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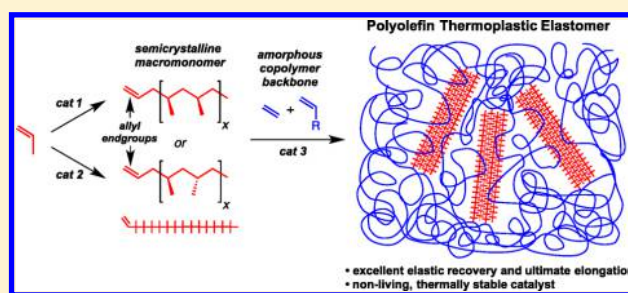
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Allyl-Terminated Polypropylene Macromonomers: A Route to Polyolefin Elastomers with Excellent Elastic Behavior

Hisashi Ohtaki,^{†,§} Fanny Deplace,[‡] Giang D. Vo,[†] Anne M. LaPointe,[†] Fumihiko Shimizu,[§] Toshihiko Sugano,[#] Edward J. Kramer,[‡] Glenn H. Fredrickson,^{*,‡} and Geoffrey W. Coates^{*,†}[†]Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States[‡]Mitsubishi Chemical Center for Advanced Materials and the Departments of Materials and Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California 93106, United States[§]Science and Technology Research Center, Inc., Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan[#]Japan Polychem Corporation, 1 Toho-cho, Mie, 510-0848, Japan

S Supporting Information

ABSTRACT: We report the design, synthesis, and physical/mechanical properties of graft copolymers containing semicrystalline polypropylene side chains and amorphous ethylene/ α -olefin copolymer backbones. These materials, a new class of semicrystalline, polyolefin-based thermoplastic elastomers, are made in two steps. First, allyl-terminated syndiotactic or isotactic polypropylene macromonomers are synthesized with controlled microstructure and molecular weight using bis(phenoxyimine)-titanium or chiral *ansa*-zirconocene catalysts, respectively. Second, a pyridyl-amido hafnium catalyst is used to copolymerize the macromonomer, ethylene, and an α -olefin with precise control of composition and side chain incorporation. With highly crystalline polypropylene side chains and amorphous backbones of low glass-transition temperatures ($<-55\text{ }^{\circ}\text{C}$), the samples have strain-to-break values up to 1400% and elastic recovery above 85% at maximum strains up to 1000%. The synthetic method described herein does not require the use of a living polymerization catalyst; in addition, the mechanical properties of these graft copolymers exceed those of the best linear block polyolefins.



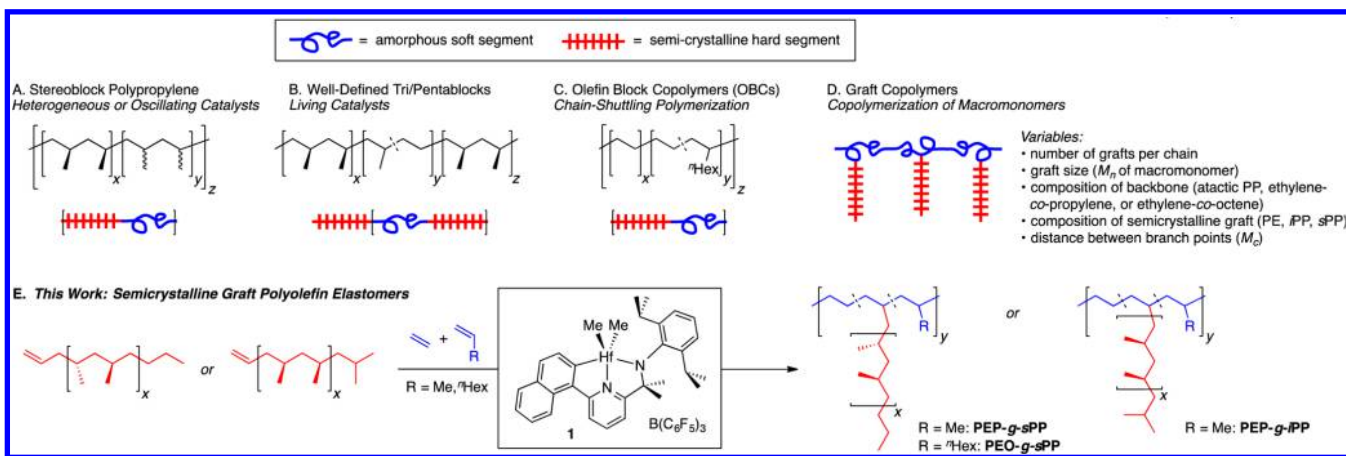
Thermoplastic elastomers (TPEs) are an important class of industrial materials that are an attractive alternative to vulcanized rubber.¹ TPEs can be melt-processed, do not require vulcanization, and, unlike thermoset rubbers, can be recycled. TPEs are blocky polymers that derive their elastomeric properties from a combination of “hard” segments with high melting points (T_m) or high glass-transition temperatures (T_g) and “soft” segments with low T_g . Elastomeric properties can be obtained in structures having at least two hard sequences separated by a soft sequence and are typically linear triblock or multiblock copolymers. In the solid state, the hard segments are dispersed throughout the amorphous matrix and form physical cross-links that produce recoverable elasticity after strain-induced deformation.¹ A well-known example of a commercial TPE is a triblock polystyrene-*block*-poly(ethylene-*co*-butene)-*block*-polystyrene copolymer (SEBS). Although many commercial TPEs are prepared via anionic polymerization and contain polystyrene, there has been longstanding interest in the synthesis and properties of TPEs based on other monomers. Bates and co-workers prepared model polyolefin TPEs by anionic polymerization followed by hydrogenation.² More recently, bio-derived TPEs have been reported.³

Given the low cost of ethylene, propylene, and α -olefins, considerable academic and industrial efforts have focused on the development of catalysts and reaction conditions to prepare blocky polyolefins.⁴ Several approaches are shown in Scheme 1. Early efforts focused on elastomeric polypropylene (Scheme 1A) prepared with nonliving catalysts. Natta reported the first elastomeric polypropylene in 1959 using $\text{TiCl}_3/\text{AlR}_3$ catalyst mixtures,⁵ and more recently similar materials were obtained using zirconium and titanium alkyl complexes supported on alumina.⁶ In the 1990s, the synthesis of elastomeric polypropylenes with more uniform composition was reported using well-defined Group 4 metallocenes. Chien,⁷ Collins,⁸ and Rieger⁹ discovered stereorigid C_1 -symmetric metallocenes that form blocky polypropylenes with isotactic-enriched regions, and Coates and Waymouth reported an “oscillating” zirconocene catalyst which produces poly(isotactic propylene-*block*-atactic polypropylene) (iPP-*b*-aPP)_n multiblocks.¹⁰ These developments represent significant advances in new polyolefin-based TPEs. However, TPEs with atactic polypropylene as the

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Scheme 1. Strategies for Preparing Semicrystalline Polyolefin Thermoplastic Elastomers



soft segment lose elasticity below their T_g , which is approximately 0 °C.^{4,11}

Over the past two decades, there have been numerous advances in the development of living alkene polymerization catalysts that offer an alternate route to precision multiblock polyolefin TPEs (Scheme 1B).^{12,13} For instance, Sita and co-workers cleverly employed degenerate chain transfer between active and inactive forms of living zirconium catalysts to produce stereoblock polypropylene.^{13c} Although these systems show good elastomeric behavior at room temperature, they may lose elasticity below 0 °C (*vide supra*).¹¹ For this reason, it would be advantageous to use soft segments with lower glass-transition temperatures than atactic polypropylene. These have been prepared using living catalysts. For example, a living bis(phenoxyimine)titanium complex has been used to synthesize syndiotactic polypropylene-*block*-poly(ethylene-co-propylene)-*block*-syndiotactic polypropylene (*synTB*),¹⁴ and a living C_2 -symmetric nickel diimine catalyst has been reported to form isotactic polypropylene-*block*-regioirregular polypropylene-*block*-isotactic polypropylene triblock (*isoTB*) and pentablock (*isoPB*) copolymers.^{14,15} These multiblock copolymers show exceptional elastic properties and exhibit some of the best mechanical properties reported for TPEs. However, living polymerizations are often performed at low reaction temperatures in batch polymerization processes and produce only one polymer chain per catalyst molecule. These drawbacks limit living transition-metal-mediated polymerizations to high-value, low-volume applications.⁴

For these reasons, the development of nonliving catalyst systems to prepare high-performance polyolefin elastomers remains an active area of research.⁴ In 2006, scientists at Dow Chemical Company reported the synthesis of elastomeric, multiblock polyolefins (Scheme 1C).¹⁶ These olefin block copolymers (OBCs), which contain hard blocks of high ethylene content and soft blocks containing both 1-octene and ethylene, are formed through an ingenious strategy where polymer chains shuttle between two catalysts with different selectivities for 1-octene incorporation. The chains are transferred between the catalysts by dialkyl zinc chain-shuttling agents, forming multiblock copolymers with blocks of varied lengths. This system produces multiple polymer chains per catalyst site, but zinc reagents are still required and, to date, the use of partially branched polyethylene hard segments limits the mechanical properties of the resulting materials.

Given the need for cost-effective routes to new high performance polyolefin-based TPEs,⁴ we envisioned a new class of well-defined graft copolymers featuring amorphous backbones and semicrystalline side chains that could be synthesized by nonliving catalysts. As is the case for multiblock TPEs, we hypothesized that the semicrystalline side chains would form physical cross-links to produce elastic recovery in the soft phase.¹ The graft copolymer could be synthesized by copolymerization of a semicrystalline macromonomer bearing a polymerizable olefin end group with ethylene and an α -olefin. This modular approach is amenable to diverse combinations of side chains and backbone compositions and provides a viable alternative to living polymerizations. Variables include distance between branch points, branch length and composition, branch distribution, and backbone length and composition (Scheme 1D). Any of these parameters can significantly influence the physical properties of the copolymer. This strategy was originally devised by Milkovich and co-workers for use in radical polymerizations¹⁷ and was later applied to metal-catalyzed olefin polymerization. Researchers at ExxonMobil have prepared polyolefin-based graft copolymer TPEs with semicrystalline side chains and amorphous backbones.¹⁸ Atactic polypropylene-*graft*-isotactic polypropylene (*aPP-g-iPP*) and atactic polypropylene-*graft*-polyethylene (*aPP-g-PE*) samples were reported, and Soares et al. used Monte Carlo simulations to model the effect of the crystalline side chains on the polymer properties.¹⁹ However, the mechanical properties of the reported polymers were found to be inferior to those of the best linear block copolymers.^{14,15} Likewise, the preparation of comb polymers containing isotactic polypropylene side chains by grafting functionalized polypropylene onto functionalized polyolefins has been reported; however, this approach requires several extra steps and introduces potentially reactive linkages into the polymers.²⁰ Herein, we report a new family of elastomeric polyolefin graft copolymers whose properties rival or exceed those of linear block copolymers (Scheme 1E). The synthesis, characterization, and physical properties are reported as well as initial studies on the effects of graft size, number of grafts, and graft composition on the mechanical properties.

Graft polymers can be prepared using three main strategies: (1) “grafting from”, in which an initiator grows a graft from an existing polymer backbone; (2) “grafting to”, in which an active polymer side chain is attached to a preformed polymer main chain; and (3) “grafting through”, in which macromonomers are incorporated into a polymer backbone during copoly-

Table 1. Characterization and Physical Properties of Graft Copolymers^a

entry	sample ^b	M_n (kDa) ^c	M_w/M_n ^c	graft/chain ^d	T_g (°C) ^e	T_m (°C) ^e	X_c^f (%)	strain at break ^g (%)	true stress at break ^g (MPa)	elastic recovery ^h	E^i (MPa)
1	(PEO _{0.96})-g-(^{8k} sPP _{0.04})	268	1.6	1.3	−66.3	139	1.5	1360	92.9	77	3.2
2	(PEO _{0.92})-g-(^{8k} sPP _{0.08})	224	1.7	2.2	−65.9	139	4.3	1290	115	85	5.0
3	(PEP _{0.96})-g-(^{5k} sPP _{0.04})	209	1.8	1.8	−58.1	121	1.1	1030	41.5	80	3.1
4	(PEP _{0.92})-g-(^{5k} sPP _{0.08})	232	2.0	3.7	−57.2	122	1.9	1000	92.1	82	7.5
5	(PEP _{0.92})-g-(^{8k} sPP _{0.08})	243	2.0	2.6	−58.5	126	5.0	1170	164	87	6.4
6	(PEP _{0.95})-g-(^{7k} iPP _{0.05})	222	1.7	1.6	−60.3	140	3.8	1050	121	86	4.6
7	(PEP _{0.92})-g-(^{7k} iPP _{0.08})	229	1.7	2.7	−59.0	138	5.5	954	169	80	8.0
8	(PEP _{0.95})-g-(^{12k} iPP _{0.05})	280	1.7	1.1	−60.6	144	4.0	1400	78.9	80	2.3
9	(PEP _{0.91})-g-(^{12k} iPP _{0.09})	215	1.8	1.6	−60.1	143	6.9	1090	118	79	5.6

^aGeneral conditions: 5.0 μ mol of catalyst **1** and 5.0 μ mol of cocatalyst B(C₆F₅)₃, 0.2 or 0.4 g of macromonomer, 2.0 mL of 1-octene or 6 psi propylene, 30 psi ethylene in toluene (54 mL) at 70 °C for 15 min. ^bGraft copolymer nomenclature: (backbone_x)-g-(^agraft_y), where x = weight fraction of backbone, y = weight fraction of the graft, and a = M_n of the graft. Weight fraction of graft was estimated based on 50% average macromonomer consumption. ^cDetermined by gel-permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 140 °C vs PE standards. ^dPredicted average number of grafts per chain, as determined by the ratio of moles of macromonomer incorporated to the moles of the graft copolymer. ^eDetermined by differential scanning calorimetry (DSC) (second heat). T_m values are peak melting transitions, and those of the polymers of entries 3–5 were broad relative to the other samples. ^fPercent crystallinity relative to *iso*PP (207 J/g). ^gMeasured at fracture in a step cycle test. ^hMeasured after the last step before fracture in a step cycle test. ⁱYoung's modulus, E , is the initial slope of the nominal stress vs nominal strain curve in the linear region ($0 < \epsilon < 0.05$) and was calculated using the most representative monotonic curve of a set of five repeat measurements. The standard deviation is estimated to be ± 0.5 MPa.

merization.²¹ For polyolefin graft copolymers, the “grafting from” and “grafting to” methods would be realized most readily using living olefin polymerization catalysts; however, “grafting through” would be possible for both living and nonliving polymerization catalysts. The synthesis of graft polyolefins via the “grafting through” strategy presents several challenges, as there are two components that must be considered—the semicrystalline macromonomer and its incorporation into the amorphous backbone.

For the macromonomer, side chains that form strong crystalline networks of physical cross-links needed for good elastic recovery were chosen. Syndiotactic polypropylene (sPP) and isotactic polypropylene (iPP) were selected because they exhibit higher T_m and lower chain mobility through crystals relative to polyethylene. As a result, they have been shown to impart excellent elastic behavior, as observed for *syn*TB, *iso*TB, and *iso*PB.^{14,15} To achieve high incorporation into the graft polymer, the polypropylene macromonomers must contain a polymerizable alkene end group. However, the most common chain termination pathway in propylene polymerization is β -hydride elimination following a 1,2 insertion of propylene, which yields disubstituted vinylidene chain ends that are not readily polymerized. Allyl-terminated macromonomers are more attractive candidates due to their ease of polymerization and can be prepared using catalysts that undergo β -hydride elimination following 2,1 insertion²² or β -methyl elimination following 1,2 insertion of propylene.²³ Although these chain transfer mechanisms are relatively rare, catalysts have recently been reported that allow the synthesis of stereoregular PP macromonomers using each of these pathways. Allyl-terminated sPP macromonomers ($[rrrr] = 0.96$) were prepared using bis(phenoxyimine)titanium(IV) catalysts developed in our group; these catalysts undergo propagation by insertion of propylene with 2,1 regiochemistry, and β -hydride elimination yields polymers with allyl end-groups. The macromonomer molecular weight and tacticity can be tuned by varying the catalyst substituents and reaction temperature.^{22,24} Allyl-terminated iPP macromonomers ($[mmmm] = 0.90$ – 0.92) were prepared via metallocene catalysts which undergo chain termination via β -methyl elimination.^{18d,25} For each type of

macromonomer, number-average molecular weights (M_n) of 5–12 kDa were tested (Table 1; sPP: $M_n = 5$ and 8 kDa; iPP: $M_n = 7$ and 12 kDa).

For the amorphous polymer backbone, we selected poly(ethylene-*co*-propylene) (PEP) and poly(ethylene-*co*-1-octene) (PEO), which performed well as soft blocks in *syn*TB and OBC polymers, respectively, due to their low T_g . In order to behave as a thermoplastic elastomer, each chain must contain on average at least two grafts per chain for effective physical cross-linking. Polymers with $M_n > 200$ kDa containing a relatively low weight percentage (5–20 wt %) of semicrystalline side chains were targeted because at higher compositions, the side chains are predicted to produce continuous semicrystalline domains whose plastic deformation of the hard segments would result in lower elastic recovery.²⁶ We focused on transition-metal catalysts that can copolymerize allyl-terminated macromonomers with ethylene and α -olefins. The polymerizations would need to be performed at high temperature to prevent macromonomer or polymer precipitation (60–80 °C for polypropylene in toluene). We chose catalysts which produce high molecular weight polymers at elevated reaction temperatures and can readily enchain sterically hindered allyl-terminated macromonomers. Orthometalated hafnium pyridyl-amido catalysts were developed by Symyx and Dow for use in high-temperature propylene polymerizations.²⁷ These catalysts are thermally robust, have high molecular weight capability, and can incorporate hindered α -olefins, such as 4-methyl-1-pentene,²⁸ which are sterically similar to the allyl end of the macromonomer. We found that the modified hafnium pyridyl-amido complex **1**²⁹ copolymerizes macromonomers with ethylene and α -olefins at 70 °C to form polymers with $M_n > 200$ kDa (Table 1). Typically, ca. 50% of the macromonomer is incorporated during the polymerization, as measured by ¹H NMR.³⁰ Using this method, we prepared three different classes of polyolefin-based graft copolymers.³¹ The first class contains PEO backbones with sPP side chains (PEO-*g*-sPP). The second and third classes contain PEP backbones with sPP (PEP-*g*-sPP) and iPP (PEP-*g*-iPP) side chains. The molecular weight, weight percentage of macromonomer, number of branches per

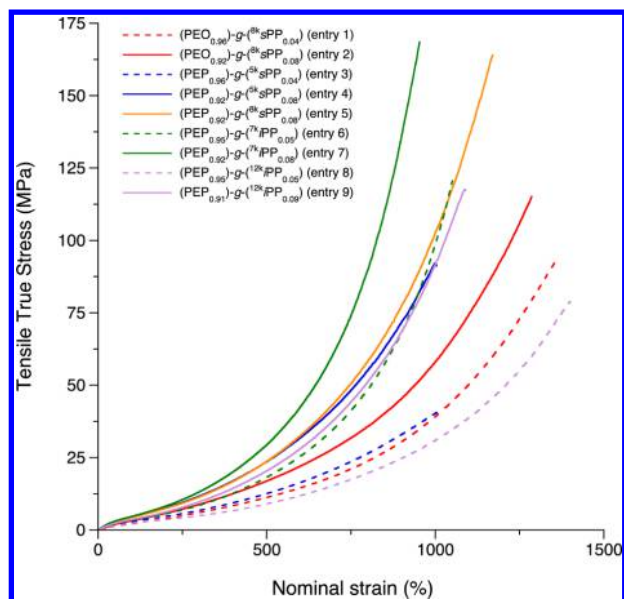


Figure 1. Plot of tensile true stress (MPa) versus nominal strain (%) at 20 °C for the samples in Table 1.

polymer, and thermal and mechanical data for the samples are summarized in Table 1.

The room-temperature true stress–strain curves of the graft copolymers are shown in Figure 1. As anticipated, an increased number of branches per chain leads to more hardening at high strain for all three classes of samples, with samples containing an average of >2 branches per chain showing more strain hardening than similar samples with fewer branches. For example, (PEP)-*g*-(⁵k sPP) and (PEP)-*g*-(⁷k iPP) show more pronounced hardening and less deformation at break with increasing number of side chains (Table 1, entries 3 vs 4 and 6 vs 7). The strain hardening observed at high deformation of all samples is similar to that observed for *syn*TB, which has been shown to be a result of the deformation of lamellar sPP crystals into long fibrillar crystals that orient in the stretching direction. This phenomenon suggests that a short fiber composite structure is formed at large strains³² and indicates that the backbone chains have been effectively cross-linked to form a network. Similar results were observed for the samples containing PEO backbones (entries 1 vs 2).³³

The fraction of maximum applied strain recovered immediately after unloading (elastic recovery) is listed in Table 1 and is plotted for selected samples as a function of maximum strain in Figure 2. The effects of side chain length, backbone structure, and number of side chains were investigated. For the samples with sPP side chains, those with side chains of $M_n = 8$ kDa have the best elastic recovery and strain at break. (PEO)_{0.92}-*g*-(⁸k sPP)_{0.08} (entry 2) has elastic recovery above 85% and up to 1100% elongation to break. (PEP)_{0.92}-*g*-(⁸k sPP)_{0.08} (entry 5) shows elastic recovery above 87% and up to 1300% elongation to break, suggesting that the PEP backbone is superior to PEO as a soft segment. Both samples have an average of two branches per chain. We hypothesize that shorter side chains ($M_n < 5$ kDa) would lead to facile deformation of the networks by chain pullout from crystals during elongation. On the other hand, side chains that are too long ($M_n > 10$ kDa) give high crystallinity with high plastic deformation of the crystalline networks. Both phenomena would result in lower elastic recovery. Indeed, we observed

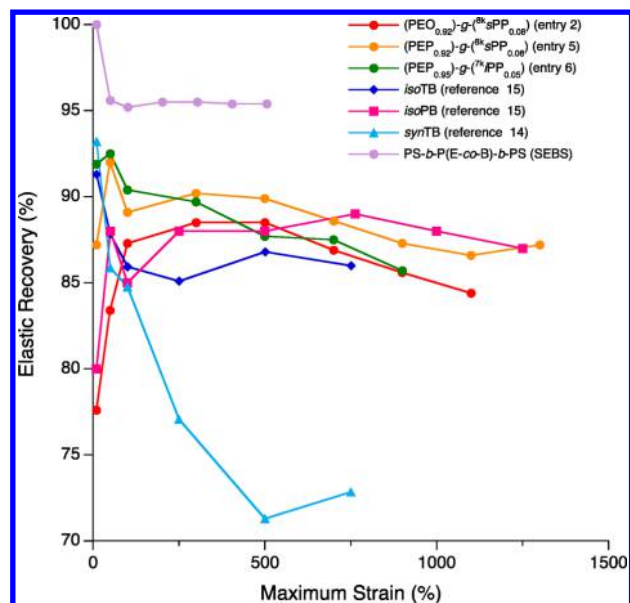


Figure 2. Plot of elastic recovery (%) versus maximum tensile strain (%) at 20 °C for selected samples in Table 1 and comparison samples.

lower elastic recovery in the samples containing iPP grafts of 12 kDa than in the samples with iPP grafts of 7 kDa (Table 1, entries 6 vs 8). Thus, samples containing side chains at intermediate length ($M_n \sim 7$ –8 kDa) have the best elastic recovery.

Although outstanding elastic recovery is observed for both sPP and iPP side chains, samples containing syndiotactic polypropylene grafts exhibit slightly better performance overall. The best sample with sPP side chains, (PEP)_{0.92}-*g*-(⁸k sPP)_{0.08} (entry 5), has better elastic recovery and strain at break (with similar stress at break) than the comparable sample with iPP side chains, (PEP)_{0.92}-*g*-(⁷k iPP)_{0.08} (entry 7). This phenomenon can be explained by the presence and lack of α_c -relaxation in iPP and sPP, respectively.³⁴ Without this relaxation process, sPP has “crystal-fixed” character that makes chain pullout from crystals more difficult than for iPP. Thus, according to this theory, sPP is a more effective anchor than iPP. However, the vast majority of industrial polypropylene is isotactic, so it is important to note that the elastic behavior of the samples containing iPP side chains is still quite good, and they may be suitable for blending with iPP resins.

The elastic recoveries of the graft elastomers were compared with those of the best *syn*TB,¹⁴ *iso*TB,^{14,15} and *iso*PB^{14,15} linear block copolymers as well as a commercial SEBS sample (Kraton G 1652) (Figure 2). The elastic recovery values of the graft polymers are similar to or better than the linear block copolymers synthesized from living transition metal-mediated polymerizations.^{14,15} For example, (PEP)_{0.92}-*g*-(⁸k sPP)_{0.08} shows elastic recovery above 87% with strain at break of 1170% (entry 5), but the elastic recovery of triblock *syn*TB drops below 80% at maximum strains above 250%.¹⁴ (PEP)_{0.96}-*g*-(⁷k iPP)_{0.05} has elastic recovery values above 86% at maximum strain of 900% or less (entry 6), which rivals the elastic recovery value of *iso*TB (85–90% at a maximum strain of 800% or less) and *iso*PB (85–89% at a maximum strain of 1300% or less).¹⁵ Thus, for polymers of similar molecular weight and composition, the introduction of crystalline sPP and iPP side chains into the graft copolymers yields comparable or better results than incorporating them into a linear block copolymer.³⁵ The elastic recovery

values of these graft copolymers also exceed those of *a*PP-*g*-iPP graft copolymers reported by researchers at ExxonMobil (87% at 150% strain).^{18c} For comparison, the elastic recovery values of PEP-*g*-*s*PP are higher even at higher strains (88% at 900% strain). The results were also compared to EO-*g*-iPP copolymers prepared by reacting amine or hydroxyl-functionalized iPP with maleic anhydride-functionalized EO. The samples prepared by postfunctionalization exhibit lower true stress at break (13–17 MPa)^{20a} than the samples reported herein (41–169 MPa) as well as lower elastic recoveries. According to a report by Hiltner and co-workers, the best elastic recovery of INFUSE OBCs is 95% at 300% strain.³⁶ However, elastic recoveries at higher strains were not reported. We observed a sharp dropoff in elastic recovery for similar OBC samples at strains above 400% using a different measurement protocol.³⁷ The mechanical performance of such OBC block copolymers should also deteriorate faster at elevated temperature than the present graft systems due to the lower T_m of PE relative to *s*PP and iPP. Although SEBS shows higher elastic recoveries than the graft copolymers reported herein, the strain at break is lower (Figure 2) and its use temperature is limited by the rather low T_g of PS.

In summary, we report a new family of polyolefin-based elastomers whose physical properties rival or exceed those of linear block copolymers. The synthesis is conducted at high polymerization temperature using a thermally stable, nonliving hafnium pyridyl-amido catalyst. The best elastic recovery was observed for elastomers with branches of intermediate length ($M_n = 7\text{--}8\text{ kDa}$). Both iPP and *s*PP grafts are highly effective in providing physical cross-links for elastic behavior. We are currently investigating the effect of graft distribution and spacing between branch points on the physical properties as well as testing new semicrystalline side chains and amorphous polymer backbones. The modularity and flexibility of synthesis will enable a wide range of structure–property studies including graft copolymers containing two or more types of side chains (e.g., *s*PP and iPP) that can produce a multiplicity of anchoring crystallite populations.

■ ASSOCIATED CONTENT

■ Supporting Information

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Synthesis and characterization of graft copolymers (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail ghf@mrl.ucsb.edu (G.H.F.).

*E-mail gc39@cornell.edu (G.W.C.).

Present Addresses

F.D.: The Dow Chemical Company, 2301 N. Brazosport Blvd., Freeport, TX 77541.

G.D.V.: DuPont Central Research and Development, 200 Powder Mill Rd., Wilmington, DE 19803.

T.S.: Toho Titanium Co., Ltd., 3-3-5, Chigasaki, Chigasaki-shi, Kanagawa Prefecture, 253-8510, Japan.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Holden, G.; Kricheldorf, H. R.; Quirk, R. P. *Thermoplastic Elastomers*, 3rd ed.; Hanser Publishers: Munich, 2004. (b) Brobny, J. G. *Handbook of Thermoplastic Elastomers*; William Andrews: New York, 2007.
- (2) Gehlsen, M. D.; Almdal, K.; Bates, F. S. *Macromolecules* **1992**, *25*, 939–943.
- (3) (a) Xiong, M.; Schneiderman, D. K.; Bates, F. S.; Hillmyer, M. A.; Zhang, K. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 8357–8362. (b) Wang, S.; Vajjala Kesava, S.; Gomez, E. D.; Robertson, M. L. *Macromolecules* **2013**, *46*, 7202–7212. (c) Jiang, F.; Wang, Z.; Qiao, Y.; Wang, Z.; Tang, C. *Macromolecules* **2013**, *46*, 4772–4780.
- (4) For an excellent overview of strategies used to produce stereoblock copolymers, see: Hustad, P. D. *Science* **2009**, *325*, 704–707.
- (5) Natta, G. *J. Polym. Sci.* **1959**, *34*, 531–549.
- (6) Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrell, J. R.; Mulhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 3851–3858.
- (7) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030–2031.
- (8) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771–3778.
- (9) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelä, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348–4355.
- (10) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217–219.
- (11) Although the T_g of atactic polypropylene is sometimes reported to be $-20\text{ }^{\circ}\text{C}$, detailed studies on model compounds suggest that it is closer to $0\text{ }^{\circ}\text{C}$ for a sample with no regiodefects. For a detailed report, see: Xu, Z.; Mays, J.; Chen, X.; Hadjichristidis, N.; Schilling, F. C.; Bair, H. E.; Pearson, D. S.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2560–2566.
- (12) (a) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30–92. (b) Edson, J. B.; Wang, Z.; Kramer, E. J.; Coates, G. W. *J. Am. Chem. Soc.* **2008**, *130*, 4968–4977. (c) Cherian, A. E.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 13770–13771. (d) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236–2257. (e) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134–5135.
- (13) (a) Shiono, T. *Polym. J. (Tokyo, Jpn.)* **2011**, *43*, 331–351. (b) Crawford, K. E.; Sita, L. R. *J. Am. Chem. Soc.* **2013**, *135*, 8778–8781. (c) Giller, C.; Gururajan, G.; Wei, J.; Zhang, W.; Hwang, W.; Chase, D. B.; Rabolt, J. F.; Sita, L. R. *Macromolecules* **2011**, *44*, 471–482. (d) Harney, M. B.; Zhang, Y.; Sita, L. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2400–2404.
- (14) Hotta, A.; Cochran, E.; Ruokolainen, J.; Khanna, V.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y.-W.; Shimizu, F.; Cherian, A. E.; Hustad, P. D.; Rose, J. M.; Coates, G. W. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15327–15332.
- (15) Rose, J. M.; Deplace, F.; Lynd, N. A.; Wang, Z.; Hotta, A.; Lobkovsky, E. B.; Kramer, E. J.; Coates, G. W. *Macromolecules* **2008**, *41*, 9548–9555.
- (16) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714–719.
- (17) Schulz, C. J.; Milkovich, R. *J. Appl. Polym. Sci.* **1982**, *27*, 4773–4786.
- (18) (a) Markel, E. J.; Weng, W. Q.; Peacock, A. J.; Dekmejian, A. H. *Macromolecules* **2000**, *33*, 8541–8548. (b) Dekmejian, A. H.; Soares, J.

- B. P.; Jiang, P. J.; Garcia-Franco, C. A.; Weng, W. Q.; Fruitwala, H.; Sun, T.; Sarzotti, D. M. *Macromolecules* **2002**, *35*, 9586–9594.
- (c) Weng, W.; Dekmezian, A. H.; Markel, E. J.; Peters, D. L. U.S. Patent 6,184,327, Feb 6, 2001. (d) Weng, W. Q.; Markel, E. J.; Dekmezian, A. H. *Macromol. Rapid Commun.* **2000**, *21*, 1103–1107.
- (19) Haag, M. C.; Simon, L. C.; Soares, J. B. P. *Macromol. Theory Simul.* **2003**, *12*, 142–152.
- (20) (a) Kuhlmann, R. L.; Wenzel, T. T.; Cheung, Y. W.; Hustad, P. D.; Carnahan, E. H.; Briggs, J. R.; Jazdzewski, B. A.; Liang, W.; Mori, R.; Kizu, K.; Kawahara, N.; Matusa, S.; Kojoh, S.; Kashiwa, N. US Patent US2009/0186985 A1, 2009. (b) Kojoh, S.; Matsugi, T.; Kashiwa, N. European Patent application EP1270647 A1, 2001. (c) Datta, S. European Patent application EP0366412 A2, 1989. (d) Krom, J. A.; Wang, X. European Patent application EP 0964022 A1, 1999.
- (21) (a) Iha, R. K.; Wooley, K. L.; Nyström, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.* **2009**, *109*, 5620–5686. (b) Tsitsilianis, C. Synthesis of Block and Graft Copolymers. In *Controlled/Living Polymerizations*; Matyjaszewski, K., Müller, A. H. E., Eds.; Wiley-VCH: Weinheim, 2009; pp 445–492.
- (22) Cherian, A. E.; Lobkovsky, E. B.; Coates, G. W. *Macromolecules* **2005**, *38*, 6259–6268.
- (23) Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145–165.
- (24) Ohtaki, H.; Coates, G. W. Manuscript in preparation.
- (25) Isotactic polypropylene (iPP) macromonomers were synthesized using the procedure described in the following patent: Ohtaki, H.; Shimizu, F.; Coates, G. W.; Fredrickson, G. H. PCT Int. Appl. WO 2013061974, 2013.
- (26) Ruokolainen, R.; Mezzenga, R.; Fredrickson, G. H.; Kramer, E. J.; Hustad, P. D.; Coates, G. W. *Macromolecules* **2005**, *38*, 851–860.
- (27) Boussie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M. K.; Murphy, V.; Shoemaker, J. A. W.; Turner, H.; Rosen, R. K.; Stevens, J. C.; Alfano, F.; Busico, V.; Cipullo, R.; Talarico, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3278–3283.
- (28) Froese, R. D. J.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *J. Am. Chem. Soc.* **2007**, *129*, 7831–7840.
- (29) (a) Domski, G. J. Doctoral Dissertation, Cornell University, 2008. (b) Coates, G. W.; Domski, G. J. PCT Int. Appl. WO 2008112133, 2008.
- (30) Residual macromonomer could not be separated from the graft copolymer due to its similar solubility to the graft copolymer. To confirm the necessity of covalent incorporation of the macromonomer, blends of the backbone and macromonomer were cast into thin films and compared qualitatively with films of the graft copolymers. In contrast to the graft copolymers, the blends did not exhibit elastic properties.
- (31) (a) *General procedure for the synthesis of PEP graft copolymers*: Inside a glovebox, a flame-dried, 6 oz. Lab-Crest pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was charged with macromonomer (0.20 or 0.40 g), toluene (50 mL), and (2,6-di-*tert*-butyl-4-methylphenoxy)diisobutylaluminum (DIBAP) (0.040 mL of 0.25 M solution, 0.010 mmol), which was added as a scavenger to remove traces of water. The reactor was then sealed, brought out of the glovebox, and equilibrated at the appropriate temperature (100 °C for iPP macromonomers and 70 °C for sPP macromonomers) for approximately 15 min to ensure the macromonomer was completely dissolved. The reactor was cooled to 70 °C, and propylene (6 psig) was added and allowed to equilibrate for 10 min at 70 °C. Then an overpressure of ethylene (30 psig) was applied. During this time, in the glovebox, **1** (3.2 mg, 5.3 μ mol) and B(C₆F₅)₃ (2.7 mg, 5.0 μ mol) were weighed into separate 20 mL vials. Toluene (2 mL) was added to each vial. The solutions were mixed and pulled into a 5 mL gas-tight syringe. The needle was capped with a septum, and the syringe was brought out of the box. The catalyst solution was injected into the reactor. The reaction was stirred for 15 min at 70 °C under a constant feed of ethylene (30 psig) and then quenched with methanol (5 mL), and the reactor was vented. The polymer was precipitated in copious amounts of methanol (300 mL), collected, washed with methanol, and dried under vacuum to constant weight. (b) *General procedure for the synthesis of PEO graft copolymers*: The procedure is similar to that described for the PEP copolymers, except 1-octene (2.0 mL, 13 mmol) is added to the reaction vessel at the same time as the solvent, macromonomer, and scavenger, and the propylene pressurization step is omitted. Instead, an overpressure of ethylene (30 psig) was added and allowed to equilibrate for 10 min at 70 °C prior to catalyst addition.
- (32) (a) Deplace, F.; Wang, Z.; Lynd, N. A.; Hotta, A.; Rose, J. M.; Hustad, P. D.; Tian, J.; Ohtaki, H.; Coates, G. W.; Shimizu, F.; Hirokane, K.; Yamada, F.; Shin, Y.-W.; Rong, L.; Toki, S.; Hsiao, B. S.; Fredrickson, G. H.; Kramer, E. J. *J. Polym. Sci., Part B: Polym. Phys.* **2010**, *48*, 1428–1437. (b) Wang, Z.; Niu, Y.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y.-W.; Shimizu, F.; Zuo, F.; Rong, L.; Hsiao, B. S.; Coates, G. W. *Macromolecules* **2010**, *43*, 6782–6788. (c) Deplace, F.; Scholz, A. K.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y.-W.; Shimizu, F.; Zuo, F.; Rong, L.; Hsiao, B. S.; Coates, G. W. *Macromolecules* **2012**, *45*, 5604–5618.
- (33) See [Supporting Information](#) (Figure S1 and S2) for individual stress–strain plots of the effect of graft density in samples containing sPP and iPP grafts, respectively.
- (34) Hu, W. G.; Schmidt-Rohr, K. *Acta Polym.* **1999**, *50*, 271–285.
- (35) The composition of the linear block copolymers is similar to that of the graft copolymers overall, with hard blocks of $M_n = 8$ –17 kDa and total $M_n = 120$ –200 kDa. The linear block copolymers contain approximately 20 wt % hard blocks. In contrast, 10–20 wt % macromonomer is added to the graft copolymerizations, but incorporations are typically 4–9 wt %.
- (36) Wang, H. P.; Khariwala, D. U.; Cheung, W.; Chum, S. P.; Hiltner, A.; Baer, E. *Macromolecules* **2007**, *40*, 2852–2862.
- (37) In the elastic recovery tests reported by Wang et al.,³⁶ there was a 10 min delay between grip release and measurement of the recovered length of the sample. This differs from the measurements reported here, in which there was no delay. The difference in protocol may account for some of the variation we observed when testing the OBC samples. Denier, C.; Deplace, F.; Kramer, E. J., unpublished results.