Ring-Opening Polymerization

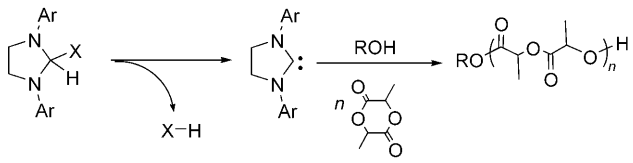
DOI: 10.1002/ange.200500723

Latent, Thermally Activated Organic Catalysts for the On-Demand Living Polymerization of Lactide**

Olivier Coulembier, Andrew P. Dove, Russell C. Pratt, Alan C. Sentman, Darcy A. Culkin, Laetitia Mespouille, Philippe Dubois, Robert M. Waymouth,* and James L. Hedrick**

The last decade has seen significant advances in carbene chemistry, including the isolation of the first heteroatom-subsituted singlet carbene and persistent triplet diarylcarbenes.[1,2] These advances have stimulated renewed interest and expanded the scope of possibilities engendered by these reactive species. Following the pioneering work by Wanzlick et al.,[3] the research groups of Bertrand[4] and Arduengo[5] isolated and characterized stable N-heterocyclic carbenes, and over the last decade the steric and electronic requirements for stable imidazolin-2-ylidene and imidazol-2-ylidene carbenes have been described.[6] Consequently, investigation into the properties and uses of N-heterocyclic carbenes (NHCs) has become a major area of research.[2,7] For example, the use of NHCs in place of phosphine ligands produces transition-metal complexes that exhibit enhanced catalytic performance and stability.[8] N-Heterocyclic carbenes have also proven to be effective organic catalysts for benzoin condensations, Stetter reactions, acylation/transesterification reactions, and the polymerization of cyclic esters.[9]

Despite advances in structural modifications to enhance the stability of N-heterocyclic carbenes[10] and the development of in situ methods for their generation,[11,12] the use of NHCs is complicated by their extreme air and moisture sensitivity, which necessitates the use of glove-box techniques. Our attention has been drawn towards the preparation and application of protected NHCs, particularly those that could be activated thermally. Many research groups realized in early studies that strongly nucleophilic carbenes underwent C–H insertion reactions with compounds containing acidic C–H bonds to form adducts in high yields.[13] Chloroform and pentafluorobenzene adducts of saturated carbenes[12] are useful precursors to transition-metal–carbene complexes; they also catalyze the ring-opening polymerization (ROP) of lactide (Scheme 1) at elevated temperatures.[12h] Grubbs



X = CCl_3, C_6F_5, etc.

Scheme 1. Polymerization of lactide with adducts of saturated N-heterocyclic carbenes.

and co-workers showed that imidazolium tetrafluoroborate salts could be treated with potassium *tert*-butoxide to reversibly generate 2-alkoxy-4,5-dihydroimidazoles.[14] Enders et al.[15] prepared alcohol adducts of the triazolylidene carbene; thermolysis of these adducts (80 °C) generated free carbene and alcohol. Our attention was drawn to alkoxytriazolines as possible unimolecular catalyst/initiator systems. Moreover, we anticipated that the hydroxy-terminated polymer and free carbene present in solution during the polymerization could react reversibly with each other to form an adduct after each propagation step,[14b] hence minimizing the concentration of the active species and possible adverse transesterification side reactions, which is a problem typical of other controlled/living polymerization procedures above 85 % conversion.[16] Herein, we describe the use of the commercially available 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2-triazol-5-ylidene carbene (**1**) for the living ROP of lactide to generate functional, block, and dendritic star copolymers.

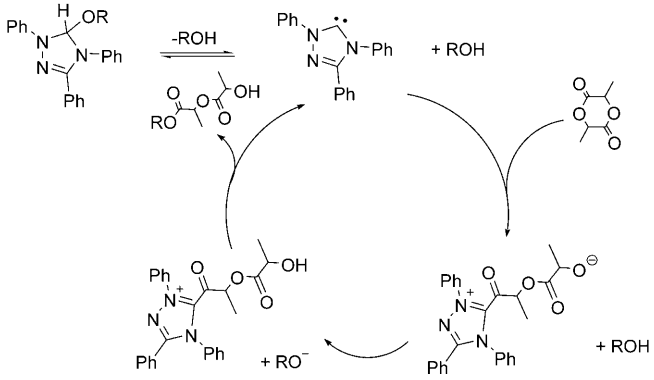
Polymerization of L-lactide (LA: 1–2 M solution in THF or toluene) by imidazolylidene carbenes in the presence of an initiator such as methanol (one equivalent of initiator to catalyst) is generally accomplished within a few minutes at 25 °C, depending on the targeted molecular weight.[14b] Only 16 % conversion was observed at 25 °C after 100 h for the polymerization of LA (1 M in toluene) with the triazolylidene carbene under similar conditions, whereas 40 % conversion was observed at 50 °C. Polymerization of LA at 90 °C proceeded with near quantitative monomer conversion in 50 h to give polylactide with a degree of polymerization (DP)

[*] O. Coulembier, L. Mespouille, Prof. P. Dubois
Laboratory of Polymeric and Composite Materials (LPCM)
University of Mons-Hainaut
Place du Parc 20, 7000 Mons (Belgium)
Fax: (+32) 65-373484
E-mail: philippe.dubois@umh.ac.bc
Dr. D. A. Culkin, Prof. R. M. Waymouth
Center for Polymeric Interfaces and Macromolecular Assemblies
Department of Chemistry
Stanford University
Stanford, CA 94305 (USA)
Fax: (+1) 650-736-2262
E-mail: waymouth@stanford.edu
Dr. A. P. Dove, Dr. R. C. Pratt, Dr. A. C. Sentman, Dr. J. L. Hedrick
IBM Almaden Research Center
650 Harry Road, San Jose, CA 95120 (USA)
Fax: (+1) 408-927-3310
E-mail: hedrick@almaden.ibm.com

[**] O.C. is grateful to the F.R.I.A. for financial support. This work was partially supported by the Belgian Federal Government Office of Science Policy (SSTC-PAI-5/3). A.P.D., R.C.P., and D.A.C. gratefully acknowledge support from the NSF Center on Polymeric Interfaces and Macromolecular Assemblies (CPIMA: NSF-DMR-0213618) and an NSF-GOALI grant (NSF-CHE-0313993). D.A.C. thanks the NIH for a postdoctoral fellowship (GM070181-01A1). Dolores Miller is gratefully thanked for the high-temperature NMR analysis. We thank Purac for the generous donation of L-lactide.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

of 70 ($M_n = 10000$) and a polydispersity (M_w/M_n) of 1.09. The diminished reactivity of the triazole carbenes for lactide polymerization compared to that observed with saturated imidazolin-2-ylidene or unsaturated imidazol-2-ylidene carbenes[9o,14b] suggested that some process was attenuating the reactivity of these carbenes towards polymerization. On the basis of the pioneering work by Enders et al. on the reactivity of triazolylidenes, we suspected that the reversible formation of alcohol adducts might be responsible for this behavior (Scheme 2).[15]



Scheme 2. Polymerization of lactide with triazole carbenes.

As reported by Enders et al.,[15] treatment of the triazolylidene with a slight excess of MeOH at room temperature readily generates the methoxytriazoline, as evidenced by resonances at $\delta = 46.8$, 101.0, and 142.9 ppm in the ^{13}C NMR (C_6D_6) spectrum. This alcohol adduct is stable at 50 °C, but dissociates at 90 °C into a mixture of the methoxytriazoline, free triazolylidene **1**, and free methanol, as evidenced by ^1H and ^{13}C NMR spectroscopic analysis. Spectroscopic analysis shows that cooling this mixture to room temperature regenerates the methoxytriazoline, thus revealing a temperature-dependent equilibrium between the triazolylidene carbene and methanol adduct: only the alcohol adduct is observed at room temperature in the presence of alcohols, and elevated temperatures are required to generate the free carbene and the alcohol.

The reversible formation of alcohol adducts provides an explanation for the low reactivity of the triazole carbenes in the polymerization of LA at room temperature. Therefore, the polymerization of LA with a variety of initiating alcohols was carried out at 90 °C (1 M in toluene). The molecular weights obtained under these conditions correlated with those predicted with monomer to initiator ratios ranging from 25:1 to 350:1 and yielded polymers with narrow dispersities (Table 1). A plot of the molecular weight and polydispersity versus conversion for the ROP catalyzed by **1** was linear (Figure 1) and the gel permeation chromatography (GPC) traces of polylactide generated with a 4-pyrene-1-butanol initiator and using both refractive index and UV detectors (410 and 350 nm, respectively) clearly show pyrene is distributed throughout the sample (Figure 1). This was corroborated by ^1H NMR analysis of the polymer end-groups which indicated the presence of one initiator per polymer chain, thus confirming the end-group fidelity.

Table 1: Selected polymerization data of L-lactide using triazolium carbene as a catalyst.

Entry	I (cat./I)[a]	M/I[b]	Time of polym. [h]	Conv.[c]	DP[d]	PDI[e]
1	MeOH (2:1)	25:1	19	72	18	
2	MeOH (4:1)	50:1	[f]	94	50	1.36
3	MeOH (4:1)	100:1	[f]	97	84	1.34
4	pyrenebutanol (1:1)	100:1	95	85	72	1.09
5	pyrenebutanol (1:1)	150:1	113	90	130	1.06
6	pyrenebutanol (1:1)	350:1	96	35		
7	PEO-OH (1:1)	100:1	63	88	90	1.17
8	bis-MPA (24:1)	40:1	42	96	38[g]	1.14

[a] Initiator (catalyst:initiator ratio). [b] Monomer:initiator ratio. [c] Conversion as measured by ^1H NMR spectroscopy. [d] Degree of polymerization determined by gel permeation chromatography using Mark–Houwink parameters from a polystrene calibration. [e] Polydispersity index, measured by gel permeation chromatography. [f] See Figure 2. [g] DP obtained for each arm of the star polymer.

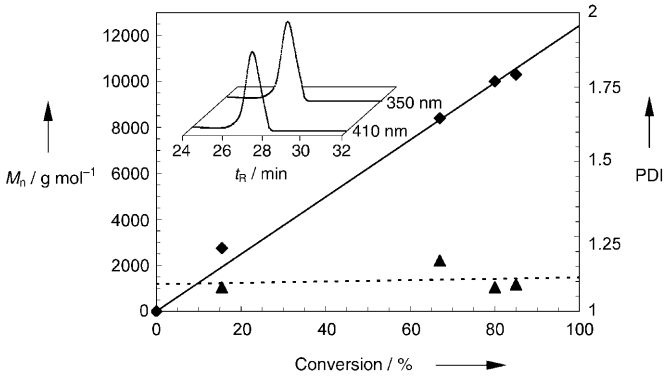


Figure 1. Evolution of molecular weight (◆), as determined by GPC, and PDI (▲) versus conversion for the polymerization of LA (Table 1, entry 4) together with GPC scans using both RI (410 nm) and UV (350 nm) detectors.

A chain-extension experiment with an initial polymerization ($[LA]_0 = 1$ M; $[\text{pyrenebutanol}]_0 = 0.04$ M; $[\text{catalyst}]_0 = 0.02$ M) was performed at 90 °C for 19 h to give polylactide of $M_n = 2500\ g\,mol^{-1}$, as determined by ^1H NMR spectroscopic analysis. L-lactide (3.47×10^{-4} mol) and **1** (2.36×10^{-5} mol) were added to this solution and the solution heated to 90 °C for an additional 7 h. The molecular weight of the sample increased to $9000\ g\,mol^{-1}$ as deduced by ^1H NMR spectroscopic analysis. GPC analysis of the sample revealed an absolute molecular weight of $7300\ g\,mol^{-1}$ and a PDI of 1.36. This solution was charged again with 3.47×10^{-4} mol of L-lactide without any further catalyst and heated to 90 °C for 7 h. The final molecular weight increased to $14000\ g\,mol^{-1}$, as determined by ^1H NMR spectroscopic analysis ($M_n(GPC) = 12000\ g\,mol^{-1}$), with no change in the polydispersity (1.34). Thus, this system exhibits the characteristics of a living polymerization.[16a]

A unique feature of this particular system is that polymerization can be reversibly terminated simply by modulating the temperature. Heating a 1 M solution of LA

to 90 °C in the presence of **1** and 4-pyrene-1-butanol results in the conversion of LA, which stops upon rapid cooling of the solution to 20 °C (Figure 2; 4-pyrene-1-butanol/catalyst = 3:1, L-lactide/4-pyrene-1-butanol = 50:1). Re-initiation of the polymerization occurs upon re-heating at 90 °C, with deactivation occurring upon cooling again to 20 °C. This process was repeated four times. Figure 2 demonstrates clearly that the polymerization can be activated/deactivated with temperature on demand. Significantly, analysis of the polymer after four successive heating and cooling cycles revealed quantitative conversion of the monomer to give polylactide with M_n = 5900 (DP = 41) and M_w/M_n = 1.13:1. Further heating of this sample at 90 °C for 720 minutes revealed little discernable change in the molecular weight or polydispersity (M_n(GPC) = 5400; PDI = 1.29), thus suggesting that the polylactides prepared under these conditions are resistant to further transesterification reactions.

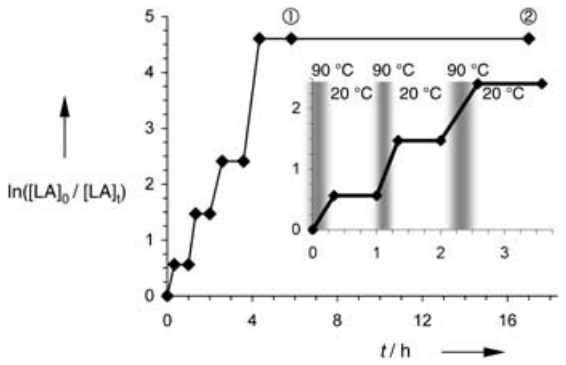
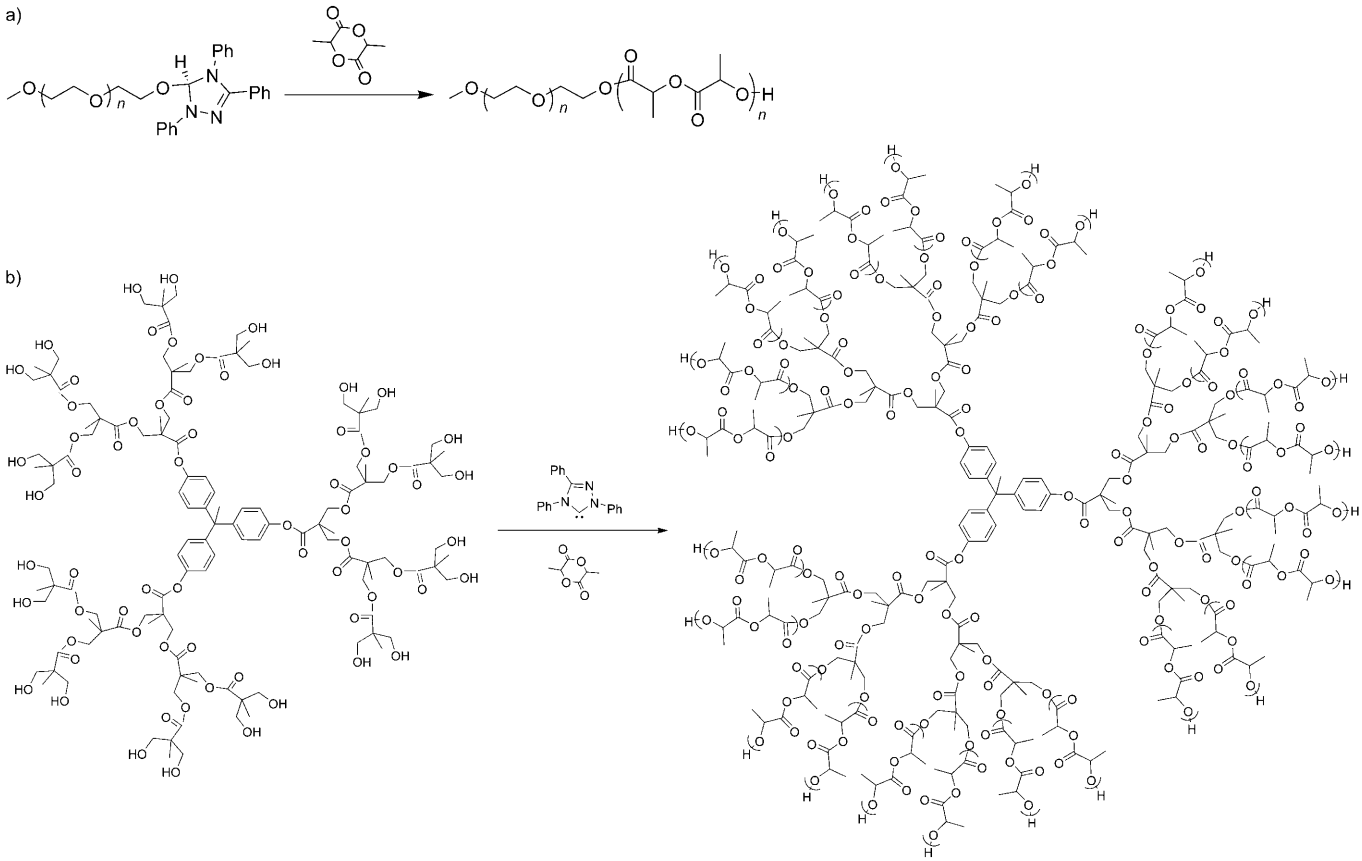


Figure 2. Time dependence of ln([LA]$_0$/[LA]) as a function of time ([LA]$_0$ = 1 M; [alcohol]$_0$ = 0.02 M; [alcohol]$_0$/[catalyst]$_0$ = 1:3) with alternation of high (90 °C) and low (20 °C) temperature. The molecular weights and polydispersity index for ① and ② are 5900 (1.13) and 5400 (1.29), respectively, as determined by GPC. Inset: the first 4 h of the reaction.

A kinetic study of the polymerization of L-lactide (LA) initiated by 4-pyrene-1-butanol (ROH) and catalyzed by **1** was performed at 90 °C using an initial monomer concentration [LA]$_0$ of 1 M. The dependence of ln([LA]$_0$/[LA]) on time at constant triazole concentration ([triaz]$_0$ = 0.02 M) was linear with an intercept at zero, which indicates that the polymerization is first order in monomer and that the number of growing species does not change during the polymerization. Plots of k_{obs} versus [triaz] or [ROH] reveal that the rate is first order both in triazole and alcohol for [triaz]/[ROH] = 1:1. These results demonstrate that the polymerization is first order with respect to catalyst, alcohol, and monomer, according to the rate law given in Equation (1), where [ROH] = [ROH]$_0$, [triaz] = [triaz]$_0$, and k_p = 530 $L^2 mol^{-2} s^{-1}$.

$$-\frac{d[LA]}{dt} = k_p[LA][ROH][triaz] \quad (1)$$



Scheme 3. Generation of block and star copolymers from triazolium alcohol adducts.

The well-defined polymerization behavior of the alkoxytriazoline catalyst systems is ideally suited for the preparation of block copolymers and complex macromolecular architectures. Several adducts of hydroxy-functionalized oligomers and multifunctional alcohols were synthesized either in situ, or isolated and used as thermally stable macroinitiators for the ring-opening polymerization of lactide at 90 °C. A monohydroxypoly(ethylene oxide) oligomer (PEO-OH) ($M_W = 2000\ g\,mol^{-1}$, PDI = 1.05) was treated with **1** in toluene at RT for 12 h to give quantitative conversion of the corresponding alkoxytriazoline. The oligo-alkoxytriazoline is stable at room temperature, but readily polymerizes LA at 90 °C to yield a narrowly dispersed diblock copolymer in near quantitative yields (ca. 90 %; Table 1, entry 7; Scheme 3 a). Dendritic star-shaped polymers were prepared from a hydroxy-functionalized third generation dendrimer derived from 2,2′-(bishydroxymethyl)propionic acid (bis-MPA).[17,18] The dendrimer, 24 equivalents of **1**, and lactide were suspended in toluene and after approximately two hours at room temperature, the solution became homogeneous. The temperature was then increased to 90 °C to yield a narrowly dispersed, 24-arm star polymer (Table 1, entry 8; Scheme 3 b, 40 h, ca. 96 % conversion). The functional groups of the bis-MPA repeating units provide sensitive markers for the spectroscopic analysis of the polymers, since the quartenary carbon atom and the protons on the methylene group are very sensitive to the substitution of the neighboring hydroxy groups.[19] ^1H and ^{13}C NMR spectroscopic analyses showed that the efficiency of the initiation was quantitative and afforded a well-defined 24-arm star polymer (Table 1, entry 8; Scheme 3 b). Significantly, the ester functionality of the dendritic core was retained, thus indicating that the catalyst polymerizes lactide without degrading the polyester-derived dendritic core under these conditions.

In summary, alkoxytriazolines were shown to reversibly dissociate at 90 °C to generate an initiating/propagating alcohol and triazolium carbene for the on-demand living polymerization of lactide. The kinetic results demonstrate that the polymerization is first order with respect to catalyst, alcohol, and monomer, thus suggesting that all the components have an equal role in the propagation step of the mechanism. We have also demonstrated that **1** reversibly forms alcohol adducts that result in an active and dormant form of the catalyst. We postulate that dissociation of the carbene and alcohol from the adduct results in activation of the monomer by the nucleophilic carbene, with propagation occurring through a step involving the activated monomer–carbene adduct and the alcohol. The recombination of the carbene with the new alcohol species results in the formation of the dormant carbene–alcohol adduct. This reversible dissociation is believed to be responsible for the exquisite control of molecular weight, narrow polydispersities, and end-group fidelity, analogous to modern controlled radical procedures.[20]

Received: February 25, 2005
Revised: April 15, 2005
Published online: July 11, 2005

Keywords: homogeneous catalysis · lactide · N-heterocyclic carbenes · ring-opening polymerization

[1] *Carbenes*, *Vol. 1* (Eds.: M. Jones, R. A. Moss), Wiley, New York, **1973**; *Carbenes*, *Vol. 2* (Eds.: M. Jones, R. A. Moss), Wiley, New York, **1975**.

[2] For general reviews, see a) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; b) H. Tomioka, *Acc. Chem. Res.* **1997**, *30*, 315; c) W. A. Herrmann, C. Kocher, *Angew. Chem.* **1997**, *109*, 2256; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162.

[3] a) H. W. Wanzlick, H. J. Kleiner, *Angew. Chem.* **1961**, *73*, 493; b) H. W. Wanzlick, *Angew. Chem.* **1962**, *74*, 129; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75; c) H. W. Wanzlick, T. Esser, H. J. Kleiner, *Chem. Ber.* **1963**, *96*, 1208.

[4] a) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand, *Angew. Chem.* **1989**, *101*, 617; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 621; b) A. Igau, A. Baceiredo, H. Gruetzmacher, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463.

[5] a) A. J. Arduengo, R. L. Dais, R. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361; b) A. Arduengo, R. L. Dias, R. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530.

[6] a) A. J. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913; b) A. J. Arduengo, R. Krfczyk, *Chem. Ztg.* **1998**, *32*, 6; c) M. K. Denk, A. Thadani, K. Hatano, A. J. Lough, *Angew. Chem.* **1997**, *109*, 2719; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2607.

[7] See, for example: a) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; b) W. Herrmann, C. Kocher, *Angew. Chem.* **1997**, *109*, 2256; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162; c) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247; d) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674; e) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2490; f) W. A. Herrmann, M. Elison, J. Fisher, C. Kocher, G. J. Artus, *Angew. Chem.* **1995**, *107*, 2602; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371; g) W. A. Herrmann, L. Goossen, C. Kocher, G. Artus, *Angew. Chem.* **1996**, *108*, 2980; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2805; h) M. J. Lappert, *J. Organomet. Chem.* **1988**, *358*, 185; i) D. Enders, K. Breuer, G. Raabe, J. Runsink, T. Henrique, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem.* **1995**, *107*, 1119; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021; j) M. C. Perry, K. Burgess, *Tetrahedron: Asymmetry* **2003**, *14*, 951; k) L. Jafarpour, S. P. Nolan, *Adv. Organomet. Chem.* **2001**, *46*, 181.

[8] See, for example: a) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; b) M. S. Stanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 749; c) W. A. Herrman, L. J. Goossen, M. Spiegler, *Organometallics* **1998**, *17*, 2162; d) T.-L. Choi, R. H. Grubbs, *Chem. Commun.* **2001**, 2648; e) J. Haung, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1998**, *17*, 2370; f) M. M. McCormick, H. A. Duong, G. Zuo, J. Louie, *J. Am. Chem. Soc.* **2005**, submitted; g) H. A. Duong, H. A. M. J. Cross, J. Louie, *J. Am. Chem. Soc.* **2004**, *126*, 11438; h) G. Zuo, J. Louie, *Angew. Chem.* **2004**, *116*, 2327; *Angew. Chem. Int. Ed.* **2004**, *43*, 2277.

[9] See, for example: a) R. Breslow, *J. Am. Chem. Soc.* **1958**, *80*, 3719; b) H. Stetter, *Angew. Chem.* **1976**, *88*, 695; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 639; c) D. Enders, J. H. Breuer, *Helv. Chim. Acta* **1996**, *79*, 1217; d) J. Teles, J. Melder, K. Ebel, D. Enders, J. H. Breuer, *Helv. Chim. Acta* **1996**, *79*, 61; e) M. S. Kerr, J. R. De Alaniz, T. Rovis, *J. Am. Chem. Soc.* **2002**, *124*, 10298; f) D. Enders, U. Kallfass, *Angew. Chem.* **2002**, *114*, 1822; *Angew. Chem. Int. Ed.* **2002**, *41*, 1743; g) G. A. Grasa, R. M. Kissling, S. P. Nolan, *Org. Lett.* **2002**, *4*, 3583; h) G. W. Nyce, J. A. Lamboy, E. F. Connor, R. M. Waymouth, J. L. Hedrick, *Org.*

Lett. **2002**, *4*, 3587; i) D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534; j) N. T. Reynolds, J. Read de Alaniz, T. Rovis, *J. Am. Chem. Soc.* **2004**, *126*, 9518; k) S. S. Sohn, E. L. Rosen, W. J. Bode, *J. Am. Chem. Soc.* **2004**, *126*, 14370; l) H. A. Duong, M. J. Cross, J. Louie, *Org. Lett.* **2004**, *6*, 4679; m) G. A. Grasa, T. Guveli, R. Singh, S. P. Nolan, *J. Org. Chem.* **2003**, *68*, 2812; n) N. T. Reynolds, J. R. De Alaniz, T. Rovis, *J. Am. Chem. Soc.* **2004**, *126*, 9518; o) G. W. Nyce, T. Glauser, E. F. Connor, A. Mock, R. M. Waymouth, J. L. Hedrick, *J. Am. Chem. Soc.* **2003**, *125*, 3046.

[10] A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* **1997**, *119*, 12742.

[11] See, for example: a) J. P. Morgan, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 3153; b) L. S. Jafarpour, S. P. Nolan, *Organometallics* **2000**, *19*, 2055.

[12] a) H.-W. Wanzlick, F. Esser, H.-J. Kleiner, *Chem. Ber.* **1963**, *96*, 1208; b) B. Cetinkaya, E. Cetinkaya, J. A. Chamizo, P. B. Hitchcock, H. A. Jasim, H. Kücükbay, M. F. Lappert, *J. Chem. Soc. Perkin Trans. 1* **1998**, 2047; c) T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 2546; d) D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J. P. Melder, K. Ebel, S. Brode, *Angew. Chem.* **1995**, *107*, 1119; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021; e) D. Enders, K. Breuer, J. Runsink, J. H. Teles, *Liebigs Ann.* **1996**, 2019; f) J. P. Morgan, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 3153; g) B. Lachmann, H. W. Wanzlick, *Liebigs Ann. Chem.* **1969**, *729*, 27; h) G. W. Nyce, S. Csihony, R. M. Waymouth, J. L. Hedrick, *Chem. Eur. J.* **2004**, *10*, 4073.

[13] See, for example: a) A. J. Arduengo, J. C. Calabrese, F. Davidson, H. V. R. Dias, J. R. Goerlich, R. Krafczyk, W. J. Marshall, M. Tamm, R. Schmutzler, *Helv. Chim. Acta* **1999**, *82*, 2348; b) H. W. Wanzlick, H. Ahrens, *Chem. Ber.* **1966**, *99*, 1580; c) Wanzlick, H. W. Kleiner, *Chem. Ber.* **1963**, *96*, 3024; d) D. Enders, K. Breuer, J. Runsink, J. H. Teles, *Liebigs Ann.* **1996**, 2019; e) J. A. Cowan, J. A. C. Clyburne, M. G. Davidson, R. L. W. Harris, J. A. K. Howard, P. Kupper, M. A. Leech, S. P. Richards, *Angew. Chem.* **2002**, *114*, 1490; *Angew. Chem. Int. Ed.* **2002**, *41*, 1432; f) L. McKenzie, J. C. Brodovitch, P. W. Percival, T. Ramnial, J. A. C. Clyburne, *J. Am. Chem. Soc.* **2003**, *125*, 11565.

[14] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953.

[15] D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J. P. Melder, K. Ebel, S. Brode, *Angew. Chem.* **1995**, *107*, 1119; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021.

[16] a) S. Penczek, T. Biela, A. Duda, *Macromol. Rapid Commun.* **2000**, *21*, 941; b) A. Lofgren, A. C. Albertsson, P. Dubois, R. Jerome, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1995**, *35*, 379.

[17] a) H. Ihre, A. Hult, *Polym. Mater. Sci. Eng.* **1997**, *77*, 71; b) H. Ihre, A. Hult, E. Soderlind, *J. Am. Chem. Soc.* **1996**, *118*, 6388.

[18] H. Ihre, O. L. Padilla De Jesu, J. M. J. Frechet, *J. Am. Chem. Soc.* **2001**, *123*, 5908.

[19] E. Malmstrom, M. Johansson, A. Hult, *Macromolecules* **1995**, *28*, 1698.

[20] a) K. Matyjaszewski, T. P. Davis, *Handbook of Radical Polymerization*, Wiley-Interscience, New York, **2002**; b) C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.* **2001**, *101*, 3661.

