Articles

Binuclear Schrock-Type Alkylidene-Triggered ROMP and Cyclopolymerization of 1,6-Heptadiynes: Access to Homopolymers and ABA-Type Block Copolymers

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Received November 15, 2005; Revised Manuscript Received January 31, 2006

ABSTRACT: The molybdenum-based binuclear Schrock-type initiator 1,4-{Mo(N-2,6-(2-Pr)$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$-CH}$_2$C$_6$H$_4$ (**1**) was used for the ring-opening metathesis polymerization (ROMP) of norborn-2-ene (NBE) and for the cyclopolymerization of a series of 1,6-heptadiynes, i.e., dimethyl dipropargylmalonate (**M1**), diethyl dipropargylmalonate (**M2**), di-*tert*-butyl dipropargylmalonate (**M3**), 4-(ethoxycarbonyl)-1,6-heptadiyne (**M4**), 4,4-bis(hydroxymethyl)-1,6-heptadiyne (**M5**), and 4-(hydroxymethyl)-1,6-heptadiyne (**M6**) to form the corresponding **M**$_n$−X−**M**$_n$ block copolymers. The polymerization systems **M1-1** (monomer **M1** polymerized by the action of initiator **1**) and **M2-1** fulfilled the criteria of a class IV and class V living system, respectively. Poly-**M1**, poly-**M2**, poly-**M3**, and poly-**M4** consisted of 40%, 50%, 58%, and 32% 1,2-(cyclopent-1-ene)vinylenes and 60%, 50%, 42%, and 68% 1,3-(cyclohex-1-ene)methylidenes, respectively. Finally, the block copolymers **M2**$_{25}$-*b*-**M1**$_{25}$-CH-1,4-C$_6$H$_4$-CH-**M1**$_{25}$-*b*-**M2**$_{25}$, **M1**$_{35}$-*b*-**M2**$_{35}$-CH-1,4-C$_6$H$_4$-CH-**M2**$_{35}$-*b*-**M1**$_{35}$, **M1**$_{25}$-*b*-NBE$_{35}$-CH-1,4-C$_6$H$_4$-CH-NBE$_{35}$-*b*-**M1**$_{25}$, **M2**$_{40}$-*b*-NBE$_{26}$-CH-1,4-C$_6$H$_4$-CH-NBE$_{26}$-*b*-**M2**$_{40}$, NBE$_{50}$-*b*-**M1**$_{35}$-CH-1,4-C$_6$H$_4$-CH-**M1**$_{35}$-*b*-NBE$_{50}$, and NBE$_{30}$-*b*-**M2**$_{25}$-CH-1,4-C$_6$H$_4$-CH-**M2**$_{25}$-*b*-NBE$_{30}$ were prepared. Using AFM, films of **M1**$_{25}$-CH-1,4-C$_6$H$_4$-CH-**M1**$_{25}$ were found to be homogeneous, while phase separation was observed for **M1**$_{25}$-*b*-NBE$_{35}$-CH-1,4-C$_6$H$_4$-CH-NBE$_{35}$-*b*-**M1**$_{25}$.

Introduction

In course of our investigations on the living cyclopolymerization of 1,6-heptadiynes[1−11] we turned our interest to the synthesis of bi- and trinuclear initiators.[12−16] On one hand, binuclear initiators offer a straightforward access to A−X−A (*pseudo*-) triblock copolymers (i.e., homopolymers separated by a small initiator-derived fragment) without the necessity of multiple, alternate monomer addition. On the other hand, A−B−A triblock (i.e., *pseudo* A−B−X−B−A pentablock) copolymers are accessible by one single change in monomer type. This method becomes an attractive alternative in case the synthesis of A−B−A block copolymers via reaction of (living) A with B to form a living A−B block copolymer is possible, however, subsequent reaction of this living diblock copolymer with A to form the desired A−B−A triblock copolymer is impossible for whatever reason.[17] The fact that synthesis is accomplished in one single step puts also reduced demands on the livingness of the entire system, thus broadening the range of catalysts that may be used for these purposes. In addition, no A−B diblock copolymers are formed as byproducts. Finally, this approach also offers access to symmetrical ditelechelic polymers. Here, we wish to report our latest results on the synthesis of a binuclear molybdenum-based initiator and its use in the cyclopolymerization of various heptadiynes and the ROMP of norborn-2-ene (NBE). The initiator gives raise to novel, cyclopolymerization-derived block-copolymer-based architectures.

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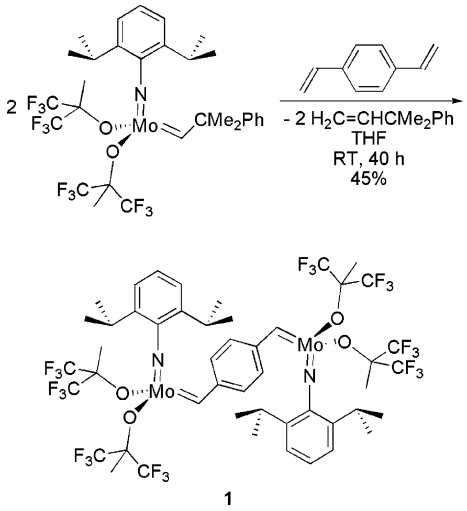
Results and Discussion

Synthesis of Binuclear Molybdenum Alkylidene 1,4-{Mo-(N-2,6-(2-Pr)$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$CH}$_2$C$_6$H$_4$ (1). Similar to a route described by Schrock et al.,[12,13] bright orange initiator **1** was synthesized via a metathesis reaction between Mo(N-2,6-(2-Pr)$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$[18] and 0.5 equiv of 1,4-divinylbenzene (Scheme 1). Although the Schrock group claimed that metathesis with 1,4-divinylbenzene proceeded too slowly to afford **1** in THF, we accomplished the synthesis of **1** in THF in 45% yield. From ^{1}H NMR spectroscopic data obtained in CDCl$_3$ at 323 K we conclude that despite the synthesis was carried out in THF, the compound was obtained as the **THF-free adduct** (see Supporting Information), which is in contrast to the X-ray supported structure published by the Schrock group.[13] However, since all polymerizations were run in THF, *syn*/*anti* ratios of the initiating species, i.e., the THF adduct of **1**, identical to those reported by the Schrock group, may be expected.

Cyclopolymerizations. Cyclopolymerization of 1,6-heptadiynes results in polyenes with cyclic recurring units along the

10.1021/ma0524373 CCC: $33.50
Published on Web 03/01/2006

Scheme 1. Synthesis of the Binuclear Schrock-type Alkylidene 1



polymer backbone. In contrast to polyenes synthesized from 1-alkynes, 1,3-interactions of the substituents, resulting in lower effective conjugation lengths (N_{eff}) in these polyenes, are absent with 1,6-heptadiyne-based cyclopolymers.[14,19] The two different reaction pathways that offer access to polyenes containing either five- (i.e., 1,2-(cyclopent-1-ene)vinylene) or six-membered (i.e., 1,3-(cyclohex-1-ene)methylidene) ring-based repetitive units are well-understood.[19] On the basis of an "alkylidene mechanism" proposed for the cyclopolymerization of 1,6-heptadiyne derivatives,[19] the backbone structure of the polymer exclusively depends on the mode of addition of the monomer to the metal alkylidene bond in the initial step. In due consequence, both the steric and electronic effects of the ligand sphere around the M═C bond of the initiator[4,5,9,20] as well as the steric demands of the substituents in the 4-position of the 1,6-heptadiyne[21] exert decisive influence on the regio- and stereoselectivity of the cyclopolymerization.

To get some further insight into both the steric effects and the influence of the polarity of the substituents in the 4-position on the cyclopolymerization mediated by initiator **1**, we chose six 1,6-heptadiyne derivatives **M1**−**M6** as model monomers (Figure 1).

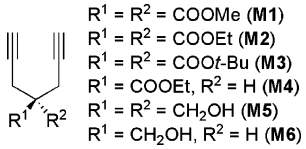


Figure 1. Structures of monomers **M1**−**M6**.

The monomers dimethyl dipropargylmalonate (**M1**),[22] diethyl dipropargylmalonate (**M2**),[23] 4-(ethoxycarbonyl)-1,6-heptadiyne (**M4**),[14] 4,4-bis(hydroxymethyl)-1,6-heptadiyne (**M5**),[14] and 4-(hydroxymethyl)-1,6-heptadiyne (**M6**)[24] were prepared according to literature procedures. Di-*tert*-butyl dipropargylmalonate (**M3**) was accessible via alkylation of the ester enolate of di-*tert*-butyl malonate formed upon deprotonation with sodium *tert*-butoxide using propargyl bromide.

Polymerizations Induced by 1. Polymerizations of **M1**−**M4** mediated by **1** were carried out in THF and were terminated in a Wittig-like capping reaction by adding excess ferrocene carbaldehyde. After precipitation from pentane, deep red or purple powders with a metal luster were obtained. Molecular weights of the resulting polyenes were determined by GPC vs polystyrene (PS) in $CHCl_3$ (Table 1).

Table 1. GPC, UV−Vis Data, and Yields for Polymers Prepared from M1−M6 Using Initiator 1[a]

polymer	M_n(calcd) (g/mol)[b]	M_n (g/mol)[c]	M_w/M_n[c]	λ_{max} (nm)[d]	yield (%)[e]
poly-**M1**$_{10}$	2600	4600	1.24	515	64
poly-**M1**$_{30}$	6700	12 400	1.27	547	97
poly-**M1**$_{50}$	10 900	20 600	1.25	554	82
poly-**M1**$_{70}$	15 100	24 300	1.31	557	70
poly-**M1**$_{100}$	21 300	38 900	1.34	559	69
poly-**M2**$_{10}$	2900	5100	1.37	499	54
poly-**M2**$_{30}$	7600	12 700	1.25	547	74
poly-**M2**$_{50}$	12 300	17 200	1.30	546	72
poly-**M2**$_{70}$	17 000	25 300	1.51	549	71
poly-**M2**$_{90}$	21 800	28 000	1.25	556	73
poly-**M2**$_{100}$	24 100	32 700	1.19	558	67
poly-**M3**$_{50}$	15 100	27 800	2.07[f]	538	51
poly-**M4**$_{50}$	8700	14 300	1.51[f]	532	77
poly-**M5**$_{100}$	15 500	12 200[g]	1.51[g,h]		∼10
poly-**M6**$_{145}$	18 000	6000[g]	1.12[g,h]		49

[a] Details of the procedure are described in the Experimental Section. [b] Assuming 100% conversion, including end groups. [c] Determined by GPC vs PS in $CHCl_3$ using RI detection. [d] In $CHCl_3$. [e] Determined gravimetrically. [f] High molecular weight shoulder/tailing. [g] Determined by GPC vs PMMA in *N*,*N*-dimethylacetamide using RI detection. [h] *N*,*N*-dimethylacetamide-soluble fraction.

GPC traces of poly-**M1** and poly-**M2** were unimodal, whereas shoulders and/or significant tailing in the high molecular weight region were observed in the GPC traces of poly-**M3** and poly-**M4**, indicating less well-behaved cyclopolymerizations. Obviously, medium-sized substituents in the 4-position of the 1,6-heptadiyne derivatives **M1** and **M2** favor the formation of uniform polyenes with narrow molecular weight distributions (PDI ≤ 1.51) when using **1** as initiating system in THF. In contrast, sterically demanding substituents in the 4-position (**M3**) as well as comparably small ones (**M4**) apparently give rise to side reactions in the cyclopolymerizations initiated by **1** as illustrated by the values of M_n and PDI (Table 1). Schrock-type alkylidenes are usually associated with low functional group tolerance.[25] However, the polar *and* protic monomers **M5** and **M6** bearing hydroxyl groups in the 4-position could in fact be polymerized using **1** though isolated yields were medium (49%) for **M6** and low (10%) for **M5** (Table 1), presumably due to gradual initiator deactivation during the polymerization process. Highly polar poly-**M5** and poly-**M6** were insoluble in common solvents such as CH_2Cl_2, THF, or $CHCl_3$ and only partially soluble in polar solvents like dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylacetamide (DMAc), whereas poly-**M1**, poly-**M2**, poly-**M3**, and poly-**M4** were soluble in several common organic solvents, e.g., CH_2Cl_2, THF, $CHCl_3$, or toluene. On the basis of these findings, we investigated the cyclopolymerization of monomers **M1** and **M2** bearing medium-sized substituents in the 4-position in some more detail. As has already been shown for the cyclopolymerization of **M2** using the DME-coordinated analogue of **1** as initiator,[14] plots of the number-average molecular weight (M_n) vs the number of monomer equivalents (N) revealed a linear dependence for both monomer-initiator systems, i.e., **M1-1** and **M2-1** (Figure 2).

This and the comparably low PDIs (≤1.51) suggest living polymerization systems. According to a ranking of living systems introduced by Matyjaszewski,[26] which is based on the ratios of the rate constants of chain transfer, propagation, and termination,[26] cyclopolymerizations of **M1** and **M2** induced by **1** fulfill at least the preconditions of a class IV and class V living systems, respectively. Thus, the polymerization system **M1-1** was still fully active after at least 30 min and **M2-1** was active even after 4 h, and polymerizations resumed quantitatively upon addition of a second monomer feed after this time to result

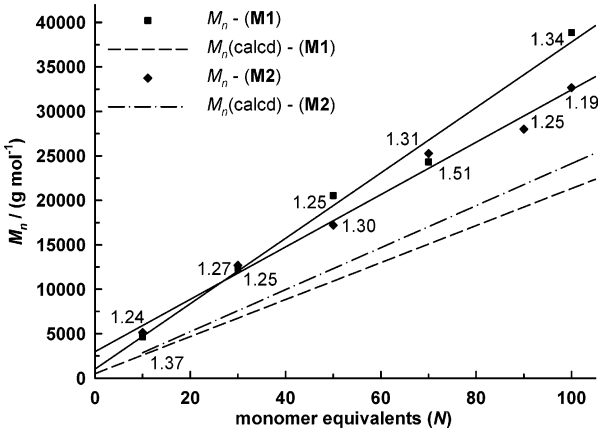


Figure 2. Plot of M_n vs number of monomer equivalents (N) and PDIs for a series of samples of **M1**$_n$-CH-1,4-C_6H_4-CH-**M1**$_n$ and **M2**$_n$-CH-1,4-C_6H_4-CH-**M2**$_n$ prepared by the action of initiator **1** (data from Table 1).

in polyenes with no significant changes in PDI. In addition to these data, the k_p/k_i values for the systems **M1**-**1** and **M2**-**1** (1 and 5, respectively; determined by ^{1}H NMR at 300 K in THF-d_8[27]), were in fact lower than those reported for various other Schrock-type alkylidenes.[4,5] The chemical shifts for the alkylidene proton (H_α) of the first, second, etc. insertion products were $\delta = 13.01$, 12.98, and 12.43 ppm for **M1** and $\delta = 13.01$, 12.99, and 12.42 ppm for **M2**.

Microstructure of Polymers Prepared by the Action of 1. More information about the ratio of five- to six-membered rings along the polymer backbones of poly-**M1**, poly-**M2**, poly-**M3**, and poly-**M4** was obtained by ^{13}C NMR spectroscopy. For poly-**M1**, poly-**M2**, and poly-**M3** both the signals of the carbon atoms bearing the ester substituents of five- and six-membered rings occurring at 57−58 and 54−55 ppm, respectively, and the carbonyl resonances at 170−173 ppm were used.[4,5,14] Apart from the carbonyl resonances in the region of 173−176 ppm, resonances of allylic carbons in the region of 26−38 ppm were used to determine the ratio of five- and six-membered rings in the case of poly-**M4**. Similar to data for poly-**M2** synthesized by Schrock et al. using Mo(N-2,6-(2-Pr)$_2$C$_6$H$_3$)(CHCMe$_2$Ph)-[OCMe(CF$_3$)$_2$]$_2$ as initiator in DME,[14] two signals for the carbonyl atoms at 170.5 and 171.5 ppm and two sets of resonances at 57 and 54 ppm were observed in poly-**M2**. Furthermore, numerous olefinic resonances in the range of 120−140 ppm and many signals for the allylic methylene carbons indicated carbons in different chemical environments within the polymer chain. Quantitative analysis of the carbonyl resonances and the sets of resonances of the quaternary carbon atoms revealed a ratio of five- to six-membered rings of approximately 1:1, irrespective of the chain length of the polyene. Detailed data are summarized in Table 2. The relevant parts of the ^{13}C NMR spectra are summarized in Figure 3, and a complete spectrum is shown in Figure 4.

Table 2. Ring Compositions[a] in Poly-M1, Poly-M2, Poly-M3, and Poly-M4 Prepared Using Initiator 1

polymer	five-membered rings (%)
poly-**M1**$_{50}$	40 ± 3
poly-**M2**$_{30}$	50 ± 0
poly-**M2**$_{70}$	50 ± 2
poly-**M2**$_{100}$	50 ± 1
poly-**M3**$_{50}$	58 ± 4
poly-**M4**$_{50}$	32 ± 3

[a] ^{13}C NMR spectra were acquired at 300 K in a 0.05 M solution of Cr(acac)$_3$ in CDCl$_3$. The percentage of five- and six-membered rings in poly-**M1**, poly-**M2**, and poly-**M3** was determined using the carbonyl resonances in the region of 170−173 ppm and quaternary carbon resonances in the region of 50−60 ppm.[4,5] For poly-**M4** carbonyl resonances in the region of 173−176 ppm and resonances of allylic carbons in the region of 26−38 ppm were used to determine the ratio of five- and six-membered rings. The average between the two is listed.

Here, an effect already described for quniuclidine-based initiators was observed again.[4,5] Thus, the fraction of 1,2-(cyclopent-1-enylene)vinylene repeat units in the polyene decreased from 50 in poly-**M2** to approximately 40% in poly-**M1**. Obviously, even an incremental reduction of steric demands of the substituents in the 4-position by replacing ethyl ester (**M2**) with methyl ester groups (**M1**) already leads to a significant increase in β-addition of **M1** compared to **M2**, consequently favoring the formation of six-membered rings.

Accordingly, further reduction of the steric demands of the substituents in the 4-position in **M4** resulted in poly-**M4** with an even higher content of six-membered rings (ca. 68%) whereas **1**-mediated cyclopolymerization of sterically demanding **M3** based on two *tert*.-butylester groups yielded poly-**M3** with approximately 58% five-membered ring-based repeat units. This is in accordance with results reported by Choi et al. using classical MoCl$_5$-based initiators.[21] Here, a decrease in the steric bulk of the monomer was reported to lead to reduced steric

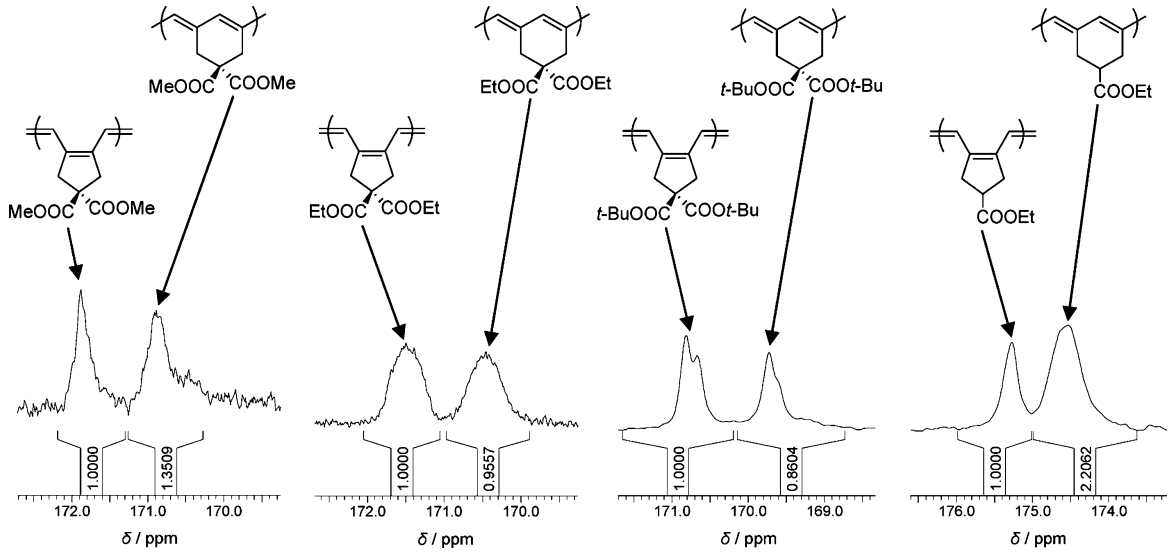


Figure 3. Carbonyl regions in the ^{13}C NMR spectra (63 MHz) of poly-**M1**$_{50}$, poly-**M2**$_{70}$, poly-**M3**$_{50}$, and poly-**M4**$_{50}$.

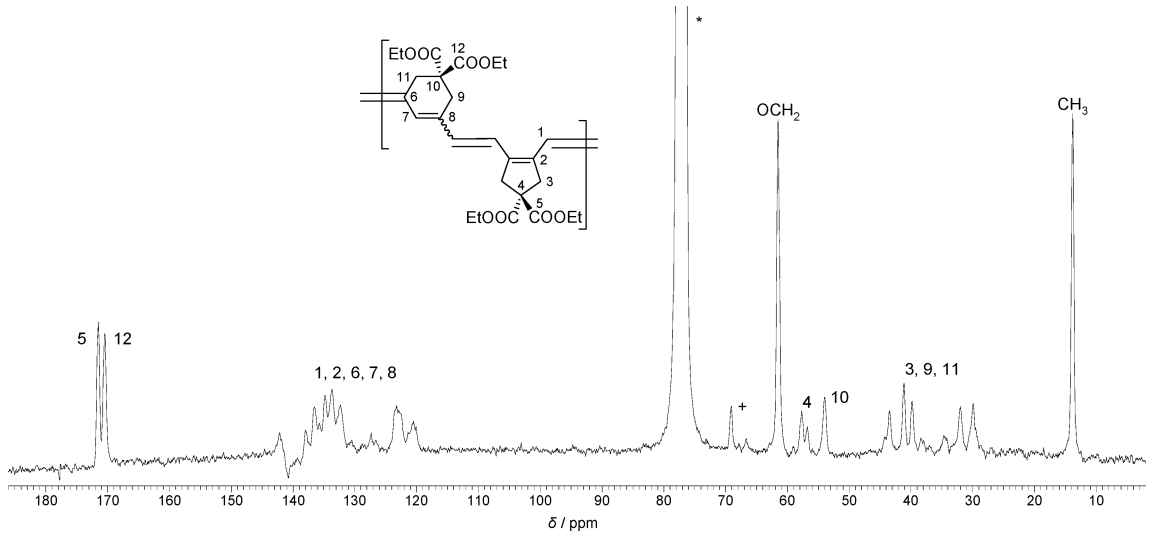


Figure 4. ^{13}C NMR spectrum (63 MHz) of poly-**M2**$_{70}$ (∗ denotes $CHCl_3$; + denotes excess ferrocene carbaldehyde).

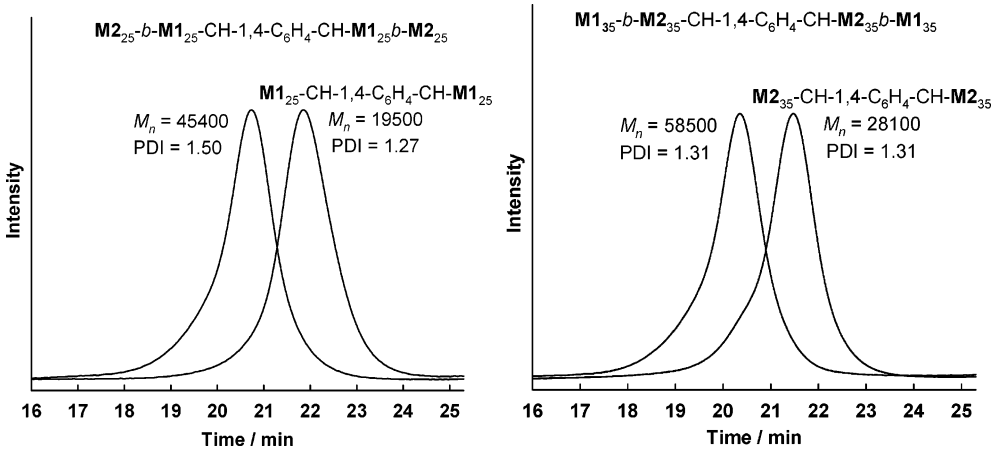


Figure 5. GPC traces vs PS with RI detection in $CHCl_3$ of **M2**$_{25}$-*b*-**M1**$_{25}$-CH-1,4-C_6H_4-CH-**M1**$_{25}$-*b*-**M2**$_{25}$ and **M1**$_{35}$-*b*-**M2**$_{35}$-CH-1,4-C_6H_4-CH-**M2**$_{35}$-*b*-**M1**$_{35}$ block copolymers obtained from monomers **M1** and **M2** using the binuclear initiator **1**.

interactions between the incoming monomer and the growing polymer chain. The UV−vis data recorded for poly-**M2** also fit these data. As reported earlier,[4,5] the absorption maximum (λ_{max}) of poly-**M2** increases from 534 to 591 nm when the 1,2-(cyclopent-1-ene)vinylene content in the polyene is increased from 0 (i.e., 100% 1,3-(cyclohex-1-ene)methylidenes) to 100%. Here, a λ_{max} of 558 nm was observed, which is significantly lower than that recorded for poly-**M2** based on pure five-membered ring structures (591 nm)[4,5] but higher than that reported for pure six-membered ring structures (534 nm).[20]

Block Copolymerizations. Synthesis of Microphase-Separated Block Copolymers. Taking the high degree of control of cyclopolymerizations of **M1** and **M2** with **1** as initiating system into account, we prepared A_n-*b*-B_m−X−B_m-*b*-A_n type block copolymers from these monomers in *two-step* polymerization processes. The first block copolymer was synthesized from living **M1**$_{25}$-CH-1,4-C_6H_4-CH-**M1**$_{25}$ by adding 50 equiv of **M2**. Termination of the polymerization with excess ferrocene carbaldehyde furnished poly-**M2**$_{25}$-*b*-**M1**$_{25}$-CH-1,4-C_6H_4-CH-**M1**$_{25}$-*b*-**M2**$_{25}$. By reversing the order of monomer addition, a different block copolymer, **M1**$_{35}$-*b*-**M2**$_{35}$-CH-1,4-C_6H_4-CH-**M2**$_{35}$-*b*-**M1**$_{35}$, was synthesized. Irrespective of the order of monomer addition, the GPC peak shifted to higher molecular weights with only minor respectively no broadening of the molecular weight distribution (Figure 5).

Since the ROMP of NBE using **1** as initiator also proceeded in a controlled manner (Figure 6), we prepared another set of

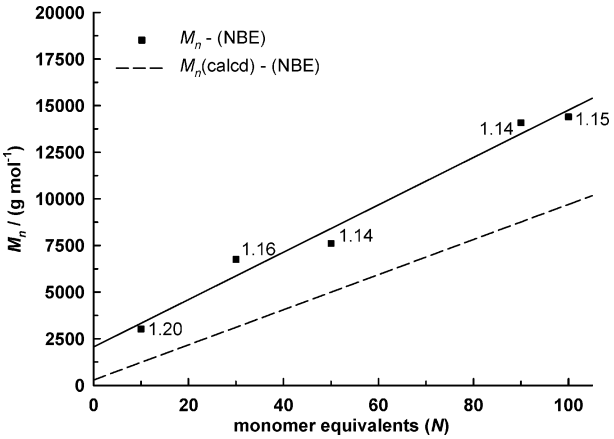


Figure 6. Plot of M_n vs number of monomer equivalents (*N*) and PDIs for a series of samples of poly-NBE prepared using initiator **1**.

block copolymers from **M1** or **M2** and NBE, respectively.

Again, irrespective of the order of monomer addition to a THF solution of **1**, the GPC signal shifted to higher molecular weights thus indicating the formation of the corresponding block copolymer (Figure 7). Supplying monomers in the order NBE, **M1**, or NBE, **M2**, respectively, afforded the corresponding block copolymers **M1**$_{25}$-*b*-NBE$_{35}$-CH-1,4-C_6H_4-CH-NBE$_{35}$-*b*-**M1**$_{25}$, **M2**$_{40}$-*b*-NBE$_{26}$-CH-1,4-C_6H_4-CH-NBE$_{26}$-*b*-**M2**$_{40}$, respectively, with low PDIs.

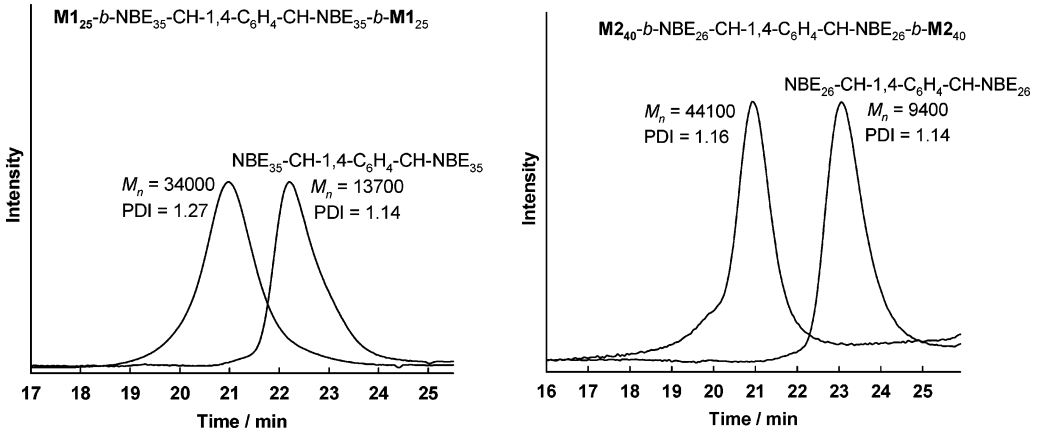


Figure 7. GPC traces of **M1**$_{25}$-*b*-NBE$_{35}$-CH-1,4-C$_6$H$_4$-CH-NBE$_{35}$-*b*-**M1**$_{25}$ and **M2**$_{40}$-*b*-NBE$_{26}$-CH-1,4-C$_6$H$_4$-CH-NBE$_{26}$-*b*-**M2**$_{40}$ block copolymers from monomers **M1**, **M2**, and NBE using the binuclear initiator **1**.

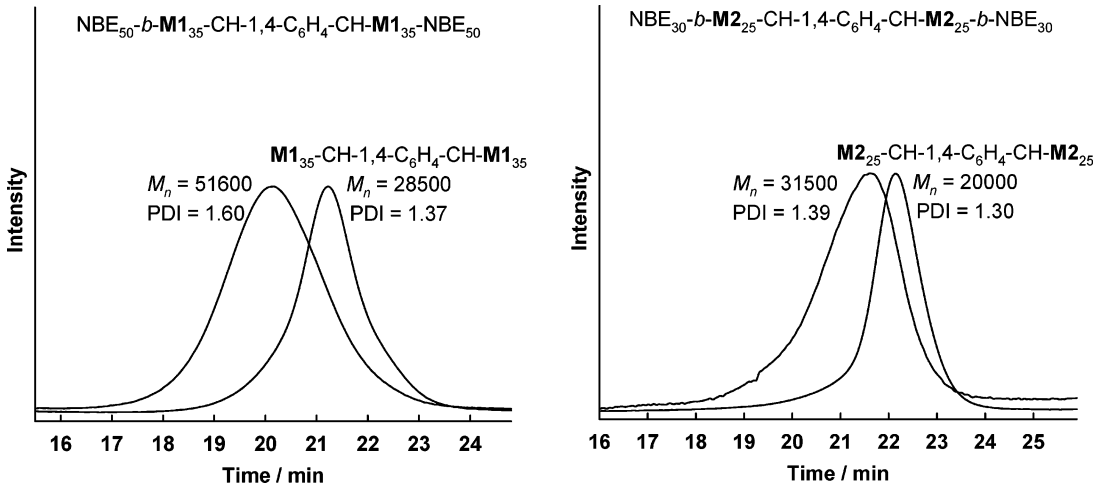


Figure 8. GPC traces of NBE$_{50}$-*b*-**M1**$_{35}$-CH-1,4-C$_6$H$_4$-CH-**M1**$_{35}$-*b*-NBE$_{50}$ and NBE$_{30}$-*b*-**M2**$_{25}$-CH-1,4-C$_6$H$_4$-CH-**M2**$_{25}$-*b*-NBE$_{30}$ block copolymers from monomers **M1**, **M2**, and NBE using the binuclear initiator **1**.

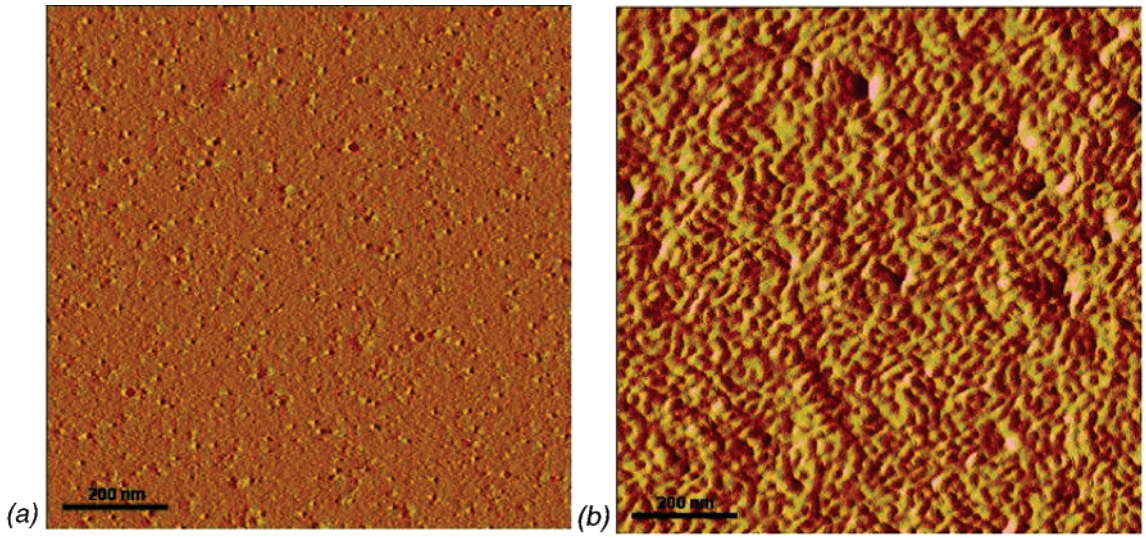


Figure 9. AFM micrographs of (a) **M1**$_{25}$-CH-1,4-C$_6$H$_4$-CH-**M1**$_{25}$ and (b) **M1**$_{25}$-*b*-NBE$_{35}$-CH-1,4-C$_6$H$_4$-CH-NBE$_{35}$-*b*-**M1**$_{25}$ (amplitude images).

Alternatively, polymerization was started using either **M1** or **M2**, followed by addition of NBE (Figure 8), resulting in the formation of NBE$_{50}$-*b*-**M1**$_{35}$-CH-1,4-C$_6$H$_4$-CH-**M1**$_{35}$-*b*-NBE$_{50}$ and NBE$_{30}$-*b*-**M2**$_{25}$-CH-1,4-C$_6$H$_4$-CH-**M2**$_{25}$-*b*-NBE$_{30}$. Though polydispersities were slightly higher, i.e., $\leq$ 1.60, in this case, it is worth mentioning that such flexibility in the order of monomer addition is hardly observed in any other living polymerization process.

To get some insight into the morphology of the A$_n$−X−A$_n$ and A$_n$-*b*-B$_m$−X−B$_m$-*b*-A$_n$ type block copolymers containing conjugated segments, AFM images were recorded from drop-casted films of **M1**$_{25}$-CH-1,4-C$_6$H$_4$-CH-*b*-**M1**$_{25}$ (Figure 9a) and **M1**$_{25}$-*b*-NBE$_{35}$-CH-1,4-C$_6$H$_4$-CH-NBE$_{35}$-*b*-**M1**$_{25}$ (Figure 9b) in dichloromethane on freshly cleaved mica. In the amplitude image of **M1**$_{25}$-CH-1,4-C$_6$H$_4$-CH-*b*-**M1**$_{25}$ a rather smooth and largely homogeneous surface was observed. In contrast, an AFM

micrograph of **M1**$_{25}$-*b*-NBE$_{35}$-CH-1,4-C_6H_4-CH-NBE$_{35}$-*b*-**M1**$_{25}$ containing poly-NBE segments clearly revealed microphase separation of the polar, conjugated poly-**M1** and nonpolar, nonconjugated poly-NBE segments of the block copolymer. However, the observed domain sizes exceed by far the calculated (estimated) domain sizes of 10 and 30 nm, respectively, suggesting some additional (supramolecular) ordering.

Conclusions

Using a 1,4-divinylbenzene bridged Mo−alkylidene initiator, controlled polymerizations of dimethyl dipropargylmalonate, diethyl dipropargylmalonate, and norborn-2-ene were realized. In addition, multistage polymerizations of these monomers are possible, offering a straightforward access to block copolymers with a well-defined number of segments. Especially A$_n$-*b*-B$_m$−X−B$_m$-*b*-A$_n$ type block copolymers with poly(NBE)-based segments show distinct microphase separation. As expected and in accordance with the literature, the use of hexafluoro-*tert*-butoxide-based molybdenum initiators yields polyenes consisting of a mixture of five- and six-membered rings along the polyene backbone. Other heptadiynes including those carrying protic functionalities can also be polymerized. Finally, the size of the substituents in 4-position of a 1,6-heptadiyne shows significant effects on the final polymer microstructure. This fact is currently further investigated since it is expected to be an additional important factor for predetermining the ring size of the repeat unit in the resulting polyene.

Experimental Section

General Details. Unless stated otherwise, all experiments were performed under an argon atmosphere in an MBraun drybox or by standard Schlenk techniques. Reagent grade tetrahydrofuran (THF), tetrahydrofuran-d_8, and pentane were distilled from sodium benzophenone ketyl under argon. Chloroform-d_1 was distilled from calcium hydride under argon. Tetrahydrofuran as polymerization solvent, chloroform-d_1, and tetrahydrofuran-d_8 were passed over a plug of activated alumina prior to use. Norborn-2-ene (NBE) was freshly distilled from calcium hydride under reduced pressure in an argon atmosphere. Benzaldehyde was distilled under reduced pressure, stored over molecular sieves (4 Å) and under argon and passed through a plug of activated alumina prior to use. All other reagents were purchased from Aldrich or Fluka and used as received without further purification.

Dimethyl dipropargylmalonate (**M1**),[22] diethyl dipropargylmalonate (**M2**),[23] 4-(ethoxycarbonyl)-1,6-heptadiyne (**M4**),[14] 4,4-bis(hydroxymethyl)-1,6-heptadiyne (**M5**),[14] 4-(hydroxymethyl)-1,6-heptadiyne (**M6**),[24] 1,4-divinylbenzene,[28] and Mo(N-2,6-(2-Pr$_2$)-C_6H_3)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$[12] were prepared as described in the literature.

Gel permeation chromatography (GPC) was carried out using PLgel 5 μm MIXED-C columns (PLgel 5 μm Guard, 50 × 7.5 mm, PLgel 5 μm MIXED-C, 300 × 7.5 mm, PLgel 5 μm MIXED-C, 600 × 7.5 mm), a 410 differential refractometer detector, and a 486 UV-detector for measurements in $CHCl_3$ (all from Waters). The flow rate was set to 1.0 mL/min. Samples were filtered through a 0.2 μm Teflon filter (Macherey-Nagel) in order to remove particles. GPC columns were calibrated vs polystyrene (PS) standards (Polymer Standards Service (PSS), molecular weights 580 to 1.57 × 10^6 g/mol). Data were processed using a Millenium software. For measurements in *N*,*N*-dimethylacetamide, GPC was carried out using PLgel 5 μm MIXED-C and PLgel 3 μm MIXED-E columns (PLgel 5 μm MIXED-C, 300 × 7.5 mm, PLgel 5 μm MIXED-C, 300 × 7.5 mm, PLgel 3 μm MIXED-E, 300 × 7.5 mm, PLgel 3 μm MIXED-E, 300 × 7.5 mm) and a 410 differential refractometer (RI) detector (Waters). The flow rate was set to 0.5 mL/min. Samples were filtered through a 0.2 μm Teflon filter (Macherey-Nagel) in order to remove particles. GPC columns were calibrated vs poly(methyl methacrylate) standards (Polymer Standards Service (PSS), molecular weights 960 to 1.64 × 10^6 g/mol). Data were processed using a Millenium software. UV−vis spectra were recorded on a Varian Cary 3 spectrophotometer in the range of 280−800 nm. Elemental analyses were performed at the Mikroanalytisches Labor, Department Chemie, Technische Universität München, Germany. NMR data were obtained at 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C) on a Bruker ARX 300 and at 250.13 MHz (^{1}H) and 62.90 MHz (^{13}C) on a Bruker AC 250 spectrometer. Chemical shifts are listed in parts per million (ppm) downfield from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: ^{1}H, δ = 7.25; ^{13}C, δ = 77.0. THF-d_8: ^{1}H, δ = 1.73; ^{13}C, δ = 67.7 ppm). FT-IR spectra were recorded on a Bruker Vector 22 or a Bruker IFS 55 spectrometer using ATR technology. AFM images were obtained in the tapping mode with a Nanoscope IIIa scanning probe microscope from Digital Instruments. AFM samples were prepared on freshly cleaved mica by slow evaporation of a dichloromethane solution of the polymers (c = 1 mg/mL).

1,4-{Mo(N-2,6-(2-Pr)$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$CH}$_2$C$_6$H$_4$ (1). To a solution of Mo(N-2,6-(2-Pr)$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (170.7 mg, 0.223 mmol) in THF (6.5 mL) was added a solution of 1,4-divinylbenzene (14.5 mg, 0.111 mmol) in THF (2 mL). Upon stirring for 40 h at room temperature, the color of the reaction mixture changed from yellow to red. The solvent was removed in vacuo, and the red-brown residue was extracted with pentane. The pentane-insoluble orange residue was washed with pentane to yield **1** as a bright orange solid (68.2 mg, 0.050 mmol, 45%). ^{1}H NMR (THF-d_8): δ = 12.94 (s, 2H, MoC*H*R); 7.34 (t, 2H, imido-H_p, $^3J_{HH}$ = 7.6 Hz); 7.19 (d, 4H, imido-H_m, $^3J_{HH}$ = 7.6 Hz); 7.11 (s, 4H, alkylidene-H_o); 3.63 (sept, 4H, C*H*Me$_2$, $^3J_{HH}$ = 6.8 Hz); 1.25 (s, 12H, OC*Me*(CF$_3$)$_2$); 1.04 (d, 24H, CH*Me*$_2$, $^3J_{HH}$ = 6.8 Hz). ^{13}C-{^{1}H} NMR (THF-d_8): δ = 280.4 (Mo*C*HR); 154.6 (C_{ipso}NAr); 149.0 (C_oNAr); 147.0 (C_{ipso}Ph); 131.0 (C_pNAr); 129.1 (C_oPh); 127.5 (q, OCMe(CF_3)$_2$, $^1J_{CF}$ = 288 Hz); 127.3 (q, OCMe(CF_3)$_2$, $^1J_{CF}$ = 287 Hz); 124.7 (C_mNAr); 82.6 (sept, O*C*Me(CF$_3$)$_2$, $^2J_{CF}$ = 29 Hz); 29.3 (*C*HMe$_2$); 24.2 (CH*Me*$_2$); 19.0 (OC*Me*(CF$_3$)$_2$). Anal. Calcd for $C_{48}H_{52}F_{24}Mo_2N_2O_4$ (1368.78): C, 42.12; H, 3.83; N, 2.05. Found: C, 42.74; H, 4.10; N, 1.86.

Di-*tert*-butyl Dipropargylmalonate (M3). Di-*tert*-butyl malonate (5.0 g, 23.12 mmol) was added to a solution of sodium *tert*-butoxide − prepared in situ from sodium (1.17 g, 50.86 mmol) dissolved in *tert*-butyl alcohol (45 mL). After a few minutes, propargyl bromide (80% w/w in toluene, 7.56 g, 50.86 mmol) was added to the colorless reaction mixture. The mixture was refluxed for 4 h, then diluted with water (100 mL), and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water (50 mL), and the solvent was removed under reduced pressure. The resulting reddish-brown material was dissolved in dichloromethane and passed over a short plug of alumina using dichloromethane as eluent. The solvent was removed in vacuo, and crystallization from pentane furnished **M3** (3.19 g, 10.91 mmol, 47%) as a white crystalline solid. IR (ATR mode, cm^{-1}): 3272 (m); 2979 (m); 2934 (w); 2125 (w); 2056 (w); 1722 (s); 1478 (w); 1454 (w); 1423 (w); 1369 (m); 1304 (m); 1249 (m); 1218 (m); 1143 (vs); 1074 (w); 1034 (w); 959 (w); 840 (m). ^{1}H NMR ($CDCl_3$): δ = 2.87 (d, 4H, $^4J_{HH}$ = 2.5 Hz, CH_2C≡CH); 2.00 (t, 2H, $^4J_{HH}$ = 2.5 Hz, CH$_2$C≡C*H*); 1.45 (s, 18H, C*Me*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 167.8 (*C*OO); 82.2 (*C*Me$_3$); 78.9 (CH$_2$-*C*≡CH); 71.3 (CH$_2$C≡*C*H); 57.0 (C_{quat}); 27.7 (C*Me*$_3$); 22.3 (*C*H$_2$-C≡CH). Anal. Calcd for $C_{17}H_{24}O_4$ (292.37): C, 69.84; H, 8.27. Found: C, 69.84; H, 8.27.

Synthesis of A$_n$—X—A$_n$-Type Block Copolymers of M1—M4 Using Initiator 1. All polymerizations were performed under argon. A solution of the monomer in THF (0.4 mL) was added to the orange solution of **1** in THF ([**1**] ca. 0.75 mmol/L) all at once under vigorous stirring. After 4−6 h at room temperature, excess ferrocene carbaldehyde was added, and the violet reaction mixture was stirred for 1 h. The mixture was concentrated to ~1 mL, and the polymer was precipitated by dropwise addition of the solution to pentane (~35 mL). The product was centrifuged and dried in vacuo to yield deep red to purple solids (51−97%).

M1$_{25}$-CH-1,4-C$_6$H$_4$-CH-M1$_{25}$. ^{1}H NMR ($CDCl_3$) δ = 6.90−5.80 (br m, 2H, $H_{olefinic}$); 3.60−2.80 (br m, 4H, C$H_{2allylic}$); 3.76 (br m, 6H, OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 171.9, 170.9 (*C*OO); 136.4, 134.7, 133.3, 132.1, 123.5, 122.7, 120.5 ($C_{olefinic}$); 57.7, 56.8, 56.5, 54.0 (C_{ipso}); 52.8 (O*C*H$_3$); 43.4, 41.1, 39.8, 32.1, 30.0, 27.5 ($C_{allylic}$). M_n = 20 600, M_w = 25 700, PDI = 1.25.

M2$_{35}$-CH-1,4-C$_6$H$_4$-CH-M2$_{35}$. ^{1}H NMR ($CDCl_3$): δ = 6.90−5.90 (br m, 2H, $H_{olefinic}$); 4.21 (br m, 4H, OCH_2Me); 3.70−2.80 (br m, 4H, C$H_{2allylic}$); 1.26 (br m, 6H, OCH$_2$*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 171.5, 170.5 (*C*OO); 137.9, 136.5, 134.7, 133.7, 132.2, 123.2, 122.4, 120.5 ($C_{olefinic}$); 61.4 (O*C*H$_2$Me); 57.6, 56.7, 54.0 (C_{ipso}); 43.5, 41.2, 39.8, 32.0, 30.0 ($C_{allylic}$); 13.7 (OCH$_2$*Me*). M_n = 25 300, M_w = 38 200, PDI = 1.51.

M3$_{25}$-CH-1,4-C$_6$H$_4$-CH-M3$_{25}$. ^{1}H NMR ($CDCl_3$): δ = 7.00−5.50 (br m, 2H, $H_{olefinic}$); 3.80−2.50 (br m, 4H, C$H_{2allylic}$); 1.45 (br m, 18H, OC*Me*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 170.8, 170.7, 169,7 (*C*OO); 136.4, 135.2, 134.0, 132.6, 128.7, 128.1, 127.5, 126.5, 122.9, 120.8 ($C_{olefinic}$); 81.1 (O*C*Me$_3$); 58.7, 57.7, 54.9 (C_{ipso}); 43.4, 41.0, 39.5, 38.9, 29.7, 28.9 ($C_{allylic}$); 27.5 (OC*Me*$_3$). M_n = 27 800, M_w = 57 700, PDI = 2.07.

M4$_{25}$-CH-1,4-C$_6$H$_4$-CH-M4$_{25}$. ^{1}H NMR ($CDCl_3$): δ = 6.90−5.70 (br m, 2H, $H_{olefinic}$); 4.18 (br m, 2H, OCH_2Me); 3.30−2.30 (br m, 5H, C$H_{2allylic}$, C*H*COOEt); 1.25 (br m, 3H, OCH$_2$*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 175.3, 174.5 (*C*OO); 138.6, 137.7, 136.9, 136.1, 135.3, 133.9, 132.1, 131.1, 129.2, 127.7, 126.7, 126.1, 122.6, 121.6, 120.6, 120.1 ($C_{olefinic}$); 60.4 (O*C*H$_2$Me); 40.6, 39.7 (*C*HCOOEt); 36.8, 35.7, 31.5, 29.1, 27.2, 26.6 ($C_{allylic}$); 14.0 (OCH$_2$*Me*). M_n = 14 300, M_w = 21 600, PDI = 1.51.

Synthesis of A$_n$—X—A$_n$-Type Block Copolymers of M5 and M6 Using Initiator 1. A solution of the monomer in THF (0.4 mL) was added to the orange solution of **1** in THF ([**1**] ca. 0.75 mmol/L) all at once under vigorous stirring. Upon addition of the monomer solution, the color immediately changed from orange to purple, and a dark precipitate formed. After 2 h at room temperature, excess benzaldehyde was added, and the purple reaction mixture was stirred for 1 h. The solvent was removed in vacuo, diethyl ether (∼10 mL) was added to the residue, and stirring was continued for 30 min after sonification. The product was centrifuged and dried in vacuo to yield a purple solid (**M5**, ∼10% yield; **M6**, 49% yield).

Synthesis of Poly-NBE Using the Molybdenum-Based Initiator 1. The initiator (**1**, 5.23 mg, 3.82 μmol) was dissolved in THF (8.2 mL), and a solution of NBE (32.38 mg, 343.88 μmol) in THF (0.4 mL) was added all at once to the orange solution of the initiator under vigorous stirring. After 1.5 h at room temperature, excess benzaldehyde (∼8 mg) was added, and the yellowish reaction mixture was stirred for a further 45 min. The mixture was concentrated to ∼1 mL, and the polymer was precipitated by dropwise addition of the solution to methanol (∼35 mL). The product was centrifuged and dried in vacuo to yield a white solid (32.0 mg, 95%).

Poly-NBE$_{90}$. ^{1}H NMR ($CDCl_3$): δ = 5.34, 5.20 (br m, 2H, $H_{olefinic}$(*trans*/*cis*)); 2.78, 2.42 (br m, 2H, C$_{ipso}$*H*); 1.80 (br m, 3H), 1.35 (br m, 2H), 1.01 (br m, 1H) (CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 134.0, 133.9, 133.4, 133.1, 133.0, 132.9 ($C_{olefinic}$); 128.6, 128.4, 128.1, 127.5, 127.3, 126.4, 125.9 (C_{aryl}); 43.4, 43.1 (C_{ipso}); 42.7, 42.1, 41.3 (CH*C*H$_2$CH); 38.6, 38.4 (C_{ipso}); 33.2, 32.9, 32.4, 32.2 (*C*H$_2$CH$_2$). M_n = 14 100, M_w = 16 100, PDI = 1.14. Spectra are in accordance with ref 29. The cis/trans-ratio of the polymer was 83:17.

Synthesis of A$_n$-*b*-B$_m$—X—B$_m$-*b*-A$_n$-Type Block Copolymers Using Initiator 1. Block copolymers from **M1**, **M2**, and NBE were prepared as described above. Instead of terminating the living chains with excess aldehyde, the reaction mixtures were divided into two parts. One part was actually terminated with excess aldehyde (ferrocene carbaldehyde for polymers that contain exclusively poly(heptadiyne) blocks; benzaldehyde for polymers that contain poly(NBE) blocks), concentrated, precipitated from pentane (block copolymers consisting of poly(heptadiyne)s) or methanol (block copolymers that contain poly(NBE) blocks), and subjected to GPC. To the second part, monomers **M1**, **M2**, or NBE, dissolved in THF (0.3 mL), were added all at once under vigorous stirring. After additional stirring for 6 h (**M1**, **M2**) or 1.5 h (NBE) at room temperature, excess aldehyde was added. The block copolymers were isolated and purified as described for the homopolymers. All copolymers with poly(NBE) blocks were precipitated from methanol, block copolymers based exclusively on poly(heptadiyne)s from pentane. Isolated yields were in the 69−98% range.

Livingness of 1-Initiated Reactions. To determine the class of livingness, samples with a degree of polymerization of 50 (**M1**, **M2**) or 70 (NBE) were prepared as described above. The corresponding reaction mixture was divided into two parts; the first part was terminated with ferrocene carbaldehyde (**M1**, **M2**) and benzaldehyde (NBE), respectively, concentrated, precipitated from pentane (**M1**, **M2**) or methanol (NBE), and subjected to GPC. The second part of the reaction mixture was stirred for 30 min (class IV) or 4 h (class V), at which time a second feed of monomer was added to result in a theoretical degree of polymerization of 100 (**M1**, **M2**) and 140 (NBE), respectively. After termination, partial removal of the solvent, and precipitation, the samples were subjected to GPC. Since significant band broadening or bimodal GPC traces, indicative of termination reactions, were not observed, class IV livingness was attributed to poly-**M1** and poly(NBE), whereas poly-**M2** fulfilled the preconditions of class V living systems.

Determination of the Ratio of k_p/k_i. Experiments were carried out at 300 K in tetrahydrofuran-d_8 according to published procedures.[27] Values for k_p/k_i of 1 and 5 were observed for the systems **M1-1** and **M2-1**, respectively.

Acknowledgment. Financial support provided by the government of the Freistaat Bayern and the government of the Freistaat Sachsen is gratefully acknowledged. Special thanks are given to Dr. D. Wang for recording some of the ^{13}C NMR spectra and to M. Steenackers for performing AFM measurements.

Supporting Information Available: Figure showing the ^{1}H NMR spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Anders, U.; Krause, J. O.; Wang, D.; Nuyken, O.; Buchmeiser, M. R. *Des. Monomers Polym.* **2004**, *7*, 151−163.
(2) Anders, U.; Nuyken, O.; Buchmeiser, M. R. *Des. Monomers Polym.* **2003**, *6*, 135−144.
(3) Anders, U.; Nuyken, O.; Buchmeiser, M. R. *J. Mol. Catal. A: Chem.* **2004**, *213*, 89−92.
(4) Anders, U.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. *Angew. Chem.* **2002**, *114*, 4226−4230; *Angew. Chem., Int. Ed.* **2002**, *41*, 4044−4047.
(5) Anders, U.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. *Macromolecules* **2002**, *35*, 9029−9038.
(6) Anders, U.; Wagner, M.; Nuyken, O.; Buchmeiser, M. R. *Macromolecules* **2003**, *36*, 2668−2673.
(7) Krause, J. O.; Nuyken, O.; Buchmeiser, M. R. *Chem.—Eur. J.* **2004**, *10*, 2029−2035.
(8) Krause, J. O.; Wang, D.; Anders, U.; Weberskirch, R.; Zarka, M. T.; Nuyken, O.; Jäger, C.; Haarer, D.; Buchmeiser, M. R. *Macromol. Symp.* **2004**, *217*, 179−190.
(9) Krause, J. O.; Zarka, M. T.; Anders, U.; Weberskirch, R.; Nuyken, O.; Buchmeiser, M. R. *Angew. Chem.* **2003**, *115*, 6147−6151; *Angew. Chem., Int. Ed.* **2003**, *42*, 5965−5969.
(10) Yang, L.; Mayr, M.; Wurst, K.; Buchmeiser, M. R. *Chem.—Eur. J.* **2004**, *10*, 5761−5770.
(11) Mayr, M.; Wang, D.; Kröll, R.; Schuler, N.; Prühs, S.; Fürstner, A.; Buchmeiser, M. R. *Adv. Synth. Catal.* **2005**, *347*, 484−492.
(12) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759−768.
(13) Schrock, R. R.; Gabert, A. J.; Singh, R.; Hock, A. S. *Organometallics* **2005**, *24*, 5058−5066.
(14) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827−2843.
(15) Risse, W.; Wheeler, D. R.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1989**, *22*, 3205−3210.
(16) Weck, M.; Schwab, P.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1789−1793.
(17) Deming, T. J.; Novak, B. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2366−2374.

(18) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185−197.
(19) Fox, H. H.; Schrock, R. R. *Organometallics* **1992**, *11*, 2763−2765.
(20) Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3295−3296.
(21) Kim, S.-H.; Kim, Y.-H.; Cho, H.-N.; Kwon, S.-K.; Kim, H.-K.; Choi, S.-K. *Macromolecules* **1996**, *29*, 5422−5426.
(22) Llerena, D.; Buisine, O.; Aubert, C.; Malacria, M. *Tetrahedron* **1998**, *54*, 9373−9392.
(23) Eglinton, G.; Galbraith, A. R. *J. Chem. Soc.* **1959**, 889−896.
(24) Halbach, T. S.; Krause, J. O.; Nuyken, O.; Buchmeiser, M. R. *Macromol. Rapid Commun.* **2005**, *26*, 784−790.
(25) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem.* **2003**, *115*, 4740−4782; *Angew. Chem., Int. Ed.* **2003**, *42*, 4592−4633.
(26) Matyjaszewski, K. *Macromolecules* **1993**, *26*, 1787−1788.
(27) 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*, 8378−8387.
(28) Gauler, R.; Risch, N. *Eur. J. Org. Chem.* **1998**, 1193−1200.
(29) Moloy, K. G. *J. Mol. Catal.* **1994**, *91*, 291−302.

MA0524373