Macromolecules **2000,** *33,* 2305−2307

Novel Coupling of Two Mechanistically Distinct Polymerizations on a Single Metal Center: Palladium-Mediated Synthesis of Poly(norbornene)−Poly(THF) Block Copolymers

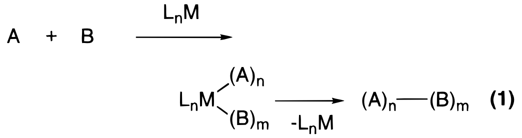
Ngiap Kie Lim and Bruce A. Arndtsen*

Department of Chemistry, McGill University,
801 Sherbrooke St. W., Montreal, Quebec H3A 2K6, Canada

Received October 28, 1999
Revised Manuscript Received January 10, 2000

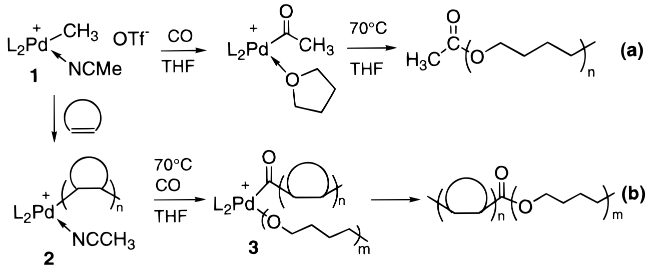
The synthesis of block copolymers with well-defined architectures represents one of the more attractive and economically viable methods to prepare new polymeric materials. This class of polymers can be considered to arise from the chemical binding of two homopolymers, and simple variations in the block length or composition with known, readily available monomers can yield materials with vastly different characteristics.[1] This is particularly true of copolymers with incompatible constitutents, whose self-organization often leads to unique micro- and macroscopic properties.[2] The synthesis of block copolymers is typically accomplished by the sequential addition of monomers in a living polymerization system. However, this technique requires that the monomers are polymerized via the same mechanism. The coupling of monomers polymerized by differing mechanisms is typically much more challenging and often involves multistep polymer syntheses.[3,4] Common methods include the coupling of two presynthesized homopolymers[3] or end group modification on a growing polymer chain.[4] Considering the variety of new materials that can be prepared by coupling two distinct classes of polymers, and the rapidly growing interest in generation of block copolymers with dramatically different blocks, this synthetic limitation is a significant research issue.

An attractive method to generate block copolymers would be to use a single polymerization initiator that can allow the growth of two different polymer chains via distinct mechanisms. This process has very recently been demonstrated in elegant studies both by Sogah[5] and by Jerome, Hedrick, and Hawker[6] using dual-functional organic initiators for the growth of two separate polymers via differing mechanisms off a single initiator site. A complementary, but particulary attractive, approach to this class of block copolymers would be to use an initiator that allows the growth of two distinct polymer blocks, followed by their coupling (eq 1). Namely, since this process would allow the liberation of the initiator after polymerization, it could, in principle, provide a novel method to catalytically synthesize well-defined block copolymers of diverse monomers. However, while there has been a significant body of research into block copolymer synthesis, to our knowledge, even the simple single operation process shown in eq 1 has not been previously observed.



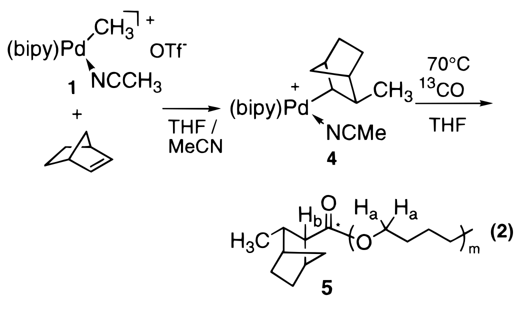
$$\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{L_nM}} \mathrm{L_nM}\begin{matrix}(\mathrm{A})_n\\(\mathrm{B})_m\end{matrix} \xrightarrow[-\mathrm{L_nM}]{} (\mathrm{A})_n\text{—}(\mathrm{B})_m \qquad (1)$$

Scheme 1



During the course of our studies with the olefin insertion polymerization catalyst (bipy)Pd(CH$_3$)(NCMe)$^+$ OTf$^-$ (**1**), we observed this complex could also mediate the cationic ring-opening polymerization of heterocycles.[7] Mechanistic studies on THF ring-opening polymerization with **1** revealed that ring-opening is initiated by CO insertion into the Pd−CH$_3$ bond and ultimately leads to the coupling of the insertion monomer CO with the ring-opened THF polymer (Scheme 1a). We report below that this reactivity of complex **1** can be elaborated into a novel method to couple insertion with cationic ring-opening polymerization. This provides a new, single site method to combine two mechanistically distinct polymerizations into block copolymers.

Olefin insertion polymerization with **1** is known to proceed via insertion into the Pd−C bond at ambient temperatures,[8] while cationic ring-opening of THF occurs at elevated temperatures (70 °C) and only after CO insertion into the Pd−R bond. Thus, complex **1** appears ideally suited for the controlled sequential growth of two polymer chains off the metal center, followed by their coupling, as illustrated in Scheme 1b. Prior to examining this block copolymer synthesis, the feasibility of this process was explored in a controlled fashion with the coupling of a single norbornene unit onto poly(THF). The insertion of norbornene into the Pd−CH$_3$ bond of complex **1** can be achieved by reaction of **1** (150 mg, 0.3 mmol) with norbornene (30 mg, 0.3 mmol) in a 8:1 THF/acetonitrile mixture for 45 min. Filtration of the solution through Celite followed by the addition of diethyl ether results in the precipitation of the single norbornene insertion product, (bipy)Pd(C$_7$H$_{10}$CH$_3$)(NCMe)$^+$ OTf$^-$ (**4**), in 94% yield (eq 2).[9]



(2)

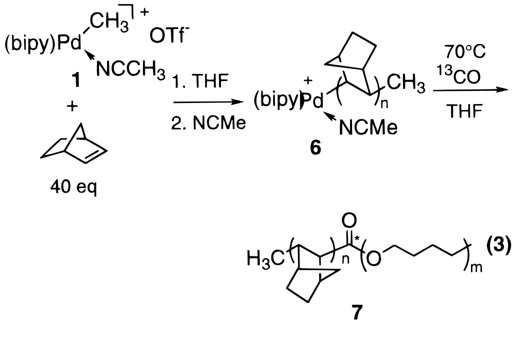
Complex **4** models the palladium−poly(olefin) complex (**2**). Thus, the ability of this complex to initiate THF polymerization and couple the methylnorbornyl fragment into the end group of the poly(THF) was examined. As anticipated, **4** does not initiate THF polymerization in the absence of carbon monoxide, similar to the behavior of **1**. However, the reaction of **4** (28 mg, 0.05

10.1021/ma991823f CCC: $19.00

mmol) with 1 atm of ^{13}CO in THF at 70 °C for 24 h leads to the formation of a gray, viscous solution. Isolation of the product upon filtration, followed by precipitation and washing with acetonitrile, yields a solid white polymer (**5**) (0.81 g). GPC analysis of the isolated polymer **5** shows it to have a $M_n = 27\,200$ (PD = 2.0). This yield and molecular weight suggests the generation of approximately one polymer chain per palladium complex. The coupling of the methylnorbornyl unit to polyTHF in polymer **5** was ascertained using ^{1}H, ^{13}C, and two-dimensional NMR experiments. The ^{1}H NMR of **5** displays poly(THF) resonances (δ 1.53 and δ 3.33), as well as broad resonances for the methylnorbornyl unit between 1 and 2.3 ppm. ^{1}H NMR integration shows approximately one methylnorbornyl unit per polymer chain, consistent with its quantitative incorporation into the end group of the polymer.[10] Importantly, the ^{13}C NMR spectrum of **5** reveals the presence of a single ^{13}C-labeled CO in the polymer in the form of an ester group (δ 174.1). Considering the previously reported ring-opening polymerization of THF with **1** to generate the acyl-terminated poly(THF) (Scheme 1), this resonance is consistent with the incorporation of ^{13}CO into **5** as a $CH_3C_7H_{10}{}^{13}CO-$ moiety on the alkoxy terminus of the poly(THF).[7]

The structure of **5** as a methylnorbornyl ester-terminated poly(THF) was confirmed by further NMR experiments. ^{13}C-decoupled ^{1}H NMR shows a three-bond coupling between the ^{13}C-labeled carbonyl carbon to H$_a$ ($^3J_{C-H} = 3.0$ Hz) and two-bond coupling to H$_b$ ($^2J_{C-H} = 8.0$ Hz). ^{1}H COSY NMR demonstrates the correlation of the norbornyl fragment to the methyl end group, as well as the connectivity of the terminal $-OCH_2-$ unit (H$_a$) to the rest of the THF polymer. These unequivocal links confirm the structure of **5** as poly(THF) with a quantitative incorporation of a methylnorbornyl ester fragment as an end group.

The above result demonstrates that it is indeed possible to use palladium complex **1** to couple a norbornene insertion monomer with the ring-opening polymerization of THF. Thus, the ability of **1** to allow the sequential growth of an insertion polymerized poly(norbornene) and a cationic ring-opened poly(THF), followed by their coupling into a block copolymer, was examined. The reaction of **1** with an excess of norbornene (40 equiv) in THF at 25 °C yields a poly(norbornene) bound palladium complex (eq 3). To facilitate characterization, acetonitrile was introduced into the reaction after 90 min to terminate the polymerization and give a small, soluble poly(norbornene) block. Evaporation of solvent followed by washing with pentane yields (bipy)Pd((C$_7$H$_{10}$)$_n$CH$_3$)(NCCH$_3$)$^+$OTf$^-$ (**6**) as a yellow powder. ^{1}H NMR of **6** shows the characteristic, broad poly(norbornene) resonances (δ 0.8−2.4) and multiplets at 7.6−8.6 ppm due to the 2,2′-bipyridyl ligand on the attached Pd(II) complex. The integration of these two sets of peaks indicates an average of eight norbornene units per palladium center. This structural assignment is confirmed by LR-MS (FAB), which reveals a (bipy)Pd- and CH$_3$-end-capped norbornene polymer with mass ranging from 935 ($n = 7$) (calcd for (bipy)Pd(C$_7$H$_{10}$)$_7$CH$_3^+$: 935) to 1405 ($n = 12$) (calcd for (bipy)Pd(C$_7$H$_{10}$)$_{12}$CH$_3^+$: 1405).



Warming of the Pd-capped poly(norbornene) (**6**) (60 mg, 0.05 mmol) to 70 °C in THF (10.0 g) with ^{13}CO (1 atm) for 24 h leads to the novel synthesis of a poly(norbornene)−poly(THF) block copolymer **7**. GPC analysis of **7** shows a higher molecular weight ($M_n = 41\,000$) and polydispersity (3.56) than observed with **5**, likely arising from the low solubility of **6** in THF. Of note, no peak for poly(norbornene) alone was found in GPC ($M_n = 500$, PD = 1.04),[11] demonstrating that the polynorbornene has been cleanly coupled with the poly(THF). The further characterization of **7** can be made through comparison with the model polymer **5**. Notably, the ^{1}H NMR reveals broad poly(norbornene) resonances between 0.8 and 2.5 ppm in addition to poly(THF) peaks at δ 1.57 and δ 3.38, integrating to approximately one poly(norbornene) unit per poly(THF).[12] The presence of an ester unit coupling these two polymer fragments can be clearly observed by ^{13}C NMR, which displays four ^{13}C-labeled signals (δ 175.6, δ 175.4, δ 174.8, δ 174.5), arising from the four possible stereoisomers on the polynorbornene block.[13] Thus, as with complex **4**, complex **6** allows the essentially quantitative coupling of the pendant Pd−(CO)poly(norbornene) “ligand” onto the alkoxy terminus of the cationic polymerized poly(THF), cleanly generating block copolymer **7**.

These results demonstrate that palladium complex **1** can provide a novel, single site route to couple two mechanistically distinct polymerizations—norbornene insertion and THF cationic ring-opening—into block copolymers. While the mechanistic details of this process have not been fully elucidated, a working mechanism consistent with these results is similar to that postulated for THF polymerization with **1** (Scheme 1),[7] in which an initial insertion of CO into the Pd−(C$_7$H$_{10}$)$_n$-CH$_3$ bond in **6** yields a Pd−acyl complex: (bipy)Pd(CO-(C$_7$H$_{10}$)$_n$CH$_3$)(THF)$^+$OTf$^-$. The electron-withdrawing acyl ligand creates a palladium center that is sufficiently Lewis acidic to initiate THF polymerization. The subsequent reductive coupling of the acyl ligand and the growing alkoxy chain ultimately produces the desired norbornene−THF block copolymer. Taken together, these series of steps provide a unique method to grow two distinct polymer chains off a single metal center, followed by their coupling into block copolymers.

In conclusion, the novel synthesis of norbornene−THF block copolymers can be achieved by utilizing the dual-functional polymerization catalyst, (bipy)Pd(Me)(NCMe)$^+$OTf$^-$ (**1**). This constitutes the first example of an insertion and ring-opening process occurring at a single metal center, followed by the coupling of the two homopolymers to generate a block copolymer. Considering the diverse variety of monomers known to undergo insertion polymerization with Pd(II) complexes,[8] as well as heterocyclic monomers that can undergo the Pd-initiated cationic ring-opening polymerization,[7] this process has the potential to provide general access to many new classes of block copolymers. As a result of the generation of Pd(0) after copolymer formation, this process is currently stoichiometric in palladium. Thus, examination of methods to reoxidize Pd(0) into an active catalyst under the polymerization conditions (e.g., via oxidative addition), as well as the generality of this copolymerization and the improvement of the polydispersities, is currently under exploration in our laboratory.

Acknowledgment. We thank NSERC of Canada and Fonds FCAR du Quebec for their financial support.

Supporting Information Available: Details of the synthesis and spectral data for **4**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Reiss, G.; Hurtrez, G.; Bahadur, P. In *Encyclopedia of Polymer Science and Engineering*; Korschwitz, J. I., Ed.; Wiley: New York, 1985. (b) Thomas, E. L.; Anderson, D. M.; Henkee, C. S.; Hoffman, D. *Nature* **1988**, *334*, 598. (c) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525. (d) Webster, O. W. *Science* **1991**, *251*, 887. (e) Bates, F. S. *Science* **1991**, *251*, 898.

(2) Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.

(3) (a) Noshay, A.; McGrath, J. E. *Block Co-Polymers*; Academic: New York, 1977. (b) Velichkova, R. S.; Christova, D. C. *Prog. Polym. Sci.* **1995**, *20*, 819. (c) Rempp, P. F.; Lutz, P. J. In *Comprehensive Polymer Chemistry*; Allen, G., Ed.; Pergamon: Oxford, 1992. (d) Rempp, P. F.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*, 3. (e) Yoshida, E.; Sugita, A. *Macromolecules* **1996**, *29*, 6422. (f) Chaumont, P.; Beinert, G. Herz, J. E.; Rempp, P. *Polymer* **1981**, *22*, 663.

(4) (a) Yagci, Y.; Mishra, M. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996; Vol. 1. (b) Schue, F. In *Comprehensive Polymer Science*, 2nd ed.; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989. (c) Nomura, R.; Narita, M.; Endo, T. *Macromolecules* **1996**, *29*, 3669. (d) Coca, S.; Paik, H.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 6513.

(5) (a) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1997**, *30*, 7050. (b) Weimer, M. W.; Scherman, O. A.; Sogah, D. Y. *Macromolecules* **1998**, *31*, 8425.

(6) (a) Hawker, C. J.; Hedrick, J. L.; Malmstrom, E. E.; Trollsas, M.; Mecerreyes, D.; Moineau, G.; Dubois, P. Jerome, R. *Macromolecules* **1998**, *31*, 213. (b) Mecerreyes, D.; Moineau, G.; Dubois, P.; Jerome, R.; Hedrick, J. L.; Hawker, C. J.; Malmstrom, E. E.; Trollsas, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1274.

(7) Lim, N. K.; Arndtsen, B. A. *Organometallics* **1999**, *18*, 3953.

(8) (a) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Drent, E.; Budzellar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (c) Abu-Surrah, A. S.; Rieger, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2475.

(9) Spectroscopic data for **2:** ^{1}H NMR (CD_2Cl_2): δ 8.63 (d, 2H), δ 8.22 (m, 4H), δ 7.73 (m, 2H), δ 2.63 (d, 1H), δ 2.56 (s, 3H), δ 2.24 (d, 1H), δ 1.93 (d, 1H), δ 1.74 (m, 2H), δ 1.60 (m, 1H), δ 1.36 (m, 2H), δ 1.21 (d, 3H), δ 1.19 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ 156.85, δ 152.11, δ 149.01, δ 148.93, δ 140.52, δ 140.01, δ 127.81, δ 127.11, δ 123.58, δ 122.61, δ 57.63, δ 45.96, δ 45.58, δ 45.23, δ 34.87, δ 30.21, δ 29.24, δ 21.87, δ 3.80. Analysis calculated for $C_{21}H_{24}F_3N_3O_3PdS$ (found): C, 44.79 (44.89); H, 4.08 (4.31); N, 7.36 (7.48).

(10) End-group quantitation was determined by comparison of M_n calculated from ^{1}H NMR integration (30 200) to M_n from GPC data (27 200).

(11) GPC analysis of polynorbornene cleaved off the Pd center by reacting **6** with CO in MeOH. The reaction of **6** with CO in MeOH causes the cleavage of the Pd−C bond to yield $CH_3(C_7H_{10})_nC(O)OCH_3$, $CH_3(C_7H_{10})_nC(O)OH$, and $CH_3(C_7H_{10})_nH$, as determined by LS-MS.

(12) End-group quantitation was determined by comparison of M_n calculated from ^{1}H NMR integration (33 000) to M_n from GPC data (41 000).

(13) A random stereochemistry in the poly(norbornene) would result in the generation of four possible triads: RRR, RRS, RSR, and RSS.

MA991823F