JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Ultrafast Cyclopolymerization for Polyene Synthesis: Living Polymerization to Dendronized Polymers

Eun-Hye Kang, In Sun Lee, and Tae-Lim Choi*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea

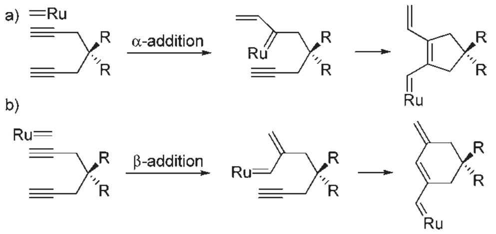
Supporting Information

ABSTRACT: We discovered that ultrafast cyclopolymerization of 1,6-heptadiyne derivatives reached completion in 1 min using a third-generation Grubbs catalyst. After optimization, this superior catalyst selectively produced conjugated polymers having a five-membered-ring structure with excellent molecular weight control and narrow polydispersity index (PDI). This living polymerization allowed us to prepare fully conjugated diblock copolymers with narrow PDIs. Lastly, this catalyst was active enough to polymerize macromonomers with G-3 dendrons in a living manner as well. This dendronized polymer with a highly regioregular polymer backbone and bulky dendrons was visualized by atomic force microscopy, which revealed the structure of a single molecular wire surrounded by insulating dendrons.

The cyclopolymerization of 1,6-heptadiyne derivatives via olefin metathesis is a powerful method for synthesizing substituted polyacetylenes. Depending on the side chains, these conjugated polymers are soluble in common organic solvents, making the polymers potential materials for use in organic electronics and optics. Over the past three decades, many catalyst systems based on transition metals have been applied to the cyclopolymerization: Ziegler-type,[1] $MoCl_5/WCl_6$,[2,3] Schrock-type alkylidene,[4−9] and modified Grubbs catalysts.[10−13] As shown in Scheme 1, α- or β-addition occurs, depending on the orientation of the metal carbene reacting with the terminal alkyne.[4] This results in two different ring-closing modes that form either five- or six-membered rings. Early catalysts as well as the Schrock catalyst produced polymers with microstructures consisting of a mixture of both five- and six-membered rings as a repeat unit.[14]

In spite of this nonselective addition mode, Schrock and coworkers demonstrated the first example of the promotion of living cyclopolymerization of 1,6-heptadiyne derivatives.[4,5] Later, using a modified Schrock catalyst, they reported selective cyclopolymerization with β-addition to give conjugated polymers with six-membered rings only.[6,7] Subsequently, Buchmeiser and coworkers succeeded in the selective synthesis of polyenes consisting of a five-membered-ring structure in a living manner, using Mo alkylidene with quinuclidine.[3,8,9] This result is more useful because the polymer with a five-membered-ring unit contains a coplanar polymer backbone, resulting in a longer conjugation length.[15] Nevertheless, a major drawback is that Mo- and W-based catalysts are air- and moisture-sensitive.

Scheme 1. Cyclopolymerization of 1,6-Heptadiyne Derivatives: (a) Five-Membered-Ring Unit Produced from α-Addition of a Metal Carbene and (b) Six-Membered Ring from β-Addition



Ru-based Grubbs catalysts are widely used in synthesis because they are not only highly active but also highly tolerant to air, moisture, and many functional groups. Despite their superior reactivity in various metathesis reactions, including ring-opening metathesis polymerization (ROMP), the cyclopolymerization of 1,6-heptadiyne derivatives had not been achieved using classic Grubbs-type initiators.[10] Recently, the Buchmeiser group disclosed groundbreaking results on cyclopolymerization using modified Ru initiators.[10−13] They substituted a chloride ligand on the second-generation Grubbs catalyst with an electron-withdrawing ligand (e.g., trifluoroacetate) and succeeded in achieving cyclopolymerization with controlled molecular weights. They also found that these modified Ru catalysts underwent selective α-addition to produce conjugated polymers with only five-membered rings. However, the drawback was that the prepared polymers generally had broad polydispersity indices (PDIs) because many of the modified catalysts had large k_p/k_i values of 1000, implying slow initiation.[10] Therefore, a more rapidly initiating catalyst would be desirable to achieve more precisely controlled polymerization.[16] Herein we report living cyclopolymerization of 1,6-heptadiyne derivatives for selective preparation of conjugated polymers with five-membered-ring backbones and narrow PDIs using a third-generation Grubbs catalyst. Furthermore, the synthesis of both block copolymers and dendronized polymers by the macromonomer approach was successfully carried out with excellent molecular weight control and narrow PDIs, demonstrating the powerful reactivity of our system.

Our investigations began with tests to determine whether cyclopolymerization would be possible with a highly active and ultrafast-initiating third-generation Grubbs catalyst[17] (**I**, Figure 1a),

Received: May 19, 2011
Published: June 30, 2011

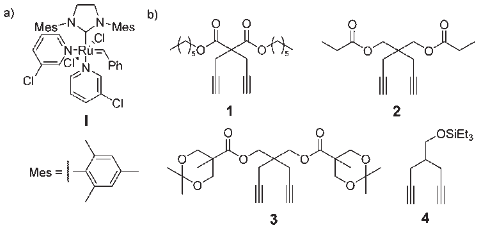


Figure 1. Structures of (a) initiator **I** and (b) monomers **1**−**4**.

which has been found to promote living ROMP of norbornene derivatives with high functional-group tolerance.[18] Initially, the most common monomer, diethyl dipropargylmalonate (DEDPM),[2,3−11,14,15] was tested for cyclopolymerization in dichloromethane (DCM), a common solvent for this reaction.[8−11] However, only low conversion of DEDPM was observed, similar to the previous report that used a second-generation Grubbs catalyst.[10] To improve the conversion, several solvents were screened, and this cyclopolymerization showed a remarkable solvent effect. When tetrahydrofuran (THF) was used instead of DCM, a huge enhancement of the monomer conversion up to 92% occurred in a short reaction time; however, poly(DEDPM) precipitated out from the solution because of its low solubility in THF.

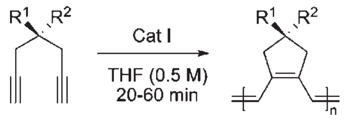
With the partial success of the cyclopolymerization in THF, we changed the momoner to dihexyl dipropargylmalonate (DHDPM, **1**) to improve the solubility. Indeed, the cyclopolymerization by **I** produced readily soluble poly(**1**) with high conversion in a short reaction time. Just like the previous report, **I** also produced highly regioregular poly(**1**) by selective α-addition. This uniform polymer microstructure having a five-membered ring as the repeat unit was confirmed by the reported ^{13}C NMR analysis (Figure S1 in the Supporting Information), which showed only one peak for the carbonyl carbon of malonate at 172 ppm and a peak for the quaternary C4 atom at 57 ppm.[5,9] In addition, UV−vis analysis showed well-resolved absorption spectra of two peaks with $\lambda_{\max}$ = 548 and 590 nm (Figure S2), providing another indication of a planar five-membered ring structure in the regioregular polymer.[15])

Prompted by the accelerated cyclopolymerization in THF, we monitored the polymerization kinetics in an NMR tube. Amazingly, ^{1}H NMR analysis in THF-d_8 revealed that greater than 95% of **1** was consumed within 2 min after the addition of 2 mol % **I**, whereas the reaction in DCM-d_2 showed much slower propagation (Figure S3). Our preliminary study suggested that using a weakly coordinating solvent (e.g., THF or diethyl ether) greatly improved the catalyst lifetime by stabilizing the propagating species through solvent coordination.[19] Contrarily, the signal for the propagating carbenes disappeared within 10 min during the cyclopolymerization in DCM-d_2, implying rapid decomposition of the active carbenes in noncoordinating solvents. We believe that this vast difference in the stability of the propagating species containing the long conjugated carbene may be the key factor that allowed great enhancement of the conversion when the cyclopolymerization was performed in THF.

Even with the fast-initiating catalyst, the PDI of the polymer from **1** was still broad (Table 1, entry 1). With the enhanced activity of the catalyst in THF, it seemed that PDI broadening was caused by a chain-transfer reaction. Therefore, the reaction temperature was lowered to 0 °C in order to suppress this reaction,[18] and indeed, the cyclopolymerization of **1** produced a polymer having a narrow PDI of 1.1 with complete consumption of the monomer. With this narrow PDI, the molecular weight of poly(**1**) was linearly controlled by changing the [M]/[I] ratio from 25:1 to 150:1 (Table 1, entries 2−5; Figure 2). The reactions reached completion within 30 min to 1 h, despite the low reaction temperature. To understand the origin of the narrow PDI, the k_i/k_p value was measured by ^{1}H NMR analysis[20] at 0 °C, and a value of 0.84 was obtained; this is the highest k_i/k_p value reported to date, indicating that the initiation was fast enough to show much narrower PDIs than those in the previous reports.[8,10,11]

To broaden the monomer scope, various mono- and bis-substituted 1,6-heptadiyne derivatives (**2**−**4** in Figure 1b) were prepared, and these ester- and ether-containing monomers also underwent fast and efficient cyclopolymerization to form five-membered-ring structures that were confirmed by ^{13}C NMR

Table 1. Cyclopolymerization of 1−4



entry	monomer	[M]/[I]	temp (°C)	M_n (kDa)[a]	PDI[a]	yield (%)[b]
1	1	100	RT	41.7	1.81	87
2	1	25	0	12.3	1.09	>99
3	1	50	0	25.4	1.19	81
4	1	100	0	40.6	1.16	97
5	1	150	0	54.4	1.44	94
6	2	25	0	14.6	1.06	93
7	2	50	0	27.3	1.10	93
8	2	100	0	46.7	1.28	96
9	2	150	0	57.6	1.29	>99
10	3	25	0	14.3	1.06	85
11	3	50	0	24.0	1.14	80
12	3	100	0	34.9	1.15	>99
13	3	150	0	50.7	1.28	87
14	4	25	−10	8.9	1.13	97
15	4	50	−10	19.3	1.11	79
16	4	100	−10	39.6	1.2	89
17	4	150	−5	54.9	1.43	87

[a] Determined by THF SEC calibrated using polystyrene (PS) standards. [b] Isolated yields after purification. Monomer conversions of all entries were >95% except entry 1 (94%).

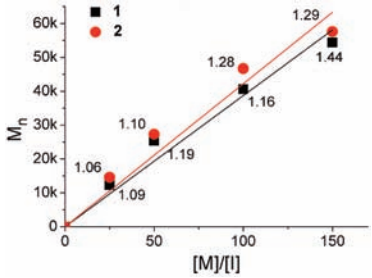


Figure 2. Plots of M_n vs monomer-to-initiator ratio for poly(**1**) and poly(**2**). The PDI values are shown as labels. Plots for the other polymers are shown in Figure S4.

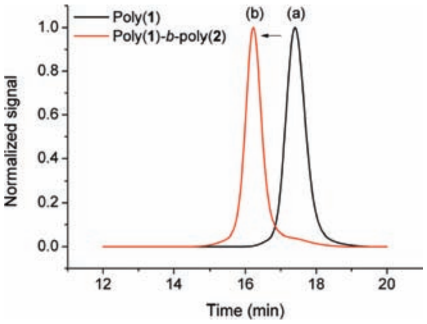


Figure 3. THF SEC traces for a homopolymer and a block copolymer: (a) poly($\mathbf{1}$)$_{25}$ (M_n = 13.6 kDa, PDI = 1.09); (b) poly($\mathbf{1}$)$_{25}$-*b*-poly($\mathbf{2}$)$_{50}$ (M_n = 33.9 kDa, PDI = 1.14). PS standards were used for calibration.

analysis (see the Supporting Information). As in the cyclopolymerization of **1**, the polymers obtained from monomers **2**−**4** also shared the characteristics of living polymerization, with narrow PDIs and controlled molecular weights (Table 1, entries 6−17; Figure 2 and Figure S4). In particular, the monosubstituted monomer **4** underwent even faster cyclopolymerization than **1** with greater than 95% conversion in 1 min in an NMR tube at room temperature ([M]/[I] = 50). This was presumably the result of the smaller amount of steric hindrance imposed by monosubstitution, which promoted faster complexation of the catalyst. However, for the same reason, poly(**4**) was more vulnerable to the chain-transfer reaction than were the bis-substituted polymers, and as a result, its PDI broadened even at 0 °C. This problem was solved by further lowering the temperature to −10 °C, where polymers with narrow PDIs and controlled molecular weights were obtained (entries 14−17).

Previously, Schrock reported the synthesis of the diblock copolymer poly(DEDPM-*b*-norbornene), which contains a mixture of five- and six-membered rings, via cyclopolymerization followed by ROMP of norbornene derivatives.[5] However, there have been no reports of true block copolymers with fully conjugated backbones obtained by cyclopolymerization. If catalyst **I** could promote living cyclopolymerization, one should be able to prepare a block copolymer having a fully conjugated backbone with a narrow PDI. Indeed, the diblock copolymer was synthesized by the addition of the first monomer **1** followed by the sequential addition of the second monomer **2** ([**1**]:[**2**]:[**I**] = 25:50:1). Size-exclusion chromatography (SEC) traces showing the complete shift from the initial block of **1** to a higher molecular weight confirmed the validity of the block copolymerization as well as the living character of this cyclopolymerization by catalyst **I** (Figure 3, M_n = 33.9 kDa, PDI = 1.14, yield = 94%). This is the first example of block copolymerization between two different 1,6-heptadiyne derivatives with a narrow PDI and a regioregular microstructure. This shows the potential of using fully conjugated block copolymers having a polyene backbone for the study of controlling various nanostructure morphologies by phase separation.

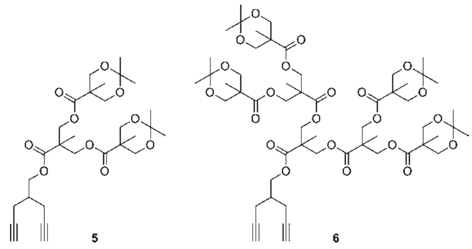
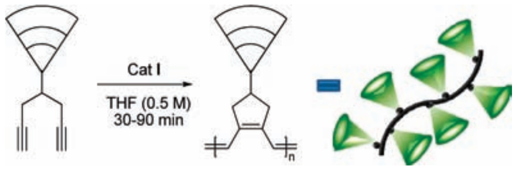


Figure 4. G2 and G3 macromonomers for dendronized polymerization.

Table 2. Cyclopolymerization of 5 and 6[a]



entry	monomer	[M]/[I]	temp (°C)	M_n (kDa)[b]	PDI[b]	yield (%)[c]
1	**5**	25	−10	12.3	1.09	88
2	**5**	50	−10	29.4	1.09	93
3	**5**	100	−10	45.4	1.10	78
4	**5**	150	−10	57.7	1.18	79
5	**6**	25	−12	15.5	1.08	92
6	**6**	50	−10	26.5	1.11	>99
7	**6**	100	0	48.7	1.12	82
8	**6**	150	−5	66.6	1.15	70
9	**6**	200	−5	78.6	1.36	86

[a] Polymerization conditions: 0.5 M THF within 1.5 h. [b] Determined by THF SEC calibrated using PS standards. [c] Isolated yields after purification. Monomer conversions were >95%.

The successful polymerization of monomer **3** containing a bulky side group showed the possibility of synthesizing dendronized polymers by the macromonomer approach. Many dendronized polymers have been prepared by stepwise methods in which the dendrons as a whole or of each generation were attached to the prepolymers with activating groups. On the other hand, the synthesis of the dendronized polymer via the macromonomer approach has the advantage of directly producing polymers without defects in the microstructures. However, the latter approach is generally more challenging because the steric hindrance of the dendrons retards the polymerization.[21−23] Encouraged by the high activity of catalyst **I** toward cyclopolymerization of the monosubstituted monomer **4**, we prepared ester-dendron-containing macromonomers **5** (G2) and **6** (G3)[24] (Figure 4). Even with the bulky G3 dendron, the dendronized polymers were prepared in a living manner; the resulting polymers exhibited narrow PDIs (1.1−1.2) and excellent molecular weight control up to a high degree of polymerization (DP = 200) (Table 2; also see Figure S4). Again, the cyclopolymerization of 200 equiv of the bulky G3 macromonomer was completed in 90 min at low temperature, reflecting the high activity of catalyst **I**. More importantly, the chain-transfer reaction seemed to be more suppressed, resulting in lower PDIs, because the large dendrons blocked the approach of the active metal carbene to the polyene backbone.

Poly(**6**) was visualized by atomic force microscopy (AFM), which provided vivid structural information on the single polymer chain; however, the AFM analysis of poly(**5**) failed because of the low height of the G2 dendron. As a result of the bulky dendrons, poly(**6**) showed an extended morphology resembling a rigid rod rather than a random coil (Figure 5). This provides a new route to the synthesis of insulated molecular wires (IMWs) with lengths of a few tens to hundreds of nanometers. Organic nanowires, as one-dimensional nanostructured electronics, have

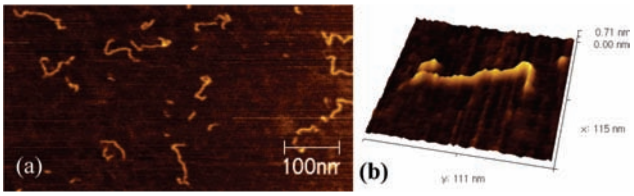


Figure 5. (a) AFM image of poly(**6**) in height mode. A polymer solution in DCM (1.25 mg/L) was spin-coated onto mica. The average height was 0.4 nm. (b) Three-dimensional view of a single polymer chain.

been developed using many organic semiconductors, including conjugated polymers.[25] In particular, the insulated form of the nanowire has the advantage of preventing short circuits or crosstalk because of its insulating cover.[26] Although various dendronized conjugated polymers have been investigated for the formation of IMWs, most were prepared by step-growth polymerization, which results in the formation of IMWs with broad PDIs and short polymer chains as a result of the large steric hindrance from high-generation dendrons.[26] Chain-growth polymerization using a Rh catalyst was adopted by the Percec group for the synthesis of substituted *cis*-polyacetylene to prepare dendronized conjugated polymers with controlled PDIs and DPs of up to 100.[27] However, the *cis*-polyacetylene backbone lacked planarity, resulting in a relatively wide band gap (>2.5 eV), whereas our approach provides IMWs with a narrow band gap (1.9−2.0 eV; Figure S2) and extended conjugation length. Furthermore, high-resolution imaging of the individual chain is rare for the conjugated polymers because of their tendency to aggregate in the form of packed nanorods.[28] In short, this method allows the preparation of IMWs with excellent molecular weight control and narrow PDIs.

In conclusion, we have used a third-generation Grubbs catalyst to achieve living cyclopolymerization of 1,6-heptadiyne derivatives to produce semiconducting polymers with controlled molecular weights and narrow PDIs. This living polymerization allowed the synthesis of a diblock copolymer with a narrow PDI from two different 1,6-heptadiyne derivatives. Additionally, up to G3-dendronized polymers were prepared in a living manner via the macromonomer approach. AFM visualization of poly(**6**) unambiguously revealed the rodlike conformation, providing a new method for synthesizing IMWs with precise control. This study has demonstrated a superior catalyst system for cyclopolymerization that may potentially lead to the formation of materials for the study of charge transport along a straight single IMW that can be applied in molecular electronics. We are currently working on the synthesis of other three-dimentional polymers such as graft polymers and star polymers using this cyclopolymerization method.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, NMR data for new compounds and polymers, UV−vis spectra of polymers, kinetics data, plots for molecular weight control, and complete ref 27b. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

tlc@snu.ac.kr

■ ACKNOWLEDGMENT

The authors dedicate this paper to Prof. Eun Lee on his retirement and 65th birthday. Financial support from the National Research Foundation of Korea, BRL, BK21, and Chungam Fellowship is acknowledged. The authors thank K.-O. Kim for support in the AFM experiments and H.-N. Bae of the National Center for Inter-University Research Facilities for assistance with the NMR experiments.

■ REFERENCES

(1) Stille, J. K.; Frey, D. A. *J. Am. Chem. Soc.* **1961**, *83*, 1697.
(2) Ryoo, M.-S.; Lee, W.-C.; Choi, S.-K. *Macromolecules* **1990**, *23*, 3029.
(3) Anders, U.; Wagner, M.; Nuyken, O.; Buchmeiser, M. R. *Macromolecules* **2003**, *36*, 2668.
(4) Fox, H. H.; Schrock, R. R. *Organometallics* **1992**, *11*, 2763.
(5) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.
(6) Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3295.
(7) Schattenmann, F. J.; Schrock, R. R. *Macromolecules* **1996**, *29*, 8990.
(8) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 4044.
(9) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Macromolecules* **2002**, *35*, 9029.
(10) Krause, J. O.; Zarka, M. T.; Anders, U.; Weberskirch, R.; Nuyken, O.; Buchmeiser, M. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 5965.
(11) Mayershofer, M. G.; Nuyken, O.; Buchmeiser, M. R. *Macromolecules* **2006**, *39*, 3484.
(12) Vygodskii, Y. S.; Shaplov, A. S.; Lozinskaya, E. I.; Vlasov, P. S.; Malyshkina, I. A.; Gavrilova, N. D.; Kumar, P. S.; Buchmeiser, M. R. *Macromolecules* **2008**, *41*, 1919.
(13) Kumar, P. S.; Wurst, K.; Buchmeiser, M. R. *J. Am. Chem. Soc.* **2009**, *131*, 387.
(14) Choi, S.-K.; Gal, Y.-S.; Jin, S.-H.; Kim, H.-K. *Chem. Rev.* **2000**, *100*, 1645.
(15) Anders, U.; Nuyken, O.; Buchmeiser, M. R. *Des. Monomers Polym.* **2003**, *6*, 135.
(16) Matyjaszewski, K. *Macromolecules* **1993**, *26*, 1787.
(17) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035.
(18) Choi, T.-L.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1743.
(19) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.
(20) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
(21) Zhang, A.; Shu, L.; Bo, Z.; Schlüter, A. D. *Macromol. Chem. Phys.* **2003**, *204*, 328.
(22) Frauenrath, H. *Prog. Polym. Sci.* **2005**, *30*, 325.
(23) Rajaram, S.; Choi, T.-L.; Rolandi, M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2007**, *129*, 9619.
(24) (a) Ihre, H.; Hult, A. *Macromolecules* **1998**, *31*, 4061. (b) Ihre, H.; De Jesús, O. L. P.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2001**, *123*, 5908.
(25) Kim, F. S.; Ren, G.; Jenekhe, S. A. *Chem. Mater.* **2011**, *23*, 682.
(26) Frampton, M. J.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 1028.
(27) (a) Percec, V.; Rudick, J. G.; Wagner, M.; Obata, M.; Mitchell, C. M.; Cho, W.-D.; Magonov, S. N. *Macromolecules* **2006**, *39*, 7342. (b) Percec, V.; et al. *Chem.—Eur. J.* **2006**, *12*, 5731.
(28) Stocker, W.; Karakaya, B.; Schürmann, B. L.; Rabe, J. P.; Schlüter, A. D. *J. Am. Chem. Soc.* **1998**, *120*, 7691.