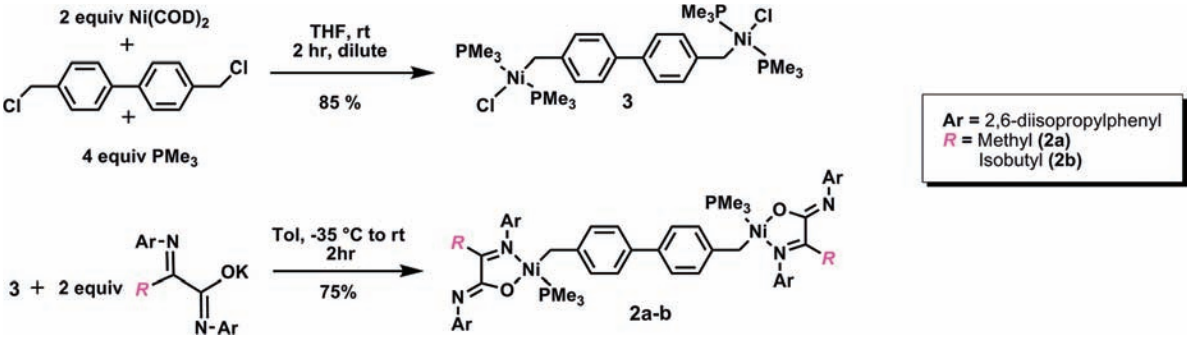
Scheme 1. Synthesis of Binuclear Complexes **2a**,**b**



centers, where the proximity of the metals results in cooperative behavior. In contrast, we designed the binuclear complexes **2a**,**b** shown in Figure 1b, such that the two initiating sites are *covalently* linked through a bis(benzyl) fragment. Unlike previously reported bimetallic olefin polymerization initiators, the metal centers in **2a**,**b** propagate away from each other as the polymer grows.

Here, we disclose the synthesis and characterization of **2a**,**b**. We show that **2a**, in the presence of Ni(COD)$_2$, can prepare PE in a quasi-living fashion, as indicated by a linear dependence of the number-average molecular weight (M_n) and narrow polydispersity indices (PDIs). The molecular weights of the products obtained are approximately double those achieved with the mononuclear analogue **1a**, indicating that the two propagating sites behave independently of each other. Subsequently, we use **2b** to prepare triblock and pentablock PE copolymers with grafted nBA chains that show a significant improvement in elastomeric performance relative to the materials prepared using mononuclear initiator **1b** (Figure 1c vs 1d).

Results and Discussion

Synthesis and Characterization of 2a,b. Complexes **2a**,**b** were prepared according to the series of steps shown in Scheme 1. In THF at room temperature, 2 equiv of Ni(COD)$_2$ undergoes oxidative addition with 1 equiv of 4,4′-bis(chloromethyl)biphenyl in the presence of 4 equiv of trimethylphosphine to yield 4,4′-bis{[*trans*-bis(trimethylphosphine)chloronickel]methyl}-1,1′-biphenyl (**3**) in 85% yield. This compound must be prepared under dilute conditions, as more concentrated conditions lead to undesirable side reactions. Compound **3** was subsequently reacted with 2 equiv of potassium [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidate (**a**) or potassium [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-4-methylpentanamidate (**b**) at −35 °C in toluene, leading to **2a** (79%) or **2b** (73%), respectively. After recrystallization from toluene, compounds **2a** and **2b** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. The NMR spectra of **2a**,**b** complexes are similar to those of the corresponding mononuclear **1a**,**b** analogues.[2] Single crystals of **2a** suitable for X-ray diffraction studies were obtained by vapor diffusion of pentane into a concentrated toluene solution. The ORTEP depiction of the resulting molecular structure is shown in Figure 2. Metrical parameters show that the ligand is bound in the desired *N*,*O*-coordination mode, as opposed to the thermodynamically favored and polymerization-inactive *N*,*N*-coordination mode.[37] Bond lengths and angles for **2a** are similar to those observed for **1a**.[38] Additional details are provided in the Supporting Information (Table S1). These data demonstrate that the desired binuclear connectivity can be achieved without significant perturbations in the coordination sphere of the nickel center.

Ethylene Homopolymerization. As shown in Scheme 2, a series of ethylene (C$_2$H$_4$) homopolymerizations was performed to confirm that the nickel centers in the **2a**,**b** system behave as independent polymerization sites and that the polymer propagation proceeds in a telechelic fashion. Under these conditions, the PE prepared from a binuclear system should exhibit twice the M_n value as that from an analogous mononuclear system. Polymerizations of C$_2$H$_4$ with **2a**/Ni(COD)$_2$ were carried out under conditions similar to those used for **1a**/Ni(COD)$_2$, which has been investigated previously.[9,39] In a typical reaction, 5 μmol of **2a** was combined with 25 μmol of Ni(COD)$_2$ in 30 mL of toluene in a steel autoclave reactor. The vessel was pressurized with 100 psi of C$_2$H$_4$ to initiate the reaction, and the polymerization was terminated by quenching with acetone. The results from this study are summarized in Table 1, together with previously reported data for **1a**.[39]

Entries 3−6 show that the M_n of the PE prepared by **2a** increases linearly with time, as determined by gel permeation

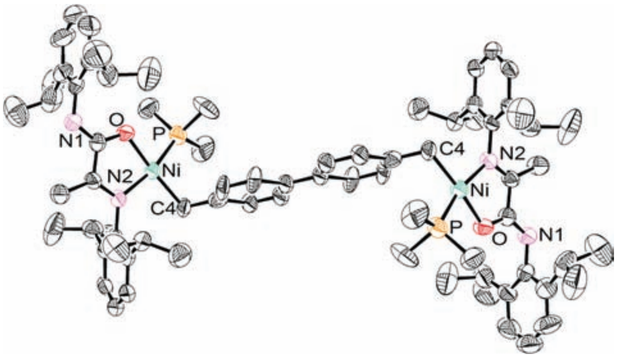
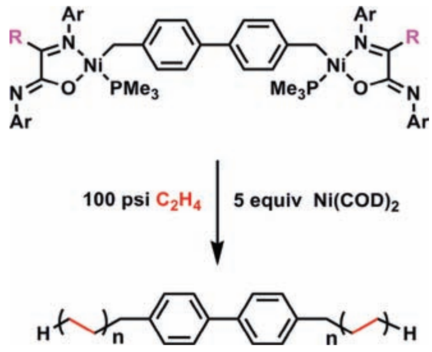


Figure 2. Molecular structure of complex **2a** with thermal ellipsoids set at 50% probability. Hydrogen atoms and cocrystallized pentane are omitted for clarity.

Scheme 2. Ethylene Homopolymerization Using **2a**,**b**[a]



[a] Ar = 2,6-diisopropylphenyl and R = methyl or isobutyl.

Table 1. Summary of Ethylene Polymerizations[a]

entry	precatalyst	time (min)	activity (kg/mol · h)	M_n (kg/mol)	PDI
1	**1a**	5	153	23	1.4
2	**1a**	10	180	44	1.4
3	**2a**	2.5	96	17	1.4
4	**2a**	5	146	40	1.4
5	**2a**	10	180	80	1.4
6	**2a**	12.5	175	92	1.5
7	**1b**	44	310	230	1.4
8	**2b**	22	350	240	1.5

[a] Polymerization conditions: 20 °C, 100 psi, 10 μmol of **1a** or 5 μmol of **2a** and 25 μmol of Ni(COD)$_2$; 5 μmol of **1b** or 2.5 μmol of **2b** and 12.5 μmol of Ni(COD)$_2$.

chromatography (GPC) at 150 °C in 1,2,4-trichlorobenzene. Comparison of entries 1 and 4 with entries 2 and 5 reveals that the M_n of the products obtained with **2a** is indeed nearly double that of **1a**. Entry 6 demonstrates that the M_n growth departs from linearity after 10 min, which is also observed with **1a**/Ni(COD)$_2$[10] and is presumed to be a result of product precipitation. In addition to PE, copolymers of C_2H_4 and 5-norbornen-2-yl acetate were prepared using **2a**/Ni(COD)$_2$, and the evolution of M_n over time is shown in the Supporting Information (Figure S2). Although the molecular weights of these copolymers are less than double those observed using **1a**, the products have narrow polydispersities and molecular weights that increase linearly with time, indicating a significant degree of control over the copolymerization process.

The reactivities of **1b** and **2b** were also examined in the presence of C_2H_4, and the results are shown in entries 7 and 8 in Table 1. As demonstrated with **2a**, binuclear complex **2b** produces a polymer with the same molecular weight as mononuclear **1b**, in half the time. It should also be noted that initiators with an isobutyl backbone (**1b**) have been previously shown to be more reactive than those with a methyl backbone (**1a**).[39] Our results are consistent with these observations, which show a nearly 2-fold increase in activity with the isobutyl analogue **2b**. Further, the isobutyl variant is more tolerant of functionalized norbornenes and can thus produce PE macroinitiators with higher molecular weights and narrower PDIs in comparison to the methyl counterpart. We therefore utilized **1b** and **2b** in the synthesis of PE macroinitiators discussed in the next section.

Synthesis and Characterization of Triblock and Pentablock PE Macroinitiators. A series of PE macroinitiators was prepared by copolymerizing C_2H_4 with 5-norbornen-2-yl 2-bromo-2-methylpropanoate (**4**), as shown in Scheme 3. Compound **4** is capable of initiating ATRP and will be referred to as an inimer henceforth. A steel autoclave reactor was charged with 2.5 μmol of **2b** or 5 μmol of **1b** and 12.5 μmol of Ni(COD)$_2$ in 30 mL of toluene. Because Ni(COD)$_2$ decomposes in the presence of **4**, it is necessary to initiate the polymerization by growing a short PE block (approximately 12 kg/mol for $t_1 = 1$ min) prior to introducing **4** into the reaction mixture; this technique has been shown to produce PE macroinitiators in a quasi-living fashion.[13] The copolymers are named according to the complex used in their synthesis (**MN** is **1b** and **BN** is **2b**) and also the length of reaction time of each block, as measured in minutes. For example, **MN 1-15** denotes a copolymer prepared from **1b** that has $t_1 = 1$ min and $t_2 = 15$ min. Additionally, pseudo "pentablock" structures were produced by increasing the polymerization pressure from 100 to 500 psi at the completion of t_2 and allowing the polymer to grow until t_3. The physical properties of the PE macroinitiators are summarized in Table 2, with the ^{1}H NMR spectra and DSC thermograms provided in the Supporting Information (Figures S3−S8).

When **1b**/Ni(COD)$_2$ is exposed to a 0.6 M concentration of **4** at t_2, in the presence of 100 psi of C_2H_4, a diblock copolymer with $M_n = 62$ kg/mol and an inimer content of 15 mol % is produced (**MN 1-15**). The molecular weight, PDI, and thermal properties of **MN 1-15** are similar to those of a 16 mol % copolymer prepared previously.[14] When **2b** is employed under identical conditions, a triblock macroinitiator with $M_n = 97$ kg/mol and an inimer content of 14 mol % is generated (**BN 1-15**). While the molecular weight of the macroinitiator obtained from **2b**/Ni(COD)$_2$ is not quite double the M_n achieved using **1b**/Ni(COD)$_2$, the thermal characteristics of the products are comparable (see Table 2). To confirm the proposed structure of **BN 1-15**, and also to demonstrate that it is fundamentally different from any structure that can be prepared using the **1b** system, we synthesized a higher M_n diblock macroinitiator. Specifically, by shifting t_2 from 15 to 30 min, we achieved an increase in M_n from 62 to 88 kg/mol. Comparison of **MN 1-30** and **BN 1-15** will enable us to elucidate key structural differences between macroinitiators prepared from **1b** vs **2b**.

A different macroinitiator structure was prepared by using the pressure-pulsing technique, as shown in Scheme 3.[10] GPC traces of the triblock and pentablocks are provided in Figure 3. As t_3 is increased from 0 to 6 min, the M_n increases in a predictable manner, while the PDIs remain relatively low (PDI ≤ 1.5). With the addition of a PE block produced at an increased C_2H_4 pressure ($t_3 = 2$ min) to the triblock **BN 1-15**, the resulting pentablock **BN 1-15-2** exhibits a decrease in T_g from 35 to 32 °C and an increase in crystallinity from 0.1 to 0.3%. This trend is expected for a material with ethylene-rich segments incorporated at the chain ends. When t_3 is increased to 6 min, macroinitiator **BN 1-15-6** exhibits an X_c of nearly 1%, which represents a 9-fold increase in the crystalline content compared to **BN 1-15**. These results indicate that the pressure-pulsing technique can be used to effectively modify the physical properties of PE macroinitiators. Furthermore, the structure of the products prepared by this method is akin to an ABABA pentablock copolymer where the A-blocks are PE-rich segments and the B-blocks are a random copolymer of C_2H_4 and **4**.

Synthesis and Characterization of Graft Copolymers. Semicrystalline PE does not become soluble until it is heated to more than 100 °C in chlorinated aromatic or hydrocarbon solvents.[40] Meanwhile, the "grafting-from" technique is preferably performed at lower temperatures to minimize unwanted reactions that may result in cross-linking.[41] Specific precautions thus need to be taken to mitigate these conflicting requirements. The use of anisole as the solvent results in a controlled ATRP process, as does the addition of a small amount of deactivator, CuBr$_2$.[13,42] Accordingly, we prepared a series of graft copolymers in the manner illustrated in Scheme 4. Briefly, the macroinitiator was dissolved in an anisole solution containing CuBr and CuBr$_2$ ligated with *N*,*N*,*N*′,*N*″,*N*″-pentamethyldieth-

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Scheme 3. Synthesis of Triblock and Pentablock PE Macroinitiators Using **2b**

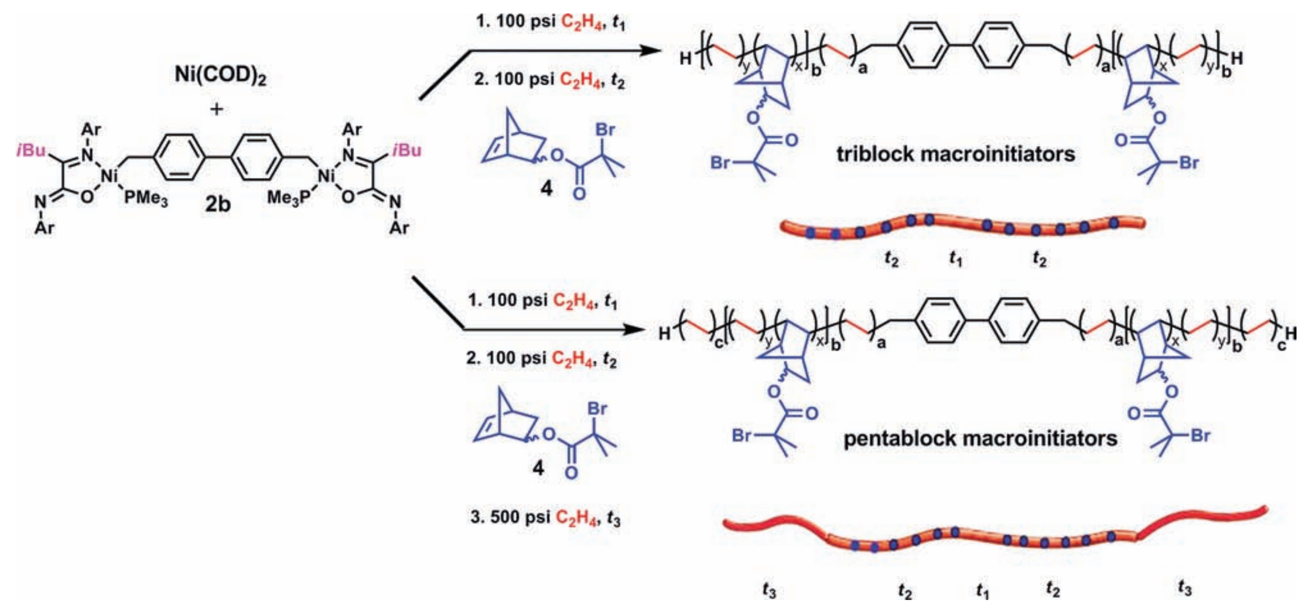


Table 2. Physical Properties of PE Macroinitiators[a]

macroinitiator	t_1 (min)	t_2 (min)	t_3 (min)	mol % **4**[b]	M_n (kg/mol)[c]	PDI[c]	T_g (°C)[d]	T_m (°C)[d]	X_c (%)[d]
MN 1-15	1	15	0	15	62	1.3	48	114	0.1
MN 1-30	1	30	0	15	88	1.4	38	116	0.2
BN 1-15	1	15	0	14	97	1.4	35	113	0.1
BN 1-15-2	1	15	2	12	112	1.4	32	111	0.3
BN 1-15-6	1	15	6	8	128	1.5	27	94, 110	0.9

[a] Copolymerization conditions: 20 °C,100 psi, 0.6 M [**4**]$_0$, 5 μmol of **1b** or 2.5 μmol of **2b**, 12.5 μmol of Ni(COD)$_2$. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by GPC. [d] Determined by DSC.

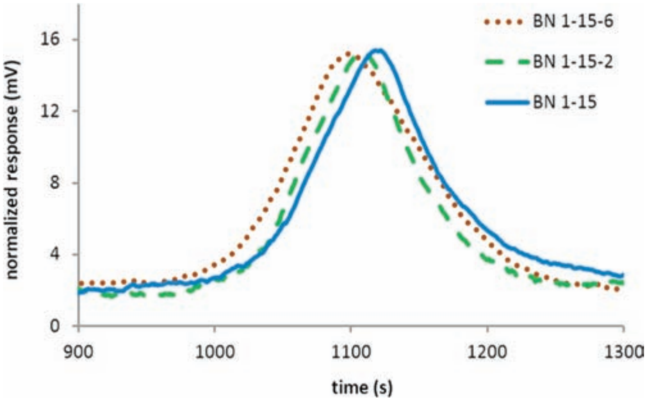
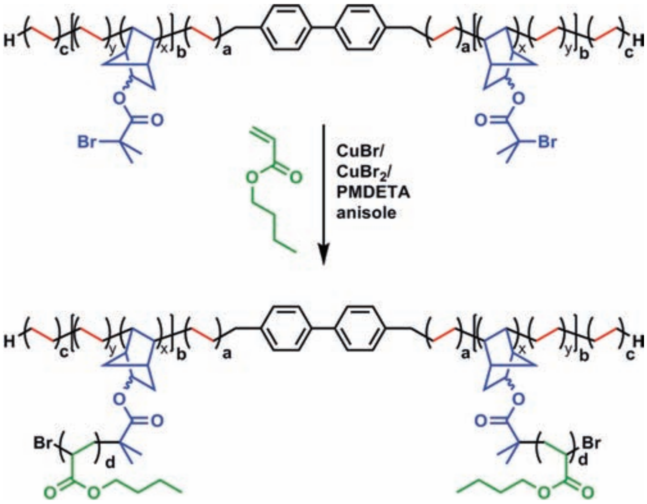


Figure 3. GPC traces of triblock and pentablock PE macroinitiators.

ylenetriamine (PMEDTA). A specified amount of degassed nBA was then introduced. The mixture was then heated to 85 or 95 °C to initiate the polymerization, followed by quenching with methanol. Due to the considerable inimer content of the macroinitiators, all except **BN 1-15-6** were soluble in anisole at 85 °C; **BN 1-15-6** requires heating to 95 °C to achieve a homogeneous solution. The results of the grafting experiments, along with the physical properties of products, are summarized in Table 3.

Scheme 4. Synthesis of Graft Copolymers[a]



[a] PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine.

When nBA is grafted from both diblock (**MN 1-15** and **MN 1-30**) and triblock (**BN 1-15**) macroinitiators, the products **G1**−**G3** exhibit an nBA incorporation of approximately 30 mol %, as determined by high-temperature ^{1}H NMR spectroscopy (Figures S9 and S10). However, when pentablock copolymers (**BN 1-15-2** and **BN 1-15-6**) are subject to the same grafting conditions, a lower nBA mol % is observed due to the decreased fractional content of inimer in the parent macroinitiators (**G4**, **G5**). Likewise, increasing [nBA]$_0$ from 0.46 to 0.7 M leads to a nearly 2-fold increase in nBA incorporation (**G5**, **G6**). The effect of grafting was also monitored by high-temperature GPC; the results are shown in Table 3, and the trace for **G4** is provided in the Supporting Information (Figure S11). All grafts show an increase in M_n relative to that of the parent macroinitiators, without a substantial increase in the PDI, verifying the controlled nature of the grafting process. For example, when **BN 1-15-2**

Table 3. Physical Properties of Graft Copolymers[a]

graft	macroinitiator	yield (mg)	M_n (kg/mol)	PDI	mol % nBA[c]	T_g (°C)[d]	T_m (°C)[d]	X_c (%)[d]
G1	**MN 1-15**	89	110	1.5	30	−28	114	0.1
G2	**MN 1-30**	90	122	1.6	31	−27	115	0.2
G3	**BN 1-15**	92	143	1.5	28	−30	107	0.1
G4	**BN 1-15-2**	95	178	1.4	26	−30	112	0.3
G5	**BN 1-15-6**	94	195	1.5	23	−31	101	0.8
G6	**BN 1-15-6**[b]	126	239	1.4	40	−35	101	0.4

[a] Grafting conditions: 0.46 M nBA, 85−95 °C, 1 h. [b] $[\text{BA}]_0 = 0.70$ M. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by DSC.

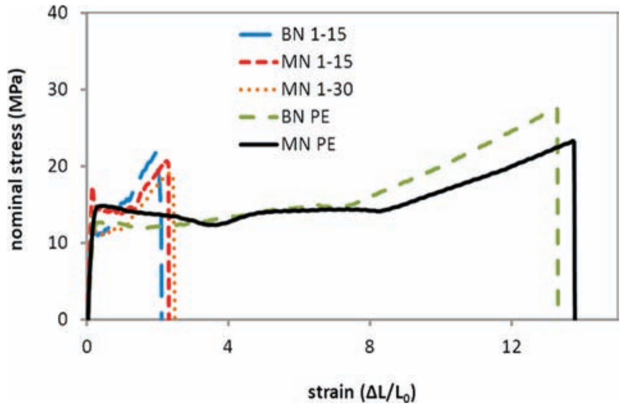


Figure 4. Monotonic stress vs strain curves of PE homopolymers and diblock and triblock macroinitiators.

Table 4. Mechanical Properties of PE Homopolymers, Diblock and Triblock Macroinitiators

					strain at break	
macroinitiator	T_g (°C)[a]	T_m (°C)[a]	X_c (%)[a]	Young's modulus (MPa)[b]	(%)[b]	(MPa)[b]
MN PE		131	50.2	106	1390	23
BN PE		133	44.7	115	1310	27
MN 1-15	48	114	0.1	125	210	20
MN 1-30	38	116	0.2	136	250	19
BN 1-15	35	113	0.1	118	200	22

[a] Determined by DSC. [b] Determined by monotonic stress−strain tests.

is grafted with nBA, the M_n shifts from 112 to 178 kg/mol. Thermal properties of grafts were also examined using DSC, and the thermograms are provided in the Supporting Information (Figures S12−S15). All graft copolymers exhibit a softening relative to the parent macroinitiators, as evidenced by a decrease in T_g from an average of 35 °C to an average of −28 °C. Increasing nBA content from 23 to 40 mol % results in a T_g decrease from −31 to −35 °C for grafts **G5** and **G6**. Altogether, the thermal properties change in accord with the anticipated structural modification from the grafting reactions.

Mechanical Properties of Diblock and Triblock Macroinitiators and Their Grafts. Mechanical properties of diblock and triblock macroinitiators and their grafts were investigated using monotonic tensile stress−strain tests; the results are provided in Figure 4 and summarized in Table 4. These studies were carried out to highlight how molecular structure, and thereby the choice of initiator in the polymerization, translates into materials with optimized properties. PE prepared from **1b**/Ni(COD)$_2$ and **2b**/Ni(COD)$_2$ was also examined as a baseline measurement. As expected, both PE homopolymers display deformation behavior typical of a plastically deforming material, with an initial elastic regime at low strains, followed by strain hardening at approximately 800% strain. Both materials exhibit an elongation at break of 1300% and a Young's modulus of 100 MPa, which is in line with the moderately branched, semicrystalline structure of the PE produced.[43] The slightly higher stress at break of the PE obtained from **2b** may be explained by its higher melting point and crystallinity, relative to the product from **1b**.

As can be seen in Figure 4, both diblock and triblock macroinitiators are significantly less extensible than the PE homopolymers, with a strain-at-break of roughly 200%, consistent with the incorporation of a high T_g norbornene unit.[44] Increasing the molecular weight from 62 to 88 kg/mol does not significantly alter the mechanical properties of the resulting macroinitiator (**MN 1-15** vs **MN 1-30** in Table 4). The slight increase in the melting point and degree of crystallinity of the higher M_n copolymer correlates with a slightly higher Young's modulus. The triblock macroinitiator prepared from the **2b** system exhibits properties comparable to those of the two materials prepared using the **1b** system. This is not unexpected since the mechanical properties of **BN 1-15**, as well as those prepared from the monometallic system, are dominated by the glassy, norbornene-rich segments.

As described above, although there were minimal differences in the stress−strain response of diblock and triblock macroinitiators, the effect of the polymer structure, and thereby the impact of the telechelic polymerization on the mechanical properties of the products, will become evident upon examination of the graft copolymers. In addition to monitoring the deformation behavior under monotonic stress, the elastic recovery was also investigated by using step-cyclic stress−strain tests, wherein the material was elongated in successive loading and unloading cycles and the elastic recovery from a maximum applied strain ($\varepsilon_{\max}$) was recorded. The results from both tests are summarized in Table 5. The nominal stress vs nominal strain plots are provided in the Supporting Information (Figure S16).

As shown in Figure 5, the true stress vs true strain relationship of **G1** under monotonic elongation reveals necking behavior presumed to be caused by insufficient crystallinity.[13] Comparison of **G1** and **G2**, prepared from a mononuclear complex, demonstrates that increasing the M_n of the macroinitiator has little effect on the mechanical properties of the graft copolymer, with a similar strain at break (1095% and 1025%) and true stress (5 MPa) observed for the two materials (Table 5). In contrast, when triblock macroinitiator **BN 1-15** is grafted with nBA, the product **G3** shows a 2-fold increase in the strain at break to 2000%, while the true stress at break increases to 20 MPa. Further, the elastomeric performance of **G3** is also improved, as shown in Figure 6, where elastic recoveries (ER) are plotted against $\varepsilon_{\max}$. Unlike the grafts **G1** and **G2**, **G3** exhibits high ER from applied stress, even at strains above 500%, with an average ER of 79%. These findings reveal an improvement in the mechanical properties of the elastomers that cannot be achieved simply by increasing the M_n of the parent macroinitiator. Therefore, the value of the telechelic initiator as a convenient tool to access polymer structures with enhanced mechanical properties becomes apparent.

Mechanical Properties of Pentablock Macroinitiators and Their Grafts. Having demonstrated significant differences between diblock and triblock graft copolymers, we next examined the effect of the pressure-pulsing technique on the mechanical properties of the pentablock macroinitiators and their

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(43) Kennedy, M. A.; Peacock, A. J.; Mandelkern, L. *Macromolecules* **1994**, *27*, 5297–5310.

(44) Scrivani, T.; Benavente, R.; Perez, E.; Pereña, J. *Macromol. Chem. Phys.* **2001**, *202*, 2547–2553.

Table 5. Mechanical Properties of Diblock and Triblock Graft Copolymers

		% ER[a]						
graft	macroinitiator	at 250% strain	at 400% strain	average	Young's modulus (MPa)[b]	nominal strain at break (%)[b]	nominal stress at yield (MPa)	true stress at break (MPa)[c]
G1	**MN 1-15**	80	73	78	0.4	1095	0.8	5
G2	**MN 1-30**	78	75	72	0.6	1025	0.8	5
G3	**BN 1-15**	76	74	79	0.4	2000	1.4	20

[a] ER = elastic recovery, determined by monotonic stress−strain tests. [b] Determined by step cyclic stress−strain tests. [c] Maximum stress (engineering stress).

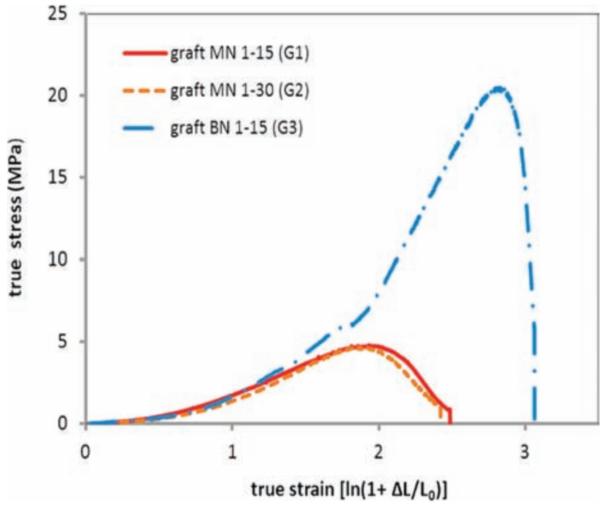

Figure 5. True stress vs true strain of diblock and triblock graft copolymers.

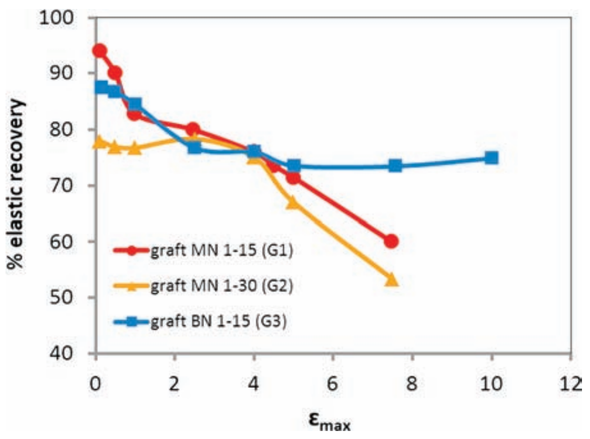

Figure 6. Elastic recoveries of diblock and triblock graft copolymers.

graft copolymers. Results from these studies are depicted in Figure 7 and summarized in Table 6. With the addition of an ethylene-rich end-block to the triblock **BN 1-15**, a significant transformation is observed, including a 2-fold decrease in Young's modulus, from 118 to 57 MPa, and a 2-fold increase in strain-at-break for the pentablock **BN 1-15-2**. When t_3 is increased from 2 to 6 min, the elongation at break shifts from 470 to 540% strain, while Young's modulus increases to 70 MPa. Additionally, **BN 1-15-6** shows a higher stress at break relative to **BN 1-15-2**, confirming that longer ethylene end-blocks give rise to a tougher material. These results correlate well with the gradual increase in the crystalline content of the pentablock macroinitiators demonstrated by the DSC analysis discussed earlier.

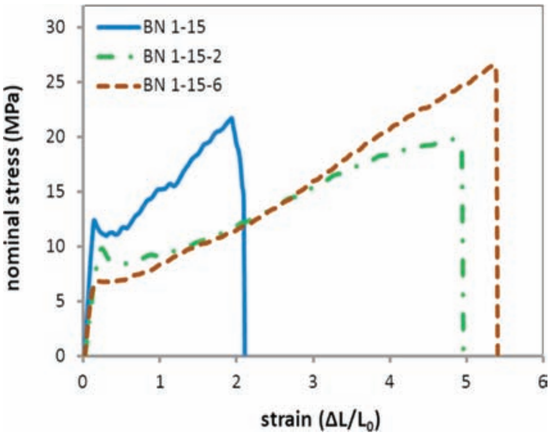

Figure 7. Monotonic stress vs strain curves of triblock and pentablock macroinitiators.

Table 6. Mechanical Properties of Triblock and Pentablock Materials

block	T_g (°C)[a]	T_m (°C)[a]	X_c (%)[a]	Young's modulus (MPa)[b]	strain at break (%)[b]	stress at break (MPa)[b]
BN 1-15	35	113	0.1	118	200	22
BN 1-15-2	32	111	0.3	57	470	19
BN 1-15-6	27	94, 110	0.9	70	540	26

[a] Determined by DSC. [b] Determined by monotonic stress−strain tests.

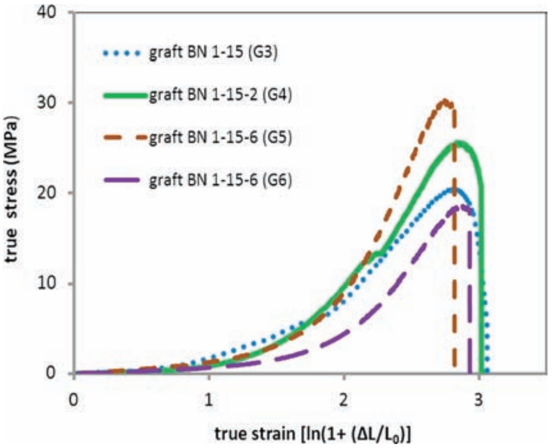

Figure 8. True stress vs true strain plots of triblock and pentablock graft copolymers.

Grafts prepared from the pentablock macroinitiators were subject to the same monotonic and step-cyclic stress−strain tests that were performed on the diblock and triblock graft copolymers. The true stress vs true strain results are depicted in Figure 8, while the elastic recoveries are shown in Figure 9, and all results are summarized in Table 7. Grafts generated from macroinitiators with increasing C_2H_4 content show an increase in Young's modulus and true stress at break and a slight decrease in the strain at break (**G4**, **G5**). Again, this trend is consistent with a shift in the crystalline content of the materials. Com-

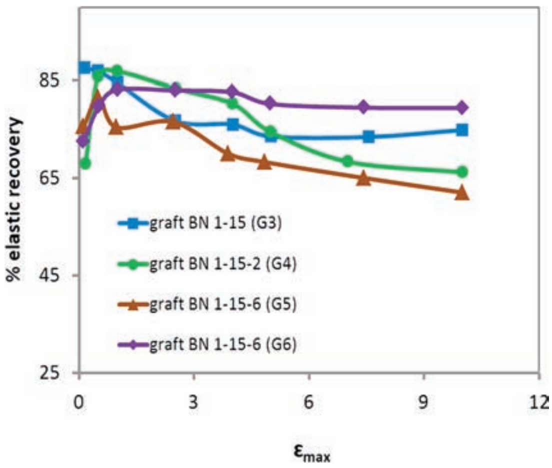

Figure 9. Elastic recoveries of triblock and pentablock graft copolymers.

parison of **G5** and **G6** reveals that increasing nBA content leads to improvement in elastomeric performance. As nBA content is varied from 23 to 40 mol % nBA, the strain at break increases from 1600 to 1800%, while the average elastic recovery shifts from 74 to 80%. Likewise, increased nBA content results in the softening of the product, as indicated by a decrease in Young's modulus from 0.7 to 0.4 MPa and a decrease in true stress at break from 30 to 16 MPa. These observations confirm that it is possible to tailor the "softness" and "elasticity" of the graft copolymer by modulating the nBA incorporation, thereby highlighting the versatility of this system.

Summary, Discussion, and Conclusions

In summary, we report the synthesis of two new binuclear Ni complexes, **2a** and **2b**. These complexes are the first examples of initiators capable of quasi-living telechelic polymerization of ethylene and copolymerization of ethylene and functionalized norbornenes. Unlike the majority of bimetallic olefin polymerization catalysts in the literature, the Ni centers in **2a**,**b** are covalently linked and are thus designed to propagate away from one other as the polymerization proceeds. NMR spectroscopy and single-crystal X-ray diffraction studies confirm that the binuclear structure does not significantly alter the coordination sphere about Ni. Ethylene polymerizations performed by activating **2a**,**b** with Ni(COD)$_2$ reveal that, for a given reaction time, the molecular weights are approximately double those obtained from analogous mononuclear systems (**1a**,**b**). This observation indicates that the Ni centers behave independently in the bimetallic system and operate with a level of control similar to that observed with the monometallic analogues.

In addition, the **2b**/Ni(COD)$_2$ system can be employed in the synthesis of triblock and pentablock PE macroinitiating copolymers, containing C_2H_4 and a norbornene comonomer, which bears a functionality useful for initiating ATRP (**4**). Diblock macroinitiators were synthesized using **1b**/Ni(COD)$_2$ for comparison. Pentablock macroinitiators were prepared by using a pressure-pulsing technique to produce ethylene-rich end-blocks, following the growth of the PE-*co*-**4** segment. All products generated using the **2b** system have narrow PDIs, consistent with a controlled copolymerization sequence, as well as an increase in M_n and predictable inimer content. Monotonic stress−strain analyses of the diblock and triblock macroinitiators indicate that they have similar mechanical behavior and fail at relatively low strains of 200%, due to the high T_g of the norbornene segments. Pentablock materials exhibit an increase in Young's modulus and strain at break, which is expected for materials containing semicrystalline PE end-blocks.

Upon grafting with nBA, the advantage of the binuclear catalyst system becomes apparent. When compared to the grafted diblock copolymers (**G1**, **G2**), the grafted triblock copolymer shows a 2-fold increase in elongation at break (**G3**). Additionally, the true stress at break increases 4-fold, while the average elastic recovery remains quite high (at nearly 80%) and does not decrease at higher strains, as is evident with **G1** and **G2**. Grafts prepared from the pentablock macroinitiators (**G4**, **G5**) show an increase in Young's modulus and true stress at break and a slightly lower strain at break compared to **G3**, consistent with increased crystallinity of the PE-rich segments. A comparison of pentablock grafts with different nBA content reveals that longer nBA side chains lead to improved elastic properties, as evidenced by increased strain at break and elastic recovery. These results indicate that, under identical reaction conditions, the telechelic initiator system allows access to polymer structures with improved mechanical properties over those obtained from the mononuclear system. In addition, the collected set of observations demonstrate that telechelic polymerization of olefins using well-defined organometallic initiators provides unique opportunities to access new materials with higher-order architectures, wherein the individual components can be used to modulate useful physical properties.

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. Toluene and THF were distilled from sodium benzophenone ketyl, and pentane from Na/K alloy. The toluene used in ethylene polymerizations was purchased from Aldrich (anhydrous grade) and further dried over Na/K alloy. Ethylene (research grade, 99.99%) was purchased from Matheson Trigas and purified by passing through Agilent moisture and oxygen traps. Bis(1,5-cyclooctadiene) nickel (Ni(COD)$_2$) was purchased from Strem. Unless otherwise specified, all other reagents were purchased from Aldrich and used without further purification.

Synthesis of 4,4′-Bis{[*trans*-bis(trimethylphosphine)chloronickel(II)]methyl}-1,1′-biphenyl (3). The synthesis of **3** was carried out under minimal light exposure. To a solution of Ni(COD)$_2$ (550 mg, 1 mmol) in 125 mL of THF at −35 °C was added a solution of trimethylphosphine (304 mg, 2 mmol) in 1 mL of THF, followed immediately by a solution of 4,4′-bis(chloromethyl)biphenyl (504 mg, 1 mmol) in 10 mL of THF. The reaction was stirred for 2 h at room temperature, after which time the solvent was removed in vacuo. The residue was redissolved in 100 mL of toluene and filtered through Celite. The solvent was removed until about 50 mL remained, and then the solution was stored at −35 °C overnight, resulting in the precipitation of a red-pink powder (555 mg, 82% yield).

^{1}H NMR (399.95 MHz, benzene-d_6, 295 K): $\delta = 7.66$ (d, 4H, $^3J_{HH} = 7.6$ Hz, Bn), 7.61 (d, 4H, $^3J_{HH} = 7.6$ Hz, Bn), 1.80 (s, 4H, CH_2Ph), 1.04 (s, 36H, $P(CH_3)_3$). ^{31}P NMR (162 MHz, benzene-d_6, 295 K): $\delta = -16.7$. Accurate elemental analysis was not possible due to the reactive nature of this compound.

4,4′-Bis{[*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-propanamidato-κ^2-*N*,*O*-(trimethylphosphine)nickel(II)]methyl}-1,1′-biphenyl (2a). To a stirred suspension of **3** (250 mg, 0.372 mmol) in 5 mL of toluene at −35 °C was added a chilled solution of potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamidate (350 mg, 0.78 mmol) in 5 mL of toluene. The reaction was stirred at room temperature for 2 h, resulting in an orange-brown solution. The solution was filtered through Celite, and the solvent was removed. The residue was then dissolved in a

Table 7. Mechanical Properties of Graft Copolymers Prepared from Triblock and Pentablock Macroinitiators

		% ER[a]						
graft	macroinitiator	at 250% strain	at 400% strain	average	Young's modulus (MPa)[b]	nominal strain at break (%)[b]	nominal stress at break (MPa)[c]	true stress at break (MPa)[b]
G3	**BN 1-15**	76	74	79	0.4	2000	1.4	20
G4	**BN 1-15-2**	80	83	77	0.5	1960	1.6	25
G5	**BN 1-15-6**	77	67	74	0.7	1600	2.0	30
G6	**BN 1-15-6**[d]	83	83	80	0.4	1800	1.1	16

[a] Determined by monotonic stress−strain tests. [b] Determined by step cyclic stress−strain tests. [c] Maximum engineering stress. [d] Increased nBA content relative to G5.

minimal amount of toluene ($\sim$2 mL), then layered with 5 mL of pentane, and cooled to -35 °C for 24 h, yielding 365 mg (79%) of reddish orange crystals.

^{1}H NMR (500 MHz, benzene-d_6, 295 K): $\delta = 7.51$ (d, 4H, $^3J_{HH} = 7.9$ Hz, Bn), 7.35 (d, 4H, $^3J_{HH} = 8.1$ Hz, Bn), 7.27 (d, 4H, $^3J_{HH} = 7.5$ Hz), 7.19−7.11 (m, 2H), 7.08−6.99 (m, 6H), 3.68 (sept, 4H, $^3J_{HH} = 6.8$ Hz, *i*Pr−C*H*), 3.47 (sept, 4H, $^3J_{HH} = 6.8$ Hz, *i*Pr−C*H*), 2.20 (s, 6H, CH_3 ligand backbone), 1.58−1.38 (br m, 24H, *i*Pr−CH_3), 1.32 (d, 12H, $^3J_{HH} = 6.7$ Hz, *i*Pr−CH_3), 1.13 (d, 12H, $^3J_{HH} = 6.8$ Hz, *i*Pr−CH_3), 1.11 (s, 4H, benzyl CH_2) 0.47 (d, 18H, $^2J_{HP} = 10.2$ Hz, P(CH_3)$_3$). ^{13}C NMR (125.7 MHz, benzene-d_6, 295 K): $\delta = 181.37$ (carbonyl), 164.99 (imine), 149.86, 147.69, 141.75, 140.44, 138.68, 130.57, 129.66, 128.89, 126.03, 122.86, 29.78, 29.23, 24.52, 24.26, 23.06, 21.77, 20.38, 12.45 (d, $^1J_{CP} = 38$ Hz, PCH$_3$). ^{31}P NMR (161.0 MHz, benzene-d_6, 295 K): $\delta = -8.2$. Anal. Calcd for $C_{74}H_{104}N_4Ni_2O_2P_2$: C, 70.48; H, 8.31; N, 4.44. Found: C, 70.51; H, 8.46; N, 4.10.

X-ray crystallography, single-crystal data for **2a**: empirical formula (including cocrystallized pentane), $C_{42}H_{64}N_2NiOP$, $M = 702.63$; monoclinic, space group *P*2(1)/*c*; $a = 12.593(4)$, $b = 15.007(5)$, and $c = 17.257(7)$ Å; $\alpha = 90°$, $\beta = 91.519(0)°$, $\gamma = 90°$, $V = 4159(2)$ Å^3, $Z = 4$, $D_{calc} = 1.122$ Mg/m^3, $\mu = 0.563$ mm^{-1}, Mo Kα, $\lambda = 0.71073$, $T = 150$ K; *R*(F242s) = 0.0412, R_w (F^2, all data) = 0.1248, goodness-of-fit =1.071 for all 2132 unique data (6509 measured, 1105 refined), $R_{int} = 0.1200$, 2yo 54.98. Deposited with CCDC as no. 736656. The single crystal was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[45] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[46] and SADABS[47] to yield the reflection data file. Subsequent calculations were carried out using SHELXTL[48] program. The structure was solved by direct methods and refined on F^2 by matrix least-squares techniques. Analytical scattering factors of 49 for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference Fourier map and refined (*x*, *y*, *z*, and U_{iso}).[50]

4,4′-Bis{[*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-4-methylpentanamidato-κ^2-*N*,*O*-(trimethylphosphine)nickel(II)]methyl}-1,1′-biphenyl (2b). To a stirred suspension of **3** (200 mg, 0.3 mmol) in 5 mL of toluene at -35 °C was added a chilled solution of potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino))-4-methylpentanamidate[18] (300 mg, 0.6 mmol) in 5 mL of toluene. The reaction was stirred at room temperature for 2 h, resulting in an orange-brown solution. The solution was filtered through Celite, and the solvent was removed. The residue was then dissolved in a minimal amount of toluene ($\sim$2 mL), layered with 5 mL of pentane, and cooled to -35 °C for 24 h, yielding 365 mg (73%) of reddish orange crystals. Due to the limited solubility of **2b** in C_6D_6, ^{13}C spectra were obtained in THF-d_8.

^{1}H NMR (500 MHz, benzene-d_6, 295 K): = 7.79 (d, 4H, $^3J_{HH} = 8$ Hz, Bn), 7.54 (d, 4H, $^3J_{HH} = 8$ Hz, Bn), 7.40 (d, 4H), 7.30−7.08 (m, 8H, ph−H), 3.79−3.63 (m, 8H, *i*Pr−C*H*), 2.87−2.81 (m, 6H, *i*But−C*H* and *i*But−CH_2), 1.77−1.64 (br s, 12H, *i*Pr−CH_3), 1.62−1.52 (br m, 24H, *i*Pr−CH_3), 1.40 (d, 12H, *i*Pr−CH_3 $^3J_{HH} = 6.8$ Hz), 1.11 (br d, 4H, benzyl−CH_2), 1.06 (d, 12H, *i*But−CH_3, $^3J_{HH} = 6.5$ Hz), 0.53 (d, 18H, PCH_3, $^2J_{HP} = 10.1$ Hz). ^{13}C NMR (125.7 MHz, THF-d_8, 295 K): = 184.6 (carbonyl), 165.69 (imine), 148.09, 141.03, 138.78, 129.8, 126.20, 124.87, 122.51, 42.08 (imine, Ph−C), 35.21, 29.86, 23.37, 21.68, 14.56, 12.18 (d, $^1J_{CP} = 28$ Hz, PCH_3). ^{31}P NMR (161.0 MHz benzene-d_6, 295 K): $\delta = -7.95$ ppm.

Synthesis of PE and PE Macroinitiators. *N*-(2,6-Diisopropylphenyl)-2-(2,6-diisopropylphenylimino)methylamidato]-Ni(η^1-CH_2Ph)(PMe_3)[38] (**1a**), *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)isobutanamidato]-Ni(η^1-CH_2Ph)(PMe_3)[39] (**1b**), and 5-norbornen-2-yl 2-bromo-2-methylpropanoate (**4**)[13] were synthesized as previously reported. Ethylene homopolymerizations were carried out in a steel autoclave reactor, loaded with 10 μmol of **1a** or 5 μmol of **2a** and 25 μmol of Ni(COD)$_2$ in 30 mL of toluene, under an inert atmosphere. In the case of isobutyl analogues, 5 μmol of **1b** or 2.5 μmol of **2b** and 12.5 μmol of Ni(COD)$_2$ in 30 mL of toluene were employed in the reaction. The polymerization was initiated by introducing a continuous feed of ethylene at 100 psi to the mixture of initiator and Ni(COD)$_2$ at 20 °C. The polymerization was terminated by quenching the product with acetone. The polymer was collected by filtration, and dried under high vacuum overnight until a constant weight was achieved. The polymerization activities were calculated from the mass of the product obtained.

PE macroinitiators were synthesized in a steel autoclave reactor, equipped with an addition funnel, using 5 μmol of **1b** or 2.5 μmol of **2b** and 12.5 μmol of Ni(COD)$_2$ in 30 mL of toluene. The addition funnel was charged with a 0.6 M solution of **4** in toluene and prepressurized with ethylene at 150 psi for 3 min. The polymerization was initiated by introducing a continuous feed of ethylene at 100 psi to the mixture of initiator and Ni(COD)$_2$ at 20 °C, for a specified amount of time (t_1). At t_1, **4** was added to the reaction by opening the addition funnel, and the polymerization was allowed to proceed until t_2. Pentablocks were prepared by increasing the polymerization pressure from 100 to 500 psi at the completion of t_2 and allowing the polymer to grow until t_3. Polymerizations were terminated by quenching with acetone. The polymer was collected by filtration and dried under high vacuum overnight until a constant weight was achieved.

Synthesis of Graft Copolymers. A copper salt stock solution was prepared by dissolving CuBr (45 mg, 3.07×10^{-4} mol), CuBr$_2$ (3.5 mg, 1.25×10^{-5} mol), and PMDETA (115 mg, 6.6×10^{-4} mol) in 10 mL of anisole under an inert atmosphere. In a typical reaction, a 10 mL round-bottom flask was charged with 50 mg of macroinitiator, 2 mL of stock solution, and 3 mL of anisole. The flask was equipped with a septum, and degassed nBA (0.4 or 0.6 mL) was added via syringe. The flask was further degassed by bubbling argon for 10 min and then placed in an 85 °C oil bath to initiate the polymerization. When grafting with **BM 1-15-6**, it was necessary to heat the sample to 95 °C to ensure a homogeneous solution. After 1 h of reaction time, the graft copolymer was

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[45] *SMART Software Users Guide*, Version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

[46] *SAINT Software Users Guide*, Version 6.0; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

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precipitated into methanol, collected by filtration, and dried in a vacuum oven at 50 °C overnight.

Characterization of Materials. Gel Permeation Chromatography (GPC). GPC analysis of polymers was performed on a Polymer Laboratories high-temperature GPC system (model PL-220) equipped with a refractive index detector. Samples were run at 150 °C in spectrophotometric grade 1,2,4-trichlorobenzene, stabilized with BHT (0.5 g of BHT/4 L of solvent). Molecular weights were calculated by using a universal calibration from narrow polystyrene standards in the molecular weight range of from 580 to 7.5 million g/mol. Mark−Houwink parameters of $\alpha = 0.7$ and $\kappa = 47.7$ were utilized to correct for polyethylene.

Nuclear Magnetic Resonance (NMR). ^{1}H, ^{13}C and ^{31}P NMR spectra of complexes **3** and **2a,b** were obtained using Varian 400 and 500 MHz spectrometers in benzene-d_6 and THF-d_8 at room temperature. ^{1}H NMR spectra of PE macroinitiators and graft copolymers were obtained using a Bruker 500 MHz spectrometer in 1,1,2,2-tetrachloroethane-d_2 at 115 °C.

Differential Scanning Calorimetry (DSC). DSC was used to determine the thermal characteristics of the PE macroinitiators and graft copolymers using a TA Instruments differential scanning calorimeter (model Q-20). The DSC measurements were performed on 5 mg polymer samples at a rate of 10 °C/min in the temperature range of −85 to 160 °C. The melting point (T_m) and heat of fusion (H_f) were calculated using the data from the third heating/cooling cycle. The degree of crystallinity (X_c) was determined by dividing the measured H_f by 288 J/g, the accepted value for 100% crystalline high-density polyethylene (HDPE) material.[51]

Mechanical Analysis of Materials. Sample Preparation. Polymer samples were compression-molded at 110 °C into a film 0.2−0.5 mm thick using a Carver lab press (model M). Film samples were dried at 50 °C under a high vacuum overnight to remove any remaining solvent. Samples then were cut into specimens of 4−7 mm long × 2 mm wide using a dogbone die.

Tensile Testing. Samples were elongated either until fracture or to a given tensile strain ε_{max} using an Instron (Norwood, MA) 1123 testing instrument. Two types of mechanical tests were performed: (1) samples were stretched *monotonically* until fracture, and stress−strain curves were recorded; or (2) *step-cycle tests* were performed that combine a stepwise stretching with unloading−reloading cycles. In each step, the sample was extended step-by-step up to strains of 10, 50, 100, 250, 400, 500, 750 and 1000 (%). Once the sample reached the appropriate strain, the crosshead direction was reversed, and the sample strain was decreased at the same rate until zero stress was achieved. The sample was then extended again at the same constant strain rate until it reached the next targeted step-strain. The step-cycle test was performed until the sample fractured, or until the final step of 1000% was reached. The elastic recovery (ER) was calculated from the step-cycle tests, and is defined as the strain recovered upon unloading divided by the maximum strain (ε_{max}) reached during the step. Likewise, in Figures 5 and 8, the true stress versus true strain are provided, wherein true stress (σ_t) is defined as σ_n/L_0, while true strain is $[\ln(1 + \Delta L/L_0)]$, where σ_n is the nominal stress, L_0 the initial length of the specimen, and ΔL the change in the length the specimen.

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Supporting Information Available: Crystallographic data, ^{1}H NMR spectra, DSC thermograms, and other information. This material is available free of charge via the Internet at http://pubs.acs.org.

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