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Novel Elastomers Prepared by Grafting *n*-Butyl Acrylate from Polyethylene Macroinitiator Copolymers

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ABSTRACT: A series of polyethylene-based macroinitiators bearing atom transfer radical polymerization (ATRP) initiator functionalities were prepared by copolymerizing norbornen-2-yl-2-bromo-2-methylpropanoate (**3**) with ethylene using *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenyl-imino)isobutanamidato]-Ni(η^1CH$_2$Ph) (PMe$_3$) (**1**) and bis(1,5-cyclooctadiene)nickel (**2**). The content of **3** was increased from 2 to 16 mol %, and the mechanical properties of the resulting macroinitiators were investigated using monotonic and step cyclic stress−strain tests. With increasing **3** content, the product transitioned from plastically deforming PE to elastomeric PE (at 10 mol % **3**) to a brittle polynorbornene-like material. Upon grafting with *n*-butyl acrylate (nBA) using ATRP, the new materials became significantly softer and more elastomeric in comparison to their parent macroinitiators. Increasing nBA content did not break up the PE crystallites, but instead diluted the overall crystallinity and decreased the glass transition temperature of the products. The highest performing acrylate-containing polyolefin elastomer exhibited an elongation at break of 780% strain and a recovery of 83% at 400% strain.

1. Introduction

Elastomers are composed of amorphous polymer chains anchored by cross-links that enable recovery from large deformations without fracture.[1] Conventional rubber materials are prepared by chemically cross-linking amorphous polymers with sulfur or peroxides. Because the cross-links are covalent in nature, these materials cannot be melt-processed or recycled.[2] In contrast, thermoplastic elastomers (TPEs) derive their elasticity from the physical interaction between the "hard" glassy or semicrystalline and "rubbery" amorphous polymer blocks. These materials are physically cross-linked, meaning they can be melt-processed at high temperatures, but still attain excellent elastic recoveries at lower service temperatures.[3]

The first class of commercially successful TPEs included polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) triblock copolymers. Although these materials exhibit good mechanical properties, the diene center blocks are susceptible to oxidation and UV degradation, limiting their applications.[4] Upon hydrogenation, the resulting polystyrene-*b*-poly(ethylene-*alt*-butylene)-*b*-polystyrene (SEBS) materials show improved oxidative and thermal stability, but their extensibility is not as large as that of conventional rubber materials. This is due, in part, to the large Flory−Huggins parameter χ between the two blocks, which limits the molecular weight of the polystyrene end blocks.[5] For SEBS to be melt-processed, shorter end blocks must be used, but this results in polystyrene domains with lower glass transition temperatures and end blocks that may be pulled out from the crystalline domain, limiting the elastic recovery and the ultimate tensile strength of the material.[6]

Polyolefin elastomers have attracted attention in both industry and academia due to their lower cost and excellent weatherability and UV resistance.[7] The first generation of olefinic elastomers, such as poly(ethylene-*co*-propylene-*co*-diene) rubber (EPDM) and poly(ethylene-*co*-propolylene) rubber (EPR), were prepared using Ziegler−Natta catalysts.[8,9] With the development of more sophisticated catalysts, blocky polyolefin architectures could be achieved, including poly(ethylene-*b*-hexene) (PEH) and poly(propylene-*b*-hexene) (PPH).[10,11] Similarly, single-site catalysts have been employed to produce regioregular poly(propylene−ethylene) block copolymers, including syndiotactic-poly(propylene)-EPR copolymer (sPP-EPR), sPP-*b*-EPR-*b*-sPP, and iPP-*b*-EPR-*b*-iPP (isotactic-PP-*b*-ERP-*b*-isotactic-PP), that show superior mechanical properties in comparison to SEBS and conventional rubber.[12−14] For example, a pentablock composed of isotactic PP segments exhibits an elongation to break of more than 2400%, with an impressive elastic recovery of 90% at strains greater than 1000%.[15] Likewise, blocky ethylene−octene (EO) copolymers prepared using Dow's chain-shuttling method have also shown good mechanical properties, including a strain-to-break of 1200%.[16] However, because these elastomeric materials are nonpolar, they are anticipated to suffer from poor adhesion and low compatibility with polar plastics. Further, they are susceptible to absorbing hydrocarbons, which can be problematic for application in the automotive industry.[17]

TPEs prepared from acrylic monomers have enhanced adhesion and oil resistance in comparison to polyolefin elastomers.[18] Several groups have prepared linear and star block copolymers composed of "glassy" poly(methyl methacrylate) PMMA end blocks and a "rubbery" poly(*n*-butyl acrylate) PnBA center block.[19] Although fairly high molecular weights were achieved (200−300 kg/mol), the optimal strain at break was only 550%. This has been attributed to the polydispersity of the materials and the large molecular weight between entanglements of PnBA.[20] Similarly, when the PMMA blocks were replaced with poly(acrylonitrile) (PAN), the maximum elongation at break was

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~600%, although the service temperature of the elastomer increased considerably due to the high melting temperature (T_m) of the PAN (319 °C).[21]

One way to combine the desirable properties of polyacrylates and polyolefins is to covalently link the two materials in the form of a graft or block copolymer. Herein we present the first systematic investigation of the physical and mechanical properties of acrylate-containing polyolefins prepared by a combination of coordination insertion and atom transfer radical polymerizations (ATRP). Previously, we have shown that a Ni α-iminocarbaxamidato complex can copolymerize ethylene and an initiating monomer (inimer) in a controlled fashion.[22] In this contribution, we demonstrate how this polymerization system can be employed to prepare well-defined elastomeric polyethylene (PE) macroinitiators, with varying inimer content. Subsequently, we generate a series of poly(ethylene-*graft*-(*n*-butyl acrylate)) P(E-*g*-nBA) materials by grafting oligomers of *n*-butyl acrylate (nBA) from the PE macroinitiators via ATRP.

2. Results and Discussion

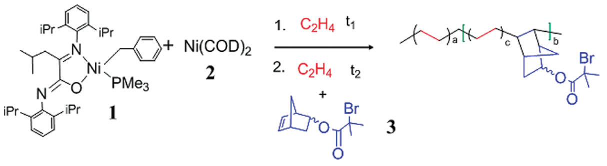
2.1. Synthesis of PE Macroinitiators. A series of PE macroinitiators were prepared using the strategy shown in Scheme 1. A steel autoclave reactor was charged with a 5 μmol solution of precatalyst (**1**) and 12.5 μmol solution of coactivator Ni(COD)$_2$ (**2**) in 30 mL of toluene, under an inert atmosphere. As discussed previously,[20] because **2** decomposes in the presence of the inimer (**3**), it is necessary to grow a short PE block (~12 kg/mol for t_1 = 1 min) before introducing **3** to the reaction mixture. Six different macroinitiators were prepared at 100 psi of ethylene and 20 °C by varying the initial concentration of **3** added to the reaction, [**3**]$_0$, from 0.06 to 0.65 M. The physical and thermal properties of the resulting materials are summarized in Table 1. The relationship between the degree of crystallinity (X_c) and inimer content is illustrated in Figure 1, and differential scanning calorimetry (DSC) thermograms of the macroinitiators are provided in the Supporting Information (Figures S2−S8). The number-average molecular weight (M_n) was determined by GPC at 135 °C in 1,2-dichlorobenzene calibrated against polystyrene standards, with Mark−Houwink parameters of $\alpha = 0.7$ and $\kappa = 47.7$ used to correct for polyethylene.

Without the addition **3**, the polyethylene obtained (**PE1**) is a moderately branched semicrystalline material, with T_m = 129 °C and an X_c of 45%, as determined by DSC. When 2 mol % of **3** is introduced into the PE backbone, the melting point decreases by 10 °C, and the X_c decreases to 26% (**PE2**). No glass transition temperature (T_g) is detected by DSC in the temperature range of −85 to 160 °C. A more substantial perturbation of the crystalline domains is observed at the inimer content of 6 mol % (**PE3**). In addition to a 2-fold decrease in the molecular weight, X_c falls to 8%. Furthermore, a weak T_g can be detected at ~0.3 °C, and the melting point separates into two peaks: one at 121 °C from the 12 kg/mol PE end block (t_1 = 1 min) and another at 74 °C from the poly(ethylene-*co*-inimer) block (t_2 = 15 min). Wide-angle X-ray scattering data reveal an identical crystalline chain packing corresponding to both melting transitions (Supporting Information, Figure S9). As the inimer content is increased, the melting transitions become less pronounced, while the T_g of the products increases in temperature and intensity. By 10 mol % of **3**, the crystallinity is sufficiently disrupted such that the amorphous middle block no longer exhibits a melting transition that can be detected by DSC (**PE5**). Above an inimer content of 12 mol %, the PE macroinitiator begins to resemble a polynorbornene more than it does polyethylene in terms of its physical and thermal properties.[23] **PE6** and **PE7** are glassy amorphous materials at room temperature, with a high T_g and negligible X_c.

To shed some light on the structure of these materials, we examined the nature of inimer incorporation by preparing macroinitiators of different molecular weights under a constant inimer feed. We found that inimer content does not change when molecular weight is varied from 36 to 98 kg/mol, which implies that the inimer is incorporated evenly throughout the PE backbone. This is also supported by the finding that only ~10 mol % of inimer is consumed under our reaction conditions.

2.2. Mechanical Properties of PE Macroinitiators. The mechanical properties of PE macroinitiators were investigated using both monotonic and step cyclic stress−strain tests. In the monotonic tests, the sample was extended in tension until fracture; while in the step cyclic tensile tests, the sample was stretched with loading and unloading cycles, and the elastic recovery from a maximum applied strain (ε_{max}) was recorded. The monotonic stress−strain curves are

Scheme 1. Synthesis of PE Macroinitiators



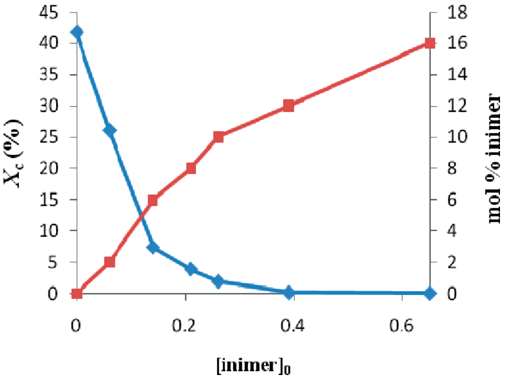


Figure 1. Degree of crystallinity and inimer incorporation as a function of [3]$_0$.

Table 1. Physical Properties of PE Macroinitiators

entry	[**3**]$_0$[a] (M)	t_1 (min)	t_2 (min)	mol % inimer[b]	inimers/chain	M_n[c] (kg/mol)	PDI[c]	T_g[d] (°C)	T_m[d] (°C)	X_c[d] (%)
PE1	0.00	1	15	0	0	105	1.3		129	45
PE2	0.06	1	15	2	61	98	1.4		119	26
PE3	0.14	1	15	6	127	63	1.4	0.3	121, 74	8
PE4	0.21	1	15	8	173	66	1.4	4	106, 55	4
PE5	0.26	1	15	10	215	67	1.4	8	112	2
PE6	0.39	1	15	12	260	69	1.3	28	115	0.2
PE7	0.65	1	15	16	300	62	1.3	50	116	0.1

[a] Initial [**3**] added at t_1. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by GPC. [d] Determined by DSC.

provided in the Supporting Information (Figure S16), while the elastic recoveries obtained from the cyclic tests are illustrated in Figure 2. In addition, pertinent results from the two tests are summarized in Table 2.

When **PE1** is extended monotonically, it exhibits deformation behavior that is characteristic of semicrystalline polyethylene.[24] After an initial elastic regime, followed by strain hardening at 40% strain, the material deforms plastically until it fractures at 1500% strain. This is also confirmed by the cyclic tests, which show a significant decrease in elastic recovery (ER) between strains of 10% and 50%. The addition of 2 mol % inimer significantly alters the mechanical properties. In contrast to **PE1**, **PE2** does not exhibit strain hardening, and the strain at break decreases to 700%. Likewise, there is a considerable improvement in the elastic performance of the macroinitiator, with a 24% increase in average ER from **PE2** to **PE1**. At 6 mol % inimer (**PE3**), the average ER rises to 64%, but the macroinitiator still deforms plastically at strains above 250%. Further increase in inimer content raises the average ER, but **PE4** breaks at a decreased strain (360%). The highest average ER of more than 80% was obtained with **PE5**, which was also the softest macroinitiator of the series, with a Young's modulus of 8 MPa. This elasticity is further confirmed by the monotonic test of **PE5**, which show a nearly linear relationship between stress and strain. As expected, with increasing inimer content T_g increases and the materials become increasingly more brittle at room temperature, exhibiting an elevated Young's modulus and reduced strain at break. These materials were not fully characterized with cyclic stress−strain tests because initial analysis of **PE6** and **PE7** revealed minimal (∼0−5%) elastic recovery, even at strains below 100%. In this manner, we have shown that the mechanical properties of PE macroinitiators can be modified by varying the content of **3**, allowing access to a variety of materials ranging from plastically deforming to elastomeric to glassy and brittle.

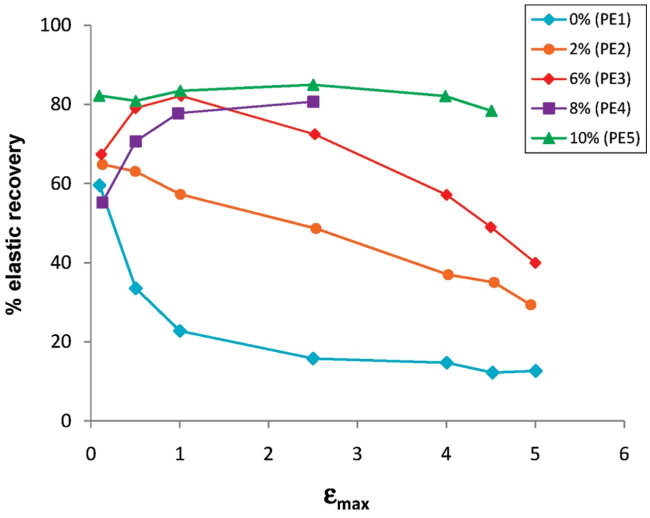


Figure 2. Comparison of elastic recoveries of PE macroinitiators. Percent elastic recovery (% ER) calculated from step cyclic stress−strain test, % ER = 100(1 − $\varepsilon_{plast}/\varepsilon_{max}$); ε_{max} is the maximum applied strain.

2.3. Synthesis of Graft Copolymers. Atom transfer radical polymerization (ATRP) of *n*-butyl acrylate (nBA) was initiated from the PE macroinitiators in Table 1 (**PE2**−**PE7**) using a strategy adopted from the literature,[25] as illustrated in Scheme 2. Typically, 50 mg of macroinitiator was treated with nBA and a solution of a copper salts in anisole and then heated to 85 °C to initiate the polymerization of nBA. Because **PE2** and **PE3** have an appreciable amount of crystallinity, it was necessary to heat these materials to 95 °C to achieve complete dissolution. A variety of graft lengths were obtained by varying the reaction time and initial nBA concentration, $[nBA]_0$. The results of the grafting experiments along with the physical and thermal properties of the graft materials are summarized in Table 3. DSC thermograms of graft copolymers **G2a**−**G2c** are provided in the Supporting Information (Figures S13−S15). The graft copolymers are numbered according to their parent macroinitiators, and the letter following the number denotes the grafting condition employed, wherein **a** is $[nBA]_0$ of 0.24 M for 1 h, **b** is $[nBA]_0$ of 0.46 M for 1 h, and **c** is $[nBA]_0$ of 0.46 M for 3 h.

In one set of experiments, macroinitiators with a varying number of inimers per chain were exposed to a $[nBA]_0$ of 0.46 M for 1 h ("**b**" conditions). The incorporation of nBA increased with increasing inimer content from 11 mol % nBA for **G2b** to 29 mol % nBA for **G7b**, as determined by ^{1}H NMR spectroscopy. By estimating the degree of polymerization (DP) of the macroinitiators from the M_n, it is possible

Table 2. Mechanical Properties of PE Macroinitiators

entry	mol % inimer	T_g (°C)	% ER[a] at 250% strain[c]	% ER[a] at 400% strain[c]	average % ER[a]	Young's modulus (MPa)[b]	strain at break (%)[b]	stress at break (MPa)[b]
PE1	0		16	15	24	150	1500	27
PE2	2		47	37	48	70	700	23
PE3	6	0.3	72	57	64	20	590	23
PE4	8	3	81		72	14	360	18
PE5	10	6	85	82	82	8	470	20
PE6	12	28				85	340	34
PE7	16	50				100	240	21

[a] %ER is % elastic recovery calculated from % ER = 100(1− $\varepsilon_{plast}/\varepsilon_{max}$). [b] Determined by monotonic stress−strain tests. [c] Determined by step cyclic stress−strain tests.

Scheme 2. Synthesis of Graft Copolymers

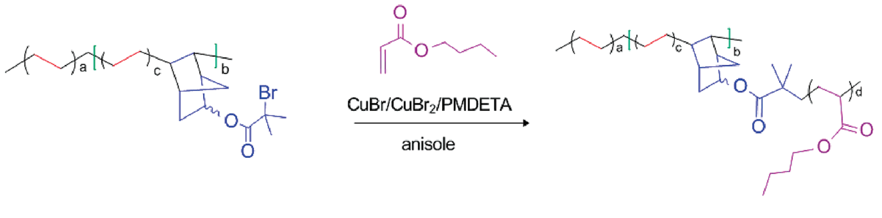


Table 3. Physical Properties of Graft Copolymers Prepared from PE Macroinitiators

entry	macroinitiator	$[\mathrm{nBA}]_0{}^a$ (M)	time (h)	T_{rxn} (°C)	yield (mg)	mol % nBA^b	overall DP nBA	DP nBA graft	$T_g{}^c$ (°C)	$T_m{}^c$ (°C)	$X_c{}^c$ (%)	PE$X_c{}^{c,d}$ (%)
G2b	**PE2**	0.46	1	95	60	11	424	7	−38	114	15	26
G3a	**PE3**	0.23	1	95	65	10	235	2	−31	120, 70	3	7
G3b	**PE3**	0.46	1	95	78	18	464	4	−36	120, 74	2	6
G3c	**PE3**	0.46	3	95	115	32	995	8	−40	120, 71	1	5
G4b	**PE4**	0.46	1	85	90	19	509	3	−32	110, 46	1	3
G4c	**PE4**	0.46	3	85	100	28	802	5	−36	110, 47	0.4	1
G5a	**PE5**	0.23	1	85	76	19	505	2	−29	112	1	4
G5b	**PE5**	0.46	1	85	96	24	680	3	−33	111	1	3
G5c	**PE5**	0.46	3	85	134	36	1211	6	−37	111	0.4	2
G6a	**PE6**	0.23	1	85	75	17	444	2	−25	112	< 0.1	0.2
G6b	**PE6**	0.46	1	85	92	26	762	3	−28	110	< 0.1	0.2
G6c	**PE6**	0.46	1	85	92	45	1774	7	−32	110	< 0.1	0.2
G7a	**PE7**	0.23	1	85	75	25	620	2	−22	112	< 0.1	0.3
G7b	**PE7**	0.46	1	85	90	29	760	3	−29	112	< 0.1	0.3

[a] Initial concentration of nBA. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by DSC. [d] PE X_c = X_c/wt % PE.

Table 4. Mechanical Properties of Graft Copolymers

entry	mol % nBA	T_g (°C)	% ER at 250% strain^b	% ER at 400% strain^b	average % ER^b	Young's modulus (MPa)^a	strain at break (%)^a	stress at break (MPa)^a
G2b	11	−38	50	42	60	30	490	15
G3a	10	−31	73	64	73	8	650	9
G3b	18	−36	67	60	72	6	630	8
G3c	32	−40	66	59	70	6	560	4
G4b	19	−32	75	55	73	3	670	3
G4c	28	−37	88	83	86	1	780	3
G5b	24	−32	78	77	80	1	740	2^c
G6b	26	−28	72	67	74	1.5	730	2.5^c
G7b	29	−29	81	76	82	0.4	1170	0.9^c

[a] Determined by monotonic stress−strain tests. [b] Determined by step cyclic stress−strain tests. [c] Maximum stress.

to calculate the overall DP of nBA and the DP of each individual graft side chain. While this estimate is not an exact calculation, largely due to inaccuracy of the M_n values obtained by using a GPC instrument calibrated relative to PS standards (corrected for PE), in addition to error inherent with NMR spectroscopy analysis, it can serve as a useful tool for comparative purposes. With the exception of **G2b**, all grafts prepared under these conditions incorporated approximately 3 ± 1 nBA repeat units at each inimer site after 1 h of reaction. The introduction of an oligomeric nBA block had a significant impact on the thermal properties of the materials. For example, in the case of **G2b**, the X_c decreased from 26% to 15% and T_m decreased from 119 to 114 °C relative to the parent **PE2**. Likewise, a weak T_g is observed at −38 °C, and no such transition was detected with **PE2**.

In addition to the measured X_c, a degree of crystallinity based on PE content (PE X_c) was calculated by dividing the measured X_c by the weight % of PE, determined from the DP of each block. Interestingly, the PE X_c was actually quite similar to the X_c of the macroinitiators for the grafts with lowest nBA content (see Table 1). These data suggest that addition of nBA does not break up the PE crystallites, but instead dilutes the overall crystallinity with the amorphous nBA material. A similar dilution effect can be observed with **G3a-c**. As nBA content increases from 10 mol % to 32 mol %, the T_g decreases from −31 to −40 °C, but PE X_c remains constant between 5 and 7%. These findings reveal that it is possible to tailor the crystallinity and glass transition temperature of the polyolefin graft copolymer independently: crystallinity and T_g are influenced by the number of inimer units, while the T_g may be changed independently of the crystallinity by varying the length of the nBA grafts.

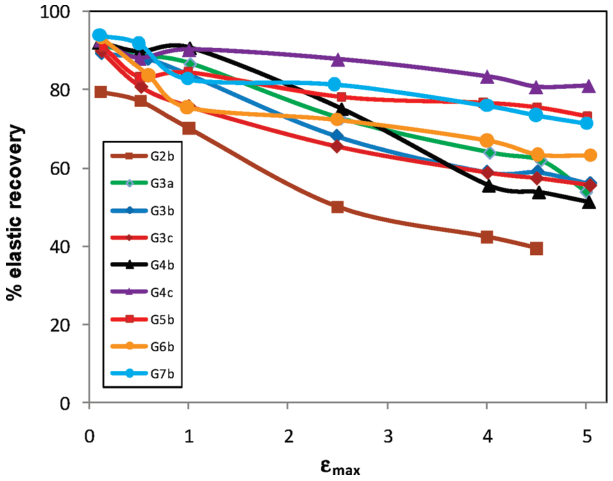


Figure 3. Comparison of elastic recoveries of graft copolymers. Percent elastic recovery (% ER) is calculated by % ER = 100(1− $\varepsilon_{\mathrm{plast}}/\varepsilon_{\mathrm{max}}$); $\varepsilon_{\mathrm{max}}$ is the maximum applied strain.

2.4. Mechanical Properties of Graft Copolymers. The graft copolymers were subjected to the same mechanical tests as the PE macroinitiators. The results for grafts with the highest extensibility and elastic recovery (ER) are summarized in Table 4. Monotonic stress−strain curves are provided in the Supporting Information (Figures S17 and S18), while the data from the cyclic tests are illustrated in Figure 3. In addition, pertinent results from the two tests are summarized in Table 4. As a whole, the grafting process renders the new materials significantly softer, as confirmed by a decrease in Young's modulus and stress at break with increasing nBA content. The monotonic tests of **G2−G4** reveal that the materials deform uniformly until fracture. In contrast, grafts prepared from macroinitiators with more than 200 inimer units per chain (**G5b−G7b**) on average show a broad maximum in the stress−strain curve around 200−400% strain due to necking. The neck achieves complete fracture at fairly high nominal strains of 700−1200%. For these materials, a maximum stress is recorded instead of stress at break.

All graft copolymers prepared in this study, with the sole exception of **G2b**, exhibit higher elongation at break and improved ER at strains above 250% relative to the parent macroinitiators. Although **G2b** breaks at 490% versus 700% for **PE2**, the average ER increases from 48% to 60%, with the most substantial improvement at 400% strain. Similarly, **G3a** shows a 7% increase in ER at 400% in comparison to its macroinitiator, **PE3**. Interestingly, additional incorporation of nBA does not lead to an increase in ER (**G3b** and **G3c**). The most dramatic improvement in elastic behavior is observed with **G4b** and **G4c**. The macroinitiator (**PE4**) shows an average ER of 72% and breaks at 360% strain. Upon grafting of 19 mol % nBA, the elongation at break increases nearly 2-fold to 670% without any significant change to the ER. Finally, upon grafting of several more nBA units from the backbone of **PE4**, the resulting graft copolymer **G4c** can be extended to nearly 9 times its initial length, with an average ER of 86% and a recovery of 83% at 400% strain. In comparison to polyolefin elastomers, **G4c** has a lower elastic recovery at 500% strain than the iPP pentablock discussed earlier (81% vs 88%) and a significantly lower strain at break (780% vs 2400%).[15] However, our graft copolymer exhibits improved elastic performance over the all-acrylate PAN−PnBA materials. For example, at a strain of 500%, the pure acrylic elastomer exhibits a recovery of only 70%, more than 10% lower than our material. Likewise, the strain at break is lower (780% vs 600%), as is Young's modulus (1 vs 0.54 MPa).[21]

The grafting process also leads to a considerable change in the mechanical properties of the glassy, amorphous macroinitiators **PE6** and **PE7**. Upon the addition of several nBA repeat units, the materials are no longer glassy at room temperature and exhibit average recoveries of 74% for **G6b** and 82% for **G7b**. Although **G6b** and **G7b** can be stretched to 740% and 1170% strain before fracture, they do not deform uniformly as evidenced by the stress−strain curves, and thus their mechanical properties are not as desirable as those of **G4c**. Future investigations will focus on preparing high inimer content macroinitiators reinforced with an additional ethylene block, which can be achieved by saturating the reaction mixture with ethylene (increasing pressure from 100 to 400 psi) at t_2 and growing a predominantly ethylene-containing block until t_3. In this manner, the materials may retain their high elasticity due to the densely grafted middle block, but they will no longer exhibit the necking behavior observed with **G6b** and **G7b** likely caused by too little crystallinity.

3. Conclusion

A series of polyethylene macroinitiators were prepared by copolymerizing ethylene with the ATRP initiating comonomer **3**. Monotonic and step cyclic stress−strain tests revealed that the mechanical properties of macroinitiators ranged from plastically deforming polyethylene to glassy and brittle polynorbornene-like materials. Elastomeric properties of the macroinitiators were observed at ∼10 mol % of comonomer. Upon grafting of the macroinitiators with nBA using ATRP, novel P(E-*g*-nBA) materials were generated, with varying amounts of nBA. The grafting process renders the new materials significantly softer and more elastic and allows access to a wide range of glass transition temperatures which are dictated by the length of the graft. The highest performing material prepared in this study exhibited an average elastic recovery of 86%, with an elongation at break of 780% strain.

4. Experimental Section

4.1. Synthesis of Materials. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. Toluene and THF was distilled from sodium benzophenone ketyl, and pentane from Na/K alloy. The toluene for reactions with ethylene 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. Reagents, unless otherwise specified, were purchased from Aldrich and used without further purification.

4.1.1. Preparation of PE Macroinitiators. *N*-(2,6-Diisopropylphenyl)-2-(2,6-diisopropylphenyl-imino)isobutanamidato]-Ni(η^1CH$_2$Ph)(PMe$_3$)[26] (**1**) and 5-norbornen-2-yl-2-bromo-2-methylpropanoate (**3**)[20] were synthesized as previously reported. Bis(1, 5-cyclooctadiene)nickel, Ni(COD)$_2$ (**2**), was purchased from Strem. A steel autoclave reactor, equipped with an addition funnel, was loaded inside the glovebox with solutions of **1** (5 μmol) and **2** (12.5 μmol) in toluene, such that the total volume was 30 mL. The addition funnel was charged with a solution of **3** of varying concentrations in toluene and prepressurized with ethylene at 150 psi for 3 min. The polymerization was initiated by introducing a continuous feed of ethylene to the mixture of **1** and **2**, to 100 psi and 20 °C for a specified amount of time (t_1). At t_1, **3** was added to the reaction by opening the addition funnel, and the polymerization was allowed to proceed until t_2. Ethylene was vented, and acetone was added to quench the active polymerization sites. The precipitated polymer was collected by filtration and dried under high vacuum overnight. Polymerization activities were calculated from the mass of the product obtained.

4.1.2. Preparation 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, 0.5−3 mL of stock solution (depending on the number of initiators), and anisole, such that the total volume was 6 mL. The flask was equipped with a septum, and degassed nBA (0.4 or 0.2 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. After a given time, the resulting graft material was precipitated into methanol, collected by filtration, and dried in a vacuum oven at 50 °C overnight.

4.2. Characterization of Materials. *4.2.1. Gel Permeation Chromatography* (*GPC*). GPC analysis of macroinitiators and grafts were performed on a Polymer Laboratories high temperature GPC system (model PL-220) equipped with a refractive index detector. Samples were run at 135 °C in HPLC grade 1,2-dichlorobenzene, stabilized with BHT (0.5 g BHT/4 L solvent). Molecular weights were calculated by using a universal calibration from narrow polystyrene standards in the molecular weight range of 580 to 7.5 million g/mol. Mark−Houwink parameters of $\alpha = 0.7$ and $\kappa = 47.7$ were utilized to correct for polyethylene.

4.2.2. Nuclear Magnetic Resonance (*NMR*). NMR spectra were obtained using Bruker 500 MHz spectrometer. ^{1}H NMR spectra of the polymers were obtained in 1,1,2,2-tetrachloroethane-d_2 at 115 °C.

4.2.3. Differential Scanning Calorimetry (*DSC*). Differential scanning calorimetry was used to determine the thermal characteristics of the PE macroinitiators and graft copolymers using a TA Instruments DSC (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 293 J/g, the accepted value, or 100% crystalline high density polyethylene (HDPE) material.[27]

4.3. Mechanical Analysis of Materials. *4.3.1. Sample Preparation*. Polymer samples were compression-molded into a small film 0.2–0.5 mm thick. Film samples were placed in a high-vacuum oven and annealed for 24 h at 50 °C. After annealing, samples were cut into specimens of 4–7 mm long × 2 mm wide using a dog-bone die.

4.3.2. Tensile Testing. Samples were either stretched to fracture or up to a given tensile strain using an Instron (Norwood, MA) 1123 testing instrument. Two types of mechanical tests were performed: (1) samples were stretched *monotonically* to 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, 450, and 500 (%). Once the sample reached the appropriate strain, the cross-head 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 500% was reached. With this step cycle test, elastic recovery of the materials was measured. The elastic recovery (% ER) is defined as the strain recovered upon unloading divided by the maximum strain reached during the step.

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Supporting Information Available: Representative characterization of macroinitiators and grafts, including NMR spectra, DSC thermograms, and mechanical testing results. This material is available free of charge via the Internet at http://pubs.acs.org.

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