Synthesis of Polyethylene Graft Block Copolymers from Styrene, Butyl Acrylate, and Butadiene

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The recent development of single-site homogeneous catalysts based on well-defined coordination compounds has created new opportunities to control the composition, molecular weight, and stereochemistry of polyolefins.[1−6] The majority of olefin polymerization catalysts are intolerant of most functionalized monomers.[1,7,8] Few methods exist for copolymerizing functionalized monomers with olefins, and these methods remain limited in the range of monomers that can be copolymerized efficiently.[9−25] We have recently described a strategy for the copolymerization of alkoxyamines with olefins; the alkoxyamine comonomers function as free-radical initiators allowing for the synthesis of graft copolymers.[13,18] Polyolefins with blocks or grafts of functionalized polymers would have improved adhesion to and compatibility with metals, glass, or other polymers and are an interesting synthetic target. In this contribution, we report the synthesis of polyethylene graft copolymers containing low levels of grafts of functionalized homopolymers and block polymers along the backbone.

We synthesized the graft polymers in two steps (Scheme 1). In the first step the polyethylene backbone was prepared by the catalytic copolymerization of ethylene, butene (approximately 10−20% weight fraction), and alkoxyamine, **1**, using bis(*n*-butylcyclopentadienyl)zirconium dichloride and methylaluminoxane (Scheme 1).[13,18,26] This metallocene was shown by others to yield highly linear polyethylene.[27] Butene was copolymerized with the ethylene to increase the solubility and ease of handling of the backbone; linear polyethylene with no short-chain branches has poor solubility in most solvents. In the second step the grafts were polymerized from the backbones using the alkoxyamines as the initiators. The levels of incorporation of the alkoxyamines (vide infra) were kept low to provide very low grafting densities on the polyethylenes. The alkoxyamine comonomer was designed to incorporate a cleavable tertiary amine and a recently developed alkoxyamine which was shown by Hawker et al. to polymerize styrenes, acrylates, and dienes in a controlled manner (Scheme 1).[28−31]

These nitroxide-based polymerizations meet most of the criteria of living systems: the polymers show a linear increase in molecular weight with respect to conversion of the monomer, the polymers have low polydispersities, and the polymerizations can be used to prepare block copolymers. We choose this method for synthesizing the grafts because of the range of monomers that could be polymerized, the control over the molecular weight and polydispersity of the grafts, and the ease of polymerization. This synthetic strategy provides a means for independently controlling the length and number of grafts as well as the olefinic composition and microstructure of the polyolefin backbone.[5,13,18,32]

The free-radical grafting reactions were carried out in the presence of a small amount (approximately 50 mg) of the initiator **2** (Scheme 1); polymerizations in the absence of **2** were not well controlled, and the resultant polymers were insoluble and believed to be cross-linked. Under these conditions, the grafts and homopolymers were synthesized simultaneously. Provided that initiation and propagation from **2** proceed as efficiently from the copolymerized **1**, the molecular weights and polydispersities of the homopolymers, $\mathbf{G_1}$, should be similar to that of the grafted chains. We tested this assumption by measuring the molecular weight and polydispersity of the grafts and comparing these to the values for the homopolymer $\mathbf{G_1}$. The grafts were bonded to the backbone through an amine; this amine was cleaved by from the backbone by reacting with a chloroformate (Scheme 2). The branches were easily recovered and characterized by GPC. The grafts of entry 1 in Table 1 that had been cleaved from the backbone had values for the M_n and polydispersity, PDI, of 67 000 g/mol and 1.20, which were very similar to those of $\mathbf{G_1}$ (Table 1). Thus, for all other entries in Table 1, we could deduce the molecular weights and polydispersites of the grafts from the characteristics of the homopolymers $\mathbf{G_1}$ and $\mathbf{G_2}$.

As we were particularly interested in low grafting densities, the determination of the number of grafts presented an analytical challenge. The number of branch points in the backbone was too low to count by NMR or IR methods so we developed a method to count them. The number of grafting sites was calculated from the molecular weights of the backbone polymers and grafts and the mole fraction of the grafts in the final polymer. First, we measured the viscosity molecular weight of the backbone. Next, we synthesized the grafts in the presence of **2** and separated the homopolymer from the grafted polymer. The homopolymer was characterized by gel permeation chromatography to find the molecular weight and polydispersity of the graft, and the grafted polymer was characterized by ^{1}H NMR to find the ratio of the grafts to the backbone. From this information the number of grafts per backbone was calculated.

The polymers that we synthesized are listed in Table 1. The viscosity molecular weights, M_v, of the backbones ranged from 268 000 to 417 000 g/mol, and the number of grafts per backbone ranged from 0.20 to 1.13. The PDI's of the grafts were mostly below 1.20. In entries 1−4 we synthesized backbones and grafts with similar molecular weights but with different numbers of grafts per backbone. In entries 5−7 we used the same backbone to synthesize grafts with decreasing molecular weights. We also prepared a series of graft block copolymers analogously (entries 6, 8, and 9). Four general types of graft block copolymers were prepared;

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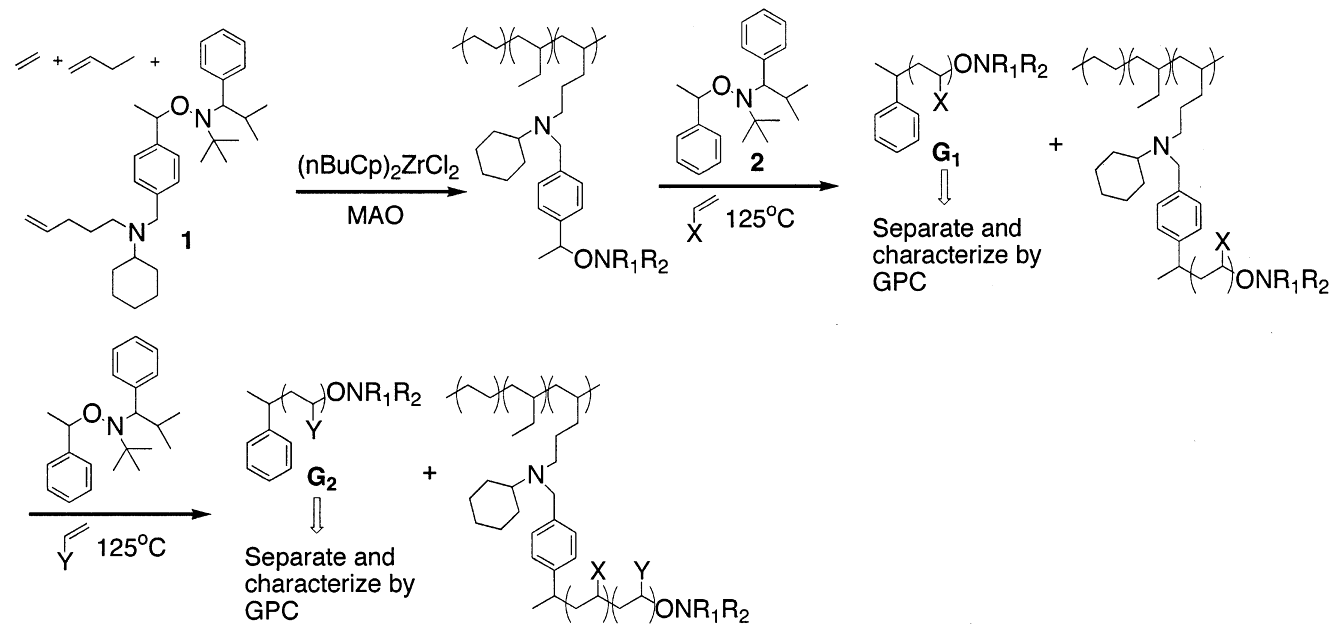
Scheme 1. Synthesis of Graft Block Copolymers



Scheme 2. Cleavage of Grafts from the Backbones

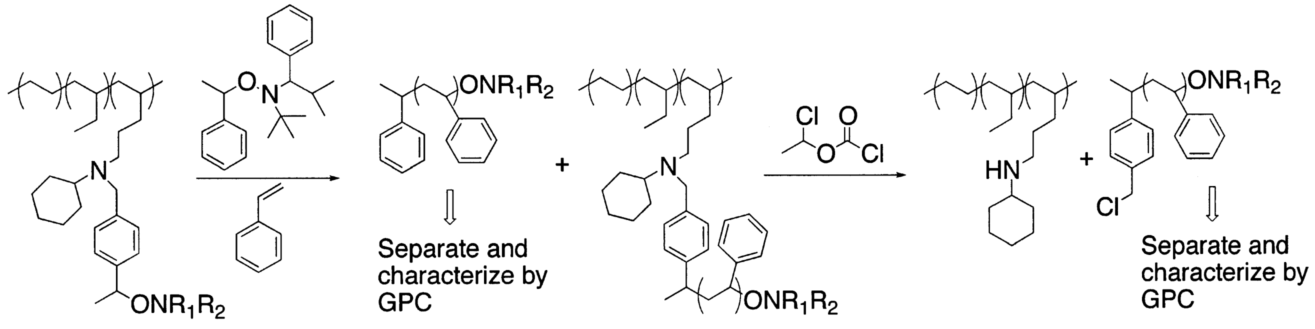


Table 1. Characterization of the Backbones and Grafts

entry	M_v[a] (g/mol)	N_B[b]	no. of grafts/chain	graft$_1$[c]	M_n of $\mathbf{G_1}$[d,e] (g/mol)	PDI of $\mathbf{G_1}$[d]	graft$_2$	M_n of $\mathbf{G_2}$[d,f] (g/mol)	PDI of $\mathbf{G_2}$[c]
1	291 000	13	1.13	S	63 000	1.20			
					67 000[g]	1.20[g]			
2	287 000	18	0.72	S	67 000	1.19			
3	318 000	13	0.39	S	65 000	1.19			
4	268 000	8.1	0.20	S	53 000	1.17			
5	417 000	10	0.93	S	65 000	1.20			
6	417 000	10	0.94	S	42 000	1.14	Bd	53 000	1.17
7	417 000	10	1.30	S	25 000	1.21			
8	417 000	10	0.90	Bd	47 000	1.18	S	24 000	1.25
9a	417 000	10	0.80	BA	22 000	1.26	S	44 000	1.16
9b	417 000	10	0.80	BA	22 000	1.26	Bd	66 000	1.18

[a] Viscosity average molecular weight of the backbone. [b] Weight fraction of butene in the backbone. [c] S = styrene, Bd = butadiene, and BA = *n*-butyl acrylate. [d] Measured against polystyrene standards by GPC. [e] $\mathbf{G_1}$ is the homopolymer synthesized concurrently with the first graft. [f] $\mathbf{G_2}$ is the homopolymer synthesized concurrently with the second graft. [g] Measured from the grafts that were cleaved from the backbone.

styrene-*block*-butadiene (entry 6), butadiene-*block*-styrene (entry 8), butyl acrylate-*block*-styrene (entry 9a), and butyl acrylate-*block*-butadiene (entry 9b).

In summary, we have shown that the copolymerization of olefinic alkoxyamines provides a general strategy to prepare polyolefin graft copolymers. A particular advantage of this approach is the ability to prepare graft block copolymers. Although many different methods to synthesize polyolefin graft copolymers are known, few allow for the controlled synthesis of blocky grafts.[12,13,17,18,33] These materials might be expected to exhibit unusual morphologies in the solid state, as observed for the linear triblock copolymers.[34−36] Further studies to investigate the phase morphology as well as to extend this method to other architectures are in progress.[16,20,27,37−43]

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

References and Notes

(1) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345.

(2) Lehmus, P.; Rieger, B. *Science* **1999**, *285*, 2081−2082.

(3) Chum, P. S.; Kruper, W. J.; Guest, M. J. *Adv. Mater.* **2000**, *12*, 1759−1767.

(4) Bochmann, M.; Pindado, G. J.; Lancaster, S. J. *J. Mol. Catal. A: Chem.* **1999**, *146*, 179−190.

(5) McKnight, A. L.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 2816−2825.

(6) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219.

(7) Stehling, U. M.; Stein, K. M.; Kesti, M. R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2019−2027.

(8) Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479−1494.

(9) Baumert, M.; Heinemann, J.; Thomann, R.; Mulhaupt, R. *Macromol. Rapid Commun.* **2000**, *21*, 271−276.

(10) Beyer, F. L.; Gido, S. P.; Buschl, C.; Iatrou, H.; Uhrig, D.; Mays, J. W.; Chang, M. Y.; Garetz, B. A.; Balsara, N. P.; Tan, N. B.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 2039−2048.

(11) Cheng, C.; Yang, N.-L. *Polym. Prepr.* **2000**, *41*, 1197−1198.

(12) (a) Chung, T. C.; Janvikul, W. *J. Organomet. Chem.* **1999**, *581*, 176−187. (b) Chung, T. C. *Prog. Polym. Sci.* **2002**, *27*, 39−85.

(13) Fox, P. A.; Waymouth, R. M.; Hawker, C. J. *Polym. Prepr.* **1999**, *40*, 872−873.

(14) Gido, S. P.; Lee, C.; Pochan, D. J.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1996**, *29*, 7022−7028.

(15) Iatrou, H.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 6697−6701.

(16) Janata, M.; Lochmann, L.; Brus, J.; Vlcek, P. *Macromolecules* **2001**, *34*, 1593−1599.

(17) Miwa, Y.; Yamamoto, K.; Sakaguchi, M.; Shimada, S. *Macromolecules* **2001**, *34*, 2089−2094.

(18) Stehling, U. M.; Malmstroem, E. E.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **1998**, *31*, 4396−4398.

(19) Velis, G.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1136−1138.

(20) Xenidou, M.; Beyer, F. L.; Hadjichristidis, N.; Gido, S. P.; Tan, N. B. *Macromolecules* **1998**, *31*, 7659−7667.

(21) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1204.

(22) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.

(23) Hong, S. C.; Pakula, T.; Matyjaszewski, M. *Macromol. Chem. Phys.* **2001**, *202*, 3392−3402.

(24) Matyjaszewski, M.; Teodorescu, M.; Miller, P. J.; Peterson, M. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2440−2448.

(25) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901−915.

(26) In a typical polymerization a Parr reactor was charged with 195 mL of toluene, 0.7 g of methylaluminumoxane, 0.5 g of **1**, and 50 g of butene. The reactor was equilibrated with 60 psi of ethylene for 30 min. The zirconium catalyst (0.7 mg) was diluted in 5 mL of toluene and injected into the Parr reactor. The polymerization was run for 1 h and quenched by the injection of methanol. A typical polymerization yielded 15−20 g.

(27) Kokko, E.; Malmberg, A.; Lehmus, P.; Lofgren, B.; Seppala, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 376−388.

(28) Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **2000**, *33*, 363−370.

(29) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904−3920.

(30) (a) Dao, J.; Benoit, D.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2161−2167. (b) Rodlert, M.; Harth, E.; Rees, I.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4749−4758. (c) Blomberg, S.; Ostberg, S.; Harth, E.; Bosman, A. W.; Van Horn, B.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1309−1320.

(31) In a typical polymerization 0.50 g of backbone polymer, 0.050 g of **2**, and 20 mL of styrene were added to a glass vial. The contents of the vial were frozen in liquid nitrogen, evacuated with a vacuum, and thawed three times. The vial was flame-sealed under vacuum. The polymerizations were run at 125 °C for 1−4 h.

(32) Fan, W.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 8619−8625.

(33) Koo, K.; Marks, T. J. *CHEMTECH* **1999**, *29*, 13−19.

(34) Avgeropoulos, A.; Dair, B. J.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1997**, *30*, 5634−5642.

(35) Brinkmann, S.; Stadler, R.; Thomas, E. L. *Macromolecules* **1998**, *31*, 6566−6572.

(36) Breiner, U.; Krappe, U.; Thomas, E. L.; Stadler, R. *Macromolecules* **1998**, *31*, 135−141.

(37) Hadjichristidis, N.; Xenidou, M.; Iatrou, H.; Pitsikalis, M.; Poulos, Y.; Avgeropoulos, A.; Sioula, S.; Paraskeva, S.; Velis, G.; Lohse, D. J.; Schulz, D. N.; Fetters, L. J.; Wright, P. J.; Mendelson, R. A.; Garcia-Franco, C. A.; Sun, T.; Ruff, C. *Macromolecules* **2000**, *33*, 2424−2436.

(38) Lee, C.; Gido, S. P.; Pitsikalis, M.; Mays, J. W.; Tan, N. B.; Trevino, S. F.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 3732−3738.

(39) Malmberg, A.; Kokko, E.; Lehmus, P.; Lofgren, B.; Seppala, J. V. *Macromolecules* **1998**, *31*, 8448−8454.

(40) McLeish, T. C. B. *Macromolecules* **1988**, *21*, 1062−1070.

(41) McLeish, T. C. B.; Larson, R. G. *J. Rheol.* **1998**, *42*, 81−110.

(42) McLeish, T. C. B.; Allgaier, J.; Bick, D. K.; Bishko, G.; Biswas, P.; Blackwell, R.; Blottiere, B.; Clarke, N.; Gibbs, B.; Groves, D. J.; Hakiki, A.; Heenan, R. K.; Johnson, J. M.; Kant, R.; Read, D. J.; Young, R. N. *Macromolecules* **1999**, *32*, 6734−6758.

(43) Shroff, R. N.; Mavridis, H. *Macromolecules* **1999**, *32*, 8454−8464.

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