

Synthesis of Poly(olefin) Graft Copolymers by a Combination of Metallocene and “Living” Free Radical Polymerization Techniques

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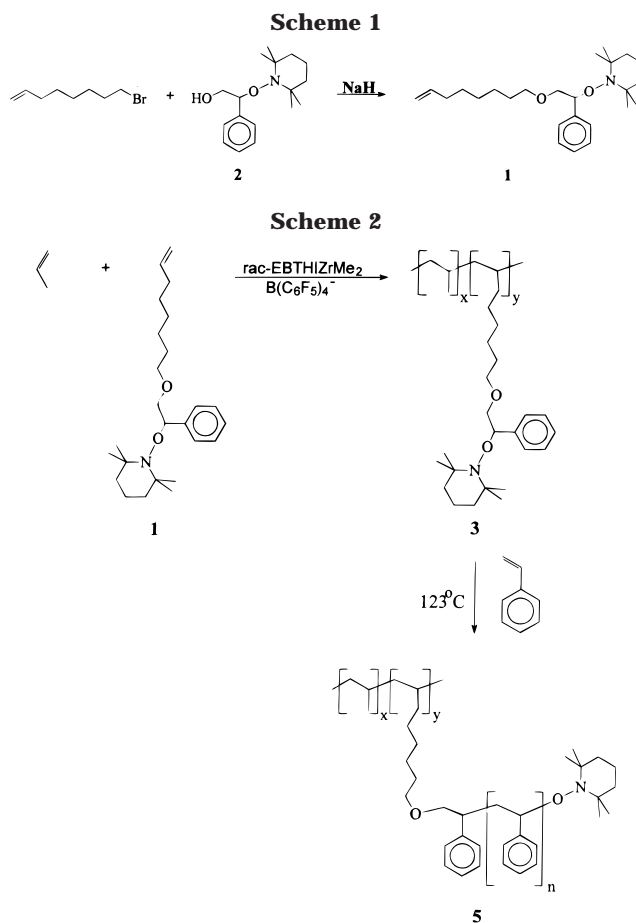
The development of novel synthetic methods is creating new opportunities for the preparation of macromolecules with defined architectures and controlled physical properties. An excellent example of this is the discovery of new catalysts for the polymerization of olefins leading to polymers of defined regio- and stereochemistry.^{1,2} However, the limited tolerance of these processes for functional groups restricts the end uses of polyolefins, especially where adhesion or compatibility with functionalized polymers, metal, or glass is desired.³ While an effective strategy for improving the compatibility of immiscible polymer systems is the use of block or graft copolymers as compatibilizing agents,^{4–6} the synthetic challenges in preparing block or graft polymers of polyolefins, particularly poly(α -olefins), has proven formidable.^{2,3,7} Chung has recently developed an interesting approach to polyolefin/poly(methyl methacrylate) graft polymers by careful introduction of oxygen to a borane-functionalized polyolefin.^{8–11}

As part of our interest in developing new routes to functionalized polyolefins,^{12,13} we were intrigued by the prospect of copolymerizing sterically hindered alkoxyamines with cationic¹⁴ group 4 metallocene catalysts.^{15–18} The use of functionalized alkoxyamines as unimolecular initiators in nitroxide-mediated “living” free radical polymerizations has recently attracted considerable attention due to the ability to accurately control the molecular weight and chain ends of narrow polydispersity vinyl polymers.^{19–24} One of the main advantages of these alkoxyamine derivatives is their stability and compatibility with a wide range of reaction conditions. This not only allows a variety of functional groups to be introduced into the alkoxyamine structure²⁵ but also may permit these functionalized alkoxyamines to be used as reactive monomers in a wide selection of polymerization reactions.²⁶ In this communication, we detail the copolymerization of an alkene substituted alkoxyamine with α -olefins, such as propylene or 4-methylpentene, using a cationic metallocene catalyst. The functionalized poly(olefin)s can then be employed as multifunctional polymeric initiators leading to novel, well-defined poly(olefin) graft and graft-block copolymers.

The alkene substituted alkoxyamine, **1**, was synthesized by reaction of the hydroxy functionalized derivative, **2**, with 1-bromooct-8-ene in the presence of sodium hydride and obtained in 81% yield after purification

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(Scheme 1). Copolymerization of **1** with propylene in the presence of *rac*-ethylene-1,2-bis(4,5,6,7-tetrahydro-1-indenyl)dimethylzirconium(IV) (*rac*-EB(THI)ZrMe₂) and *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate ([HNMe₂(C₆H₅)]⁺[B(C₆F₅)₄]⁻) afforded the copolymer **3** [*M*_n = 28 000; PD = 1.80] (Scheme 2).²⁷ Analysis of **3** by ¹H NMR revealed that the level of incorporation of the alkoxyamine unit into the copolymer correlated well with that of the feed ratio. Similar results²⁸ were obtained with 4-methylpentene to give the functionalized polyolefin, **4**, which indicates that **1** is compatible with a range of different α -olefins.

The presence of alkoxyamine initiating groups then allows grafted vinyl polymer chains to be grown from the poly(olefin) backbone, **3–4**, using “living” free radical techniques. For example, heating a mixture of **3** and styrene (200 equiv per initiating group) at 123 °C under argon in the presence of acetic anhydride gave the graft copolymer, **5b**, which was shown to have a molecular weight, *M*_n, of 210 000 and a polydispersity of 2.0. The high polydispersity of **5b** is a direct result of the polydisperse nature of the starting poly(olefin) and the statistical variation in the number of initiating groups per backbone and is not indicative of poor control during the “living” free radical grafting process.

To determine the degree of control of the free radical grafting process, the individual grafted polystyrene chains were cleaved from the poly(olefin) backbones with trimethylsilyl iodide. For example, reaction of **5b** with trimethylsilyl iodide leads to cleavage of the ether

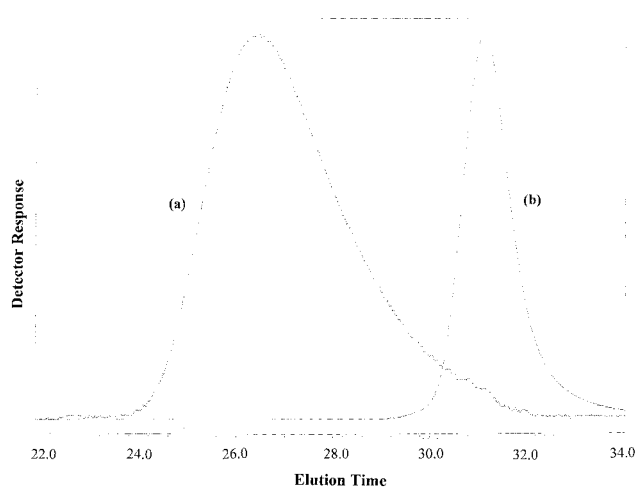


Figure 1. GPC traces for (a) the grafted polystyrene-poly(4-methylpentene) copolymer, **5b**, and (b) the product obtained from cleavage of the graft copolymer with trimethylsilyl iodide, **6b**.

Scheme 3

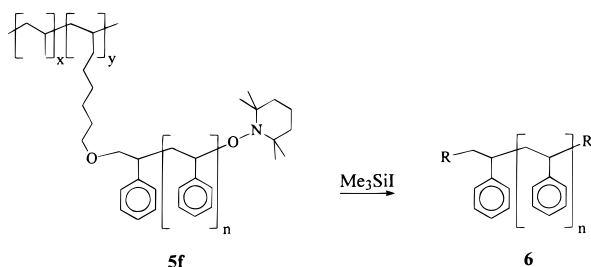


Table 1. Polystyrene Equivalent Molecular Weights and Polydispersity of Graft Copolymers Obtained from the Reaction of **3** or **4** with Styrene (Unless Otherwise Indicated) at 123 °C

starting material	compound	monomer ratio	experimental M_n	polydispersity
3	5a	100:1	130 000	1.9
3	5b	200:1	210 000	2.0
3	5c	300:1	300 000	2.2
4	5d	100:1	15 000	1.5
4	5e	200:1	32 000	1.6
4	5f	290:1	43 000	1.5
4	5g	580:1	110 000	2.4
4	5h	1150:1	165 000	2.9
4	5i^a	250:1	40 000	1.6
4	5j^b	250:1	37 000	1.5
4	5k^c	250:1	39 000	1.6
4	5l^d	250:1	35 000	1.8

^a 4-Chlorostyrene. ^b 4-Methylstyrene. ^c 3:1 Styrene/butyl acrylate. ^d 3:1 Styrene/methyl methacrylate.

groups to give, after purification, the individual polystyrene grafts, **6** (Scheme 3). The molecular weight of **6** ($M_n = 16\,500$, PD = 1.15, Figure 1b) is close to the theoretical value²⁹ of 18 700 expected from the molar ratio of styrene to initiating group and indicates that the "living" free radical polymerization of vinyl monomers from a functionalized poly(olefin) backbone is a controlled process (Figure 1). Similar results were obtained for the poly(4-methylpentene) derivatives and indicates that formation of homopolystyrene is not a major process in these graft copolymer systems.

As can be seen from Table 1 the structure of the graft copolymer, **5**, can be readily controlled with the molecular weight of **5** increasing in a systematic way with increasing molar ratio of styrene. More importantly,

Table 2. Molecular Weights and Polydispersity of Polystyrenes, **6**, Obtained after Cleavage of **5** with Trimethylsilyl Iodide

starting material	experimental M_n	polydispersity	theoretical MW
5a	8 000	1.16	9 300
5b	16 500	1.15	18 700
5c	30 500	1.20	27 000
5d	8 500	1.18	9 300
5e	17 000	1.16	18 700
5f	28 500	1.12	27 000
5g	44 000	1.31	54 000
5h	75 000	1.42	108 000

cleavage of **5** leads to low polydispersity materials with molecular weights close to the theoretical values (Table 2). This novel procedure was also used to prepare graft copolymers from functionalized styrenes such as *p*-chlorostyrene, *p*-acetoxystyrene, or mixtures of styrene and acrylate/methacrylate monomers. The latter give rise to random copolymer grafts which due to the high styrene content (75 mol %) are also expected to grow in a controlled manner.

The presence of a significant number of alkoxyamine functional groups at the chain ends of the graft copolymers, **5**, also provides the unique opportunity to prepare novel grafted, block copolymers. To investigate this possibility the polystyrene-*g*-poly(olefin), **5f**, was heated at 123 °C under argon with *p*-acetoxystyrene for 8 h to give the grafted block copolymer, **7**. As expected the molecular weight was observed to increase from $M_n = 43\,000$ (PD = 1.70) to $M_n = 130\,000$ (PD = 1.95). No significant overlap of the GPC traces was observed, indicating efficient block copolymer formation, while ¹H NMR spectroscopy supported the sequence of reactions leading to **7**. Similar behavior was observed on the reaction of **5f** with a 2:1 mixture of styrene and butyl acrylate, a 3:1 mixture of styrene and methyl methacrylate, and styrene. The efficiency of the block copolymerization was also demonstrated by comparison of the cleavage products obtained from the starting graft copolymer, **5f**, and the graft copolymer, **8**, obtained from chain extension of **5f** with styrene.

In conclusion, we have demonstrated that the metallocene/borate-catalyzed polymerization of alkoxyamine substituted alkenes is a viable process leading to poly(olefins) containing initiating groups for living free radical polymerizations. These initiating groups can then be used to prepare well-defined graft copolymers in which the molecular weight and polydispersity of the vinyl graft is accurately controlled. The presence of alkoxyamine groups at the chain ends of these graft copolymers can also be used to reinitiate polymerization leading to novel grafted block copolymer structures.

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Supporting Information Available: Text giving experimental information (4 pages). Ordering and access information is given on any current masthead page.

References and Notes

- Brintzinger, H. H.; Fischer, D.; Muelhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

- (2) Boor, J. J. *Ziegler–Natta Catalysts and Polymerizations*, Academic Press: New York, 1979.
- (3) Simonazzi, T.; Nicola, A. D.; Aglietto, M.; Ruggeri, G. In *Comprehensive Polymer Science*, 1992; Vol. 1st Supplement, Chapter 7, pp 133–158.
- (4) Aggarwal, S. L. *Block Copolymers*, Plenum Press: New York, 1970.
- (5) Riess, G.; Periard, J.; Banderet, A. *Colloidal and Morphological Behavior of Block and Graft Copolymers*, Plenum Press: New York, 1971.
- (6) Lohse, D. J.; Datta, S.; Kresge, E. N. *Macromolecules* **1991**, *24*, 561.
- (7) Ruggeri, G.; Aglietto, M.; Petragani, A.; Ciardelli, F. *Eur. Polym. J.* **1983**, *19*, 863.
- (8) Chung, T. C.; Jiang, G. J. *Macromolecules* **1992**, *25*, 4816.
- (9) Chung, T. C.; Rhubright, D.; Jiang, G. J. *Macromolecules* **1993**, *26*, 3467.
- (10) Chung, T. C.; Janvikul, W.; Bernard, R.; Jiang, G. J. *Macromolecules* **1994**, *27*, 26.
- (11) Chung, T. C.; Janvikul, W.; Bernard, R.; Hu, R.; Li, C. L.; Liu, S. L.; Jiang, G. J. *Polymer* **1995**, *36*, 3565.
- (12) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679.
- (13) Stehling, U.; Stein, K. M.; Kesti, M. R.; Waymouth, R. M. *Macromolecules* **1997**, submitted for publication.
- (14) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.
- (15) Aaltonen, P.; Fink, G.; Loefgren, B.; Seppaelae, J. *Macromolecules* **1996**, *29*, 5255.
- (16) Bruzard, S.; Cramail, H.; Duvignac, L.; Deffieux, A. *Macromol. Chem. Phys.* **1997**, *198*, 291.
- (17) Schneider, M. J.; Schaefer, R.; Muelhaupt, R. *Polymer* **1997**, *38*, 2455.
- (18) Wilen, C.-E.; Naesman, J. H. *Macromolecules* **1994**, *27*, 4051.
- (19) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722.
- (20) Kazmaier, P. M.; Moffat, K. A.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K. *Macromolecules* **1995**, *28*, 1841.
- (21) Li, I.; Howell, B. A.; Matyjaszewski, K.; Shigemoto, T.; Smith, P. B.; Priddy, D. B. *Macromolecules* **1995**, *28*, 6692.
- (22) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11314; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993.
- (23) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323.
- (24) Catala, J. M.; Bubel, F.; Hammouch, S. O. *Macromolecules* **1995**, *28*, 8441.
- (25) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* **1996**, *29*, 5245.
- (26) Sogah, D. Y.; Puts, R. D.; Trimble, A.; Sherman, O. *Polym. Prepr.*, **1997**, *38* (1), 731. Kobatake, S.; Harwood: H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* **1997**, *29*, 4238. Hawker, C. J.; Hedrick, J. L.; Malmström, E. E.; Trollsås, M.; Waymouth, R. M.; Stehling, U. M. *Polym. Prepr.* **1997**, *38* (2), 412.
- (27) Molecular weights, M_n , for the poly(olefin) derivatives were determined by end group analysis, which is accurate to ca. 30 000 amu. All poly(olefins) used in this study were within this range.
- (28) The borate (17.3 mg, 21.6 μ mol), 4-methylpentene (4.66 mL, 36.8 mmol), decane (1 mL), toluene (13.2 mL), and **1** (0.785 g, 2.02 mmol) were placed in a vial in a drybox and treated with 7.4 mg (19.2 μ mol) of *rac*-EBTHIZrMe₂. The reaction mixture was stirred at room temperature under argon for 6 h and quenched with methanol to give copolymer **3** (2.6 g, 70%). $M_n = 6080$; $M_w/M_n = 1.65$.
- (29) Theoretical molecular weights are calculated by assuming that one alkoxyamine initiating group leads to a single polymer chain, the degree of polymerization of which is governed by the ratio of styrene to initiator. The polymerizations are run to 90% conversion.

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