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Air-Initiated Radical Polymerization of Lithium Salts of *ω*-(Undecamethylcarba-*closo*-dodecaboran-1′-yl)alk-1-enes, $CH_2{=}CH(CH_2)_{n-2}C(BMe)_{11}^-\ Li^+$

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Abstract: We report an easy access to the salts of the $LiC(BMe)_{11}^-$ anion, which greatly simplifies the synthesis of compounds carrying the $-C(BMe)_{11}^-$ substituent, including the title anions. The previously recognized and puzzling spontaneous oligomerization of the solid lithium salts $CH_2{=}CH(CH_2)_{n-2}C(BMe)_{11}^-\ Li^+$ upon storage under ambient conditions is now shown to proceed by a radical mechanism, with the "naked" Li^+ cation acting as a catalyst. The degree of polymerization is higher in solution, especially when azoisobutyronitrile (AIBN) is used as initiator (up to ~50). Initiation by the thermal decomposition of AIBN is also catalyzed by naked Li^+, and this initiator is effective at room temperature. Di-*tert*-butyl peroxide and UV irradiation can also be used. The observation of Li^+ catalysis agrees with a prior prediction from ab initio calculations, according to which Li^+ complexation of ethylene strongly lowers the activation energy for methyl radical addition. The results bear on the current discussion of the possible sensitivity of radical clocks to their molecular environment and suggest that naked Li^+ will catalyze the radical polymerization of simple terminal alkenes.

Introduction

Terminal alkenes devoid of activating substituents adjacent to the double bond do not polymerize easily and are ordinarily stable indefinitely under benchtop conditions (room temperature in air). Indeed, considerable effort has been expended in developing ways to induce cationic polymerization of unactivated alkenes using coordinatively unsaturated transition metal catalysts.[1,2] In some cases, radical polymerization can be induced with standard initiators, but it is difficult and often yields low-molecular-weight polymers.[3]

In the course of a general examination of the properties of polyalkylated derivatives of the carba-*closo*-dodecaborate anion $CB_{11}H_{12}^-$ (**1**),[4] we recently made a puzzling accidental observation:[5] solid samples of the lithium salt of the alkenylcarborate anion, $CH_2{=}CH(CH_2)_{n-2}C(BMe)_{11}^-\ Li^+$ (**[*n*]2**, $n = 6$), which we prepared as a precursor for an ionic polymer, spontaneously polymerized in less than a day of storage under ambient conditions, whereas the cesium salt was perfectly stable. In the present paper, we report the results of a more detailed investigation. We (i) describe a more efficient synthesis of the lithium salts **[*n*]2** ($n > 2$), (ii) characterize the products of their room-temperature "spontaneous" (actually, oxygen-induced) polymerization, and (iii) provide evidence that this polymerization proceeds by a radical and not an ionic mechanism. The results suggest that "naked" Li^+ ions will catalyze the radical polymerization and copolymerization of simple terminal alkenes in general, as implied some time ago by quantum mechanical calculations.[6] They indeed do, and we address this issue in a separate publication.[7]

Results

An Improved Synthesis of the Terminal Alkenes [*n*]2 (*n* > 2). The original synthesis of the salts **[*n*]2** ($n = 2-7$)[5] relied on the known[8] deprotonation and alkylation of the weakly acidic CH vertex in the anion **1** (Scheme 1). The alkenyl chain was introduced in a masked form, since the conditions of a subsequent permethylation of the carborane cage with methyl triflate[9,10] are not compatible with the presence of a multiple bond, an aromatic ring, or a lone pair elsewhere in the molecule. Finally, the double bond was unmasked. Since we needed six different alkenes **[*n*]2**, the synthesis was rather tedious, especially given that the simplest form of masking the double bond in the form of an alkyl halide was not always applicable, due to unexpected complications with Grob fragmentation under the methylation conditions.[5]

We remarked ruefully at the time[5] that one could do away with the masking if only one had access to the C-deprotonated

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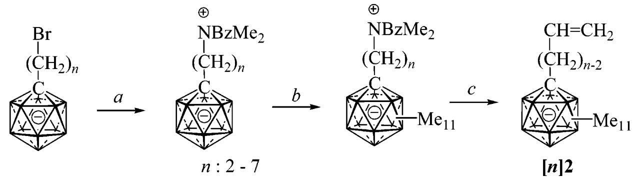
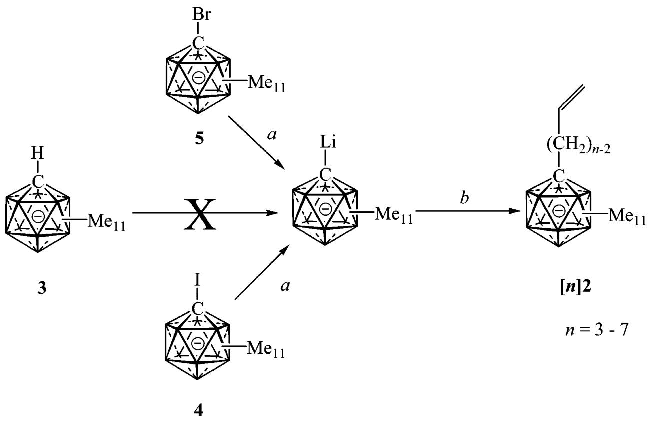
Scheme 1 ^{a}



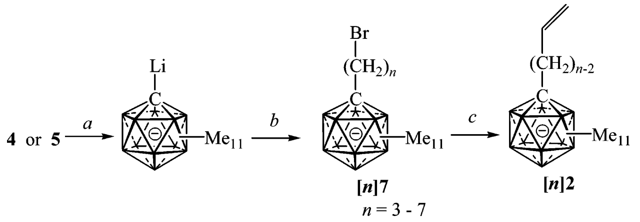
^{a} Reagents and conditions: (a) $C_6H_5CH_2NMe_2$, methanol, reflux, 3−5 d. (b) MeOTf, CaH_2, sulfolane. (c) MeLi, −10 °C, ether.

Scheme 2 ^{a}



^{a} Reagents and conditions: (a) *n*-BuLi, −78 °C. (b) $TosO{-}(CH_2)_{n-2}{-}CH{=}CH_2$, 10−15 h.

Scheme 3 ^{a}



^{a} Reagents and conditions: (a) *n*-BuLi, −78 °C. (b) $Br{-}(CH_2)_n{-}Br$, 6−18 h. (c) LiTMP.

form of the undecamethylated $HC(BMe)_{11}^-$ anion (**3**),[11−13] either by direct deprotonation or by lithium−halogen exchange on the $I{-}C(BMe)_{11}^-$ (**4**) or $Br{-}C(BMe)_{11}^-$ (**5**) anion. The C-deprotonated **3** could then be alkenylated to yield the desired product **[*n*]2** with any choice of $n > 2$.

While **3** is readily accessible by undecamethylation of **1** with methyl triflate,[11,13] it is much less acidic than **1**, and to this date we have not found a base that would deprotonate it. The lithium−halogen exchange route to the C-deprotonated form did not appear passable, either, since earlier attempts[11] to prepare **4** by exhaustive methylation of $I{-}C(BH)_{11}^-$ (**6**) had yielded only intractable mixtures of partially methylated anions.

The recent development[14] of reaction conditions that permit the undecamethylation of the 1-halo derivatives of **1** and make **4** and **5** readily available has changed the situation radically, and we now find that Scheme 2 indeed represents the route of choice for the preparation of **[*n*]2** ($n > 2$) (for $n = 2$, we use the original procedure[5]).

Under scrupulously dry conditions, the halogen−lithium exchange in **4** or **5** with *n*-BuLi or *t*-BuLi in tetrahydrofuran (THF), toluene, or 1,2-dimethoxyethane (DME) is quantitative. The lithiated anion is an extremely strong base and deprotonates THF after a few hours at room temperature. Subsequent reactions with the bromoalkenes $CH_2{=}CH{-}(CH_2)_{n-2}{-}Br$ required 15−72 h and gave the desired products in 58−77% yields. The byproduct was **3**, suggesting possible interference by electron transfer from the lithiated **3** to the C−Br bond. Such transfer would produce the radical anion $^{\bullet}C(BMe)_{11}^-$, expected to abstract a hydrogen atom from the solvent or the alkyl radical to yield **3**. Allylation ($n = 3$) was examined in more detail, and the results were compatible with the suspicion. Allyl iodide gave no **[3]2** and produced **3** quantitatively. Allyl bromide and allyl chloride reacted much more slowly but gave 69% and 52% of **[3]2**, respectively. To avoid the interference, we turned to the tosylates $CH_2{=}CH{-}(CH_2)_{n-2}{-}OTos$ and found that the products **[*n*]2** ($n > 2$) were produced in almost quantitative yields in 10−15 h.

In an alternative synthesis of **[*n*]2** ($n > 2$), the halogen−lithium exchange in **4** or **5** is followed by alkylation with a dibromoalkane, $Br{-}(CH_2)_n{-}Br$, to afford the *ω*-bromoalkyl derivative **[*n*]7** in 65−85% yields, followed by dehydrobromination with LiTMP in 87−98% yields (Scheme 3). This reagent overcomes the difficulties experienced previously[5] with the dehydrohalogenation of $C(BMe)_{11}^-$ carrying primary alkyl bromides under more usual reaction conditions.

Oligomers Formed from Solid Li$^+$ Salts of [*n*]2 Spontaneously upon Standing. Our attention was originally caught by the observation[5] that, after several weeks of storage in closed or open vials at room temperature, without any effort at protection from air or ambient moisture, the solid microcrystalline lithium salts **[*n*]2** ($n = 5$ or 6) partially lost their solubility in nonpolar solvents such as toluene. Gel permeation chromatography (GPC) examination of **[5]2** and **[6]2** revealed the presence of oligomers consisting of up to 10 monomer units.

We have now examined this curious phenomenon in more detail and found that the spontaneous oligomerization of **[*n*]2** ($n = 5{-}7$) under ambient conditions is complete in a single day (Table 1). Under the same conditions, the lithium salts with shorter alkenyl chains, $n = 2{-}4$, are stable indefinitely, as are the sodium or cesium salts with chains of any length. A mixture of 10% of the lithium and 90% of the cesium salt of **[5]2** oligomerizes entirely. The NMR spectra of the purified oligomers are those expected for polyalkenes and show no evidence for the presence of double bonds, even at the highest magnification. They show that one chain end is terminated with $-CH_2OH$ groups, and $-CHROH$ groups are not detectable.

Spontaneous Polymerization of Li$^+$ Salts of [*n*]2 in Solution. The lithium salts of **[5]2**, **[6]2**, and **[7]2**, but not their sodium or cesium salts, also polymerize in about 1 day when kept at room temperature in air in a saturated solution in benzene (Table 1). According to NMR analysis, one chain end is again terminated with $-CH_2OH$ groups, and $-CHROH$ groups are absent. The reaction of the lithium salt of **[5]2** was also attempted in 1,2-dichloroethane, where it proceeds smoothly, and THF, where it does not take place even after 2 days. When the Li$^+$ sequestering agent, 12-crown-4, is also present in the 1,2-dichloroethane solution of the lithium salt of **[5]2**, no

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Table 1. Products of Room-Temperature Polymerization of Li^+ Salts of **[*n*]2**

monomer	M_w	M_n	n (GPC)[a]	n (NMR[b])[c]	yield (%)
Solid State, Spontaneous in Air					
[5]2	5800	2300	∼6	∼5	83
[6]2	8600	3200	∼8	∼8	91
[7]2	10400	3900	∼10	∼9	87
Benzene Solution, Spontaneous in Air					
[5]2	24700	9500	∼25	∼22	80
[6]2	27900	12700	∼32	∼30	89
[7]2	33600	14600	∼36	∼33	85
Benzene Solution, AIBN-Initiated, Anaerobic					
[5]2	34700	18500	∼48		80
[6]2	34800	16600	∼42		90
[7]2	33400	20900	∼51		78
[6]2/C_6H_{12}[d,e]	29200	15400	∼24/72		75
1,2-Dichloroethane Solution, Di-*tert*-butyl Peroxide/ UV-Initiated, Anaerobic					
[5]2	4930	1700	∼4		95
[6]2	7060	2550	∼7		89
[7]2	9120	3200	∼8		90

[a] Average degree of polymerization by GPC analysis, based on polystyrene standards. [b] The ^1H and ^{13}C NMR spectra (Supporting Information) compare well with expectations based on the literature spectra of polyalkenes. ^{13}C NMR: Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334. ^1H NMR: Brandolini, A. J.; Hills, D. D. *NMR Spectra of Polymers and Polymer Additives*; Marcel Dekker: New York, 2000. [c] Average degree of polymerization from terminal group signal integration in ^1H NMR spectra. In air-initiated polymers, hydroxyl end groups were quantitated after treatment with trichloroacetyl isocyanate: Goodlett, V. W. *Anal. Chem.* **1965**, *37*, 431. The $-CHR-CH_2O-CO-NH-CO-CCl_3$ protons were observed as a doublet at 3.60−4.15 ppm ($J = 6.0-6.2$ Hz) and the $-NH-$ protons as a broad singlet at 10.46−10.49 ppm. Neither $-CHRO-CO-NH-CO-CCl_3$ protons, expected at 5.15−5.22 ppm, nor any vinylic protons were detectable. In AIBN-initiated polymers, ^{13}C NMR revealed the nitrile carbon of terminal $-CMe_2CN$ groups (δ 122.4−124.8 ppm: Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1984**, *17*, 1094), but the methyl protons were obscured. [d] Equimolar ratio with 1-hexene. [e] 60:40 copolymer (by mass, quantified by the ^1H NMR) **[6]2**:1-hexene.

reaction is observed after 4 days. When hydroquinone or TEMPO is present in the 1,2-dichloroethane solution of the lithium salt of **[5]2**, no polymer is formed even at elevated temperatures. When a fresh benzene solution of the lithium salt of **[5]2** is deoxygenated and left at room temperature, no polymer is formed even after 3 days at room temperature followed by 2 days of reflux.

Initiator-Induced Polymerization of Li^+ Salts of [*n*]2 in Deaerated Solution. In the absence of air, pure benzene solutions of the lithium salts of the monomers are stable indefinitely, but when a radical initiator is present, polymerization occurs even at relatively low temperatures at which the initiator is ordinarily stable. In the presence of 10% azoisobutyronitrile (AIBN) by weight, the room-temperature polymerization of the lithium salts of **[5]2**, **[6]2**, and **[7]2** in benzene is complete in 8 h (Table 1). The $-CMe_2CN$ terminal group was detected by ^{13}C NMR. With 1% AIBN, the reaction of **[5]2** is far slower but takes place at 60 °C. Copolymerization of **[6]2** with an equimolar amount of 1-hexene in the presence of 1% AIBN at room temperature produces a copolymer containing a 60:40 **[6]2**/hexene ratio by ^1H and ^{13}C NMR. No polymerization of the lithium salts of **[2]2**, **[3]2**, and **[4]2** is observed even after long times and at elevated temperatures.

In the presence of 10% (by weight) di-*tert*-butyl peroxide in 1,2-dichloroethane, **[5]2**, **[6]2**, and **[7]2** do not polymerize in the dark at room temperature, but after 12 h at 80 °C or upon UV irradiation at room temperature they give polymers very similar to those obtained with 10% AIBN, as described above. In the irradiation experiment, only oligomers were formed, and when 12-crown-4 was added, the polymerization reaction was suppressed altogether.

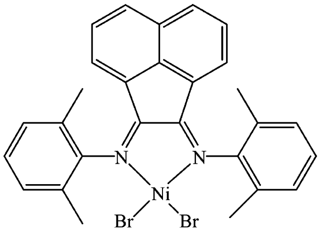
Some of the experiments were repeated in the presence of trapping agents. With 1 M *t*-BuOLi (0.1 mL) and 10% AIBN in benzene at 80 °C, polymer formation from **[5]2** still occurs but is slower. Complete conversion required 18 h. With 1% CH_3OD and 10% AIBN in benzene at 25 °C, a polymer is formed in 8 h that contains no incorporated deuterium. With 1% CD_3OD and 10% AIBN in benzene at 25 °C, a polymer is formed in 10 h that contains deuterium incorporated as CHD (δ 0.82 ppm in ^2D NMR).

The disappearance of AIBN (0.015 M) in a C_6D_6 solution containing varying concentrations of $LiCB_{11}Me_{12}$[15] followed first-order kinetics at room temperature (25 °C). The apparent rate constant k obeyed the equation $k = 0.49[LiCB_{11}Me_{12}]$/L mol^{-1} s^{-1}. In the absence of the lithium salt, no reaction was observable even after a few days.

Attempted Transition-Metal-Catalyzed Polymerization of [*n*]2. Cationic polymerization was attempted using the recently developed nonmetallocene transition metal catalysts,[2,16,17] which are more active than the classical catalysts[1] based on group 4 metallocenes. We prepared the α-diiminenickel catalyst **8**[16] and used it with MAO as cocatalyst, and we also prepared the diamide complex of titanium **9**[17] and used it with $B(C_6F_5)_3$ as cocatalyst.[18] We verified that both catalysts polymerize 1-hexene to a high-molecular-weight polymer, but all our attempts to polymerize **[*n*]2** ($n = 5$ and 6) yielded only low-molecular-weight oligomers with M_w of 1700−2600, smaller than those obtained by just allowing the solid samples of **[*n*]2** to sit on a benchtop for a day. Extended reaction times of up to 2 days did not lead to increased molecular weight.

Discussion

As suggested by their appearance and consistency and proven by GPC analysis and NMR spectroscopy, the products of the Li^+-catalyzed reactions of **[*n*]2** are polymeric and saturated. We plan to analyze their microstructure and potential ionic conductivity at a future time. Here, we address the issue of why and how they form at all, given that terminal alkenes are normally stable to polymerization under ambient conditions. We first note that poorly solvated ("naked") Li^+ cations appear to be indispensable for the polymerization to occur, regardless of the mode of initiation. When they are replaced by larger alkali



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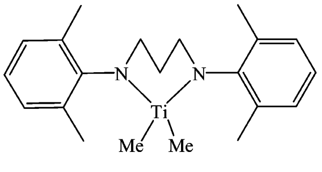

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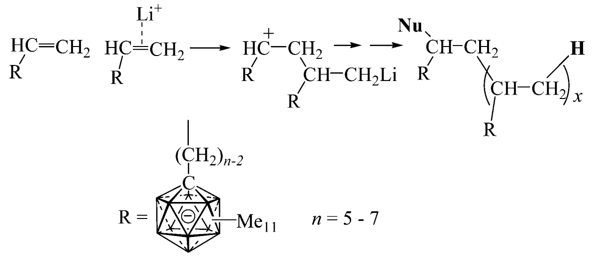
metal cations or deactivated by complexation with 12-crown-4 or THF, the reaction does not proceed. Only weakly coordinating solvents, such as benzene and 1,2-dichloroethane, or solvent-free solid samples have been used successfully. The deactivating effect of *t*-BuOLi can be attributed to its basicity, which probably allows it to tie up Li$^+$ cations in the form of *t*-BuOLi$_2^+$.

The requirement for the Li$^+$ cation to be "naked" strongly suggests that Li$^+$ plays the role of a Lewis acid in the polymerization process. Its effects on individual steps in the polymerization mechanism are not cleanly separated in most of the observations, but both initiation (radical formation) and chain propagation are evidently catalyzed: (i) In the presence of naked Li$^+$, AIBN decomposes at a useful rate already at 25 °C and di-*tert*-butyl peroxide at 80 °C, well below the normally required temperatures of ~60 °C and over 100 °C, respectively. The linear dependence of the AIBN decomposition rate constant on Li$^+$ concentration, observed even when Li$^+$ is in 2-fold excess, suggests that a small fraction of AIBN is complexed to Li$^+$ in a fast pre-equilibrium and that the complex slowly decomposes into Li$^+$, N$_2$, and radicals. (ii) Upon photoinitiation at room temperature, polymerization occurs only if naked Li$^+$ is present, and it is suppressed by the addition of 12-crown-4. This demonstrates that the propagation is catalyzed, too. The simplest mechanism for the promotion of the radical propagation step by Li$^+$ would be its complexation to the radical or to the terminal double bond.

There is considerable past analogy for catalysis by Li$^+$ ions acting as a Lewis acid for both types of processes. The decomposition of AIBN into radicals is promoted by AgClO$_4$, ZnCl$_2$, BCl$_3$, AlEt$_3$, and other Lewis acids.[19a] The propagation rate constant in the polymerization of acrylonitrile is increased upon the addition of LiCl,[20] and numerous similar catalytic metal salt effects have been reported for a variety of monomers strongly activated by functional groups capable of efficient complexation with Lewis acids.[19b] Such complexation of methacrylates and other activated double bonds has been often used to modify monomer reactivity in copolymerizations and to influence the tacticity of polymers.[21−24]

What is novel here is the proposal that even the radical polymerization of unactivated alkenes can be subject to Li$^+$ catalysis, provided that the Li$^+$ cations are sufficiently poorly solvated. The amazing Lewis acid activity of these cations in the solution of LiMeC(BMe)$_{11}$ in benzene and similar arenes is well illustrated both by the great enhancement of Lewis acid catalysis of pericyclic reactions[15] relative to the ordinarily used and in themselves quite active solution of LiClO$_4$ in ether,[25−28] which contains well-solvated Li$^+$ ions, and by their ability to abstract a methide anion from methylated carborane anions at elevated temperatures.[29]



Scheme 4. A Conceivable Mechanism for Cationic Polymerization of **[*n*]2** (n = 5−7)

Since many metal salts (but not lithium salts) and other Lewis acids are known to initiate the cationic polymerization of unactivated alkenes,[30] this route to the observed products needs to be considered in principle. If Li$^+$ were to act like other metal cations, the first steps would be complexation with a double bond and initiation of an electrophilic attack by the activated double bond on the double bond of another alkenylcarborane anion (Scheme 4). Chain growth would be terminated by an adventitious nucleophile, Nu, such as water from the air or methanol, which was used as a solvent for crystallization. Either one would also convert the initially formed CLi bond to a CH bond.

The intermediacy of an alkyllithium compound, central to this mechanism, looks highly improbable, especially when we recall that the polymerization proceeds even in ambient atmosphere, is suppressed upon removal of air, and is reactivated by addition of a radical initiator such as AIBN. We believe that this cationic mechanism, and also a mechanism initiated by a Brønsted acid, can actually be excluded safely, because the oligomers formed in the presence of CH$_3$OD do not contain incorporated deuterium, while those formed in the presence of CD$_3$OD do.

The failure of active-metal-based catalysts to induce significant polymerization of the terminal alkenes **[*n*]2**, while they catalyze the polymerization of simple terminal alkenes, also argues against a cationic mechanism. The likely reason for this curious lack of catalytic activity is deactivation of the catalyst−alkene complex by intramolecular association of the metal center with the alkenylated carborate anion. Such association of various metal-based cations with methidic (methyl anion-like) methyl groups of methylated carborate anions has been well characterized.[13,31−34] Based on the apparently facile abstraction of methide anions by *tert*-butyl cations from the MeC(BMe)$_{11}^-$ anion,[35] the chain-end carbocations involved in the mechanism under consideration would be expected not only to associate with the −C(BMe)$_{11}^-$ anion but to actually abstract a methyl group from it. They thus do not appear to be viable chain propagation intermediates in the observed polymerization of **[*n*]2**.

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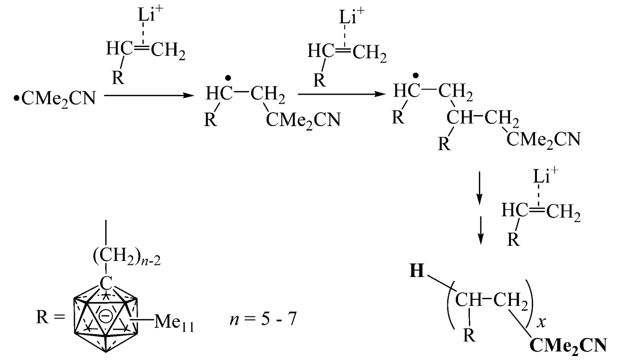
Scheme 5. Proposed Mechanism for Radical Polymerization of **[*n*]2** ($n = 5-7$)[a]



[a] The chain-terminating hydrogen abstraction is not shown explicitly.

If the polymerization proceeds by a radical mechanism, as we propose, the Li^+ cation acts both by facilitating the generation of radicals from the initiator and by facilitating a radical attack on the double bond to produce a secondary alkyl radical. Chain growth presumably terminates by chain transfer due to allylic hydrogen abstraction.

The two simple ways in which Li^+ could promote the radical propagation step are complexation with the radical and complexation with the alkene. Two decades ago,[6] ab initio calculations predicted that the activation barrier for the addition of the methyl radical to ethylene would be reduced to less than half when the latter is complexed to Li^+, and there was no indication that the Li^+ cation might prefer to move from the alkene to the radical. More recent calculations[36] predicted that the activation of a double bond by such complexation is general and not restricted to ethylene. It is perhaps not surprising that there has been no experimental verification of these computational results as far as we are aware, since soluble salts that would serve as sources of “naked” Li^+ cations capable of complexing an isolated double bond in very weakly coordinating solvents have not been readily available, and the anions **[*n*]2** are highly unusual in this regard. If we take the computational results at face value, we arrive at the mechanism shown in Scheme 5.

Although this behavior is also unprecedented for the polymerization of a terminal alkene without an activating substituent, it looks more plausible a priori, and all the evidence described above is compatible with it. Oxygen is apparently able to act as an initiator and is responsible for the presence of a terminal hydroxy group. Its removal suppresses the reaction, as does the addition of a radical scavenger. The mechanism of the oxygen-induced initiation has not been investigated. Oxygen could be activated toward addition to a double bond by complexation of Li^+ to C=C or to O_2, and it could also generate a radical center on carbon by inducing electron-transfer processes. Although one-electron oxidation of the peralkylated carborane anion is difficult,[9,37] it might conceivably also intervene. In the presence of a standard radical initiator, AIBN or di-*tert*-butyl peroxide, oxygen is not needed, and the chain end groups are those expected from these radical initiators.

The product polydispersity is high, as expected for radical polymerization. In the presence of 1-hexene, co-oligomerization is observed. The lack of reactivity of the anions with a short alkenyl chain, **[*n*]1** ($n = 2-4$), is probably attributable to steric hindrance by the bulky $-C(BMe)_{11}^-$ anion substituent.

It appears likely that Li^+ will catalyze other radical reactions as well. Indeed, the observation that the molecular weight of the oligomers of **[*n*]2** is never very high suggests that the abstraction of allylic hydrogen, which leads to chain transfer, may be catalyzed nearly as much as the radical addition process itself. If this is true under all reaction conditions, Li^+ catalysis will not be useful for the radical polymerization of these terminal alkenes to compounds of high molecular weight, but it may be useful when lower molecular weight materials are needed.

Conclusions

We have described a much improved synthesis of the functionalized carborane anions **[*n*]2**. The availability of the 1-lithiated derivative of the undecamethylated anion **3** is likely to have broad significance for the preparation of compounds containing the unusual $-C(BMe)_{11}^-$ substituent. The polymers of **[*n*]2** obtained by room-temperature polymerization with AIBN as the initiator have molecular weights suitable for a possible use as solid lithium cation conductors, and their ionic conductivities are currently under examination.

On the basis of the evidence collected, we propose that the previously only briefly reported[5] “spontaneous” Li^+-catalyzed oligomerization of **[*n*]2** proceeds by the radical mechanism and is initiated by ambient oxygen. If so, the present results support Clark’s old prediction[6] that alkene complexation with Li^+ will greatly facilitate the addition of alkyl radicals to their double bonds, and the warning[36,38] that “radical clocks” [39−41] may be less imperturbable chronometers than is currently believed.

In the lithium salts **[*n*]2**, the polymerization substrate is somewhat special in that it carries its own catalyst. However, the present results could have much wider implications. They make it quite likely that other lithium salts soluble in weakly coordinating solvents,[9,42] such as $Li^+ MeC(BMe)_{11}^-$, will activate even much simpler alkenes for radical addition and possibly for other reactions. We describe the initial results of an examination of these possibilities elsewhere[7] and postpone all detailed mechanistic investigations until optimal simple substrates have been identified.

Experimental Section

General. Experimental manipulations were carried out using standard vacuum and inert atmosphere techniques. Chemicals were reagent grade (Aldrich); some **1** was synthesized[43] and some purchased from Katchem, Ltd., Elišky Krásnohorské 6, 11000 Prague 1, Czech Republic. THF was dried over sodium and distilled before use. The nickel catalyst **8**,[16] the titanium catalyst **9**,[17] and $B(C_6F_5)_3$[44] were prepared as described in the literature. A 10% solution of MAO in toluene (Aldrich) was used. Proton shifts of BH protons were measured with boron decoupling. Chemical shifts are given in ppm (δ scale) with positive shifts downfield: all ^1H chemical shifts were referenced relative to internal residual protons from a lock solvent and ^{11}B shifts to $BF_3 \cdot Et_2O$ [$B(OMe)_3$ at 18.1 ppm]. The external reference was contained in a capillary within the same tube. The NMR solvent was $(CD_3)_2CO$ unless

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Table 2. Yields of Products **[*n*]2** in General Procedure P2

n	**4** (g, mmol)	*t*-BuLi (mL, mmol)	$CH_2=CH-(CH_2)_{n-2}-Br$ (g, mmol)	time (h)	*T* (°C)	**[*n*]2** (g, %)
3	0.100, 0.18	0.25, 0.40	0.055, 0.45	72	50	0.058, 69
4	0.075, 0.13	0.20, 0.29	0.045, 0.33	28	rt	0.042, 64
5	0.100, 0.18	0.25, 0.40	0.067, 0.45	20	rt	0.053, 58
6	0.050, 0.09	0.15, 0.20	0.036, 0.23	32	rt	0.030, 65
7	0.135, 0.24	0.35, 0.53	0.106, 0.60	15	rt	0.098, 77

noted otherwise. Electrospray negative and positive ion mass spectra were measured in methanol (monomers) or THF (polymers). All chromatographic separations were performed on Sorbent Technologies C18 (60 Å, 40 μm) reverse-phase columns. TLC was performed on C18 silica TLC plates w/UV254 aluminum backed (150 μm), with detection by rhodamine 6G (ethanolic solution) in methanol/water (1:1). All the monomers were degassed by three freeze−pump−thaw cycles and stored in Schlenk tubes.

Gel Permeation Chromatography (GPC). Molecular weights and polydispersities of the polymers were determined in THF solutions by GPC at ambient temperature and calibrated against Waters polystyrene standards. A Waters gel permeation chromatograph, differential refractometer, refractive index detector (RI 2414), and EMPOWER software were used, with a three-column bed (Styragel HR 4.6 × 300 mm columns with 5 μm bead size, for molecular weight ranges 100−10 000, 500−30 000, and 5000−6 000 000) and a flow rate of 0.3 mL/min. The results were the same for the crude polymers and those precipitated from methanol.

Kinetics of AIBN Decomposition. The disappearance of AIBN (0.015 M) in a C_6D_6 solution, monitored by ^{1}H NMR, followed first-order kinetics at room temperature (25 °C). The apparent rate constants $k \times 10^5$ s^{-1} were <0.005 for 0 M Li$^+$, 3.39 ± 0.03 for 0.007 M Li$^+$, 7.15 ± 0.10 for 0.015 M Li$^+$, 11.27 ± 0.14 for 0.023 M Li$^+$, and 15.15 ± 0.07 for 0.031 M Li$^+$. The errors shown are maximum deviations in three independent kinetic runs.

General Synthetic Procedures. Conversion to Lithium Salts, Procedure P1. A Me_3NH^+ or Cs$^+$ salt was dissolved in diethyl ether (3 × 10 mL); the ethereal layer was extracted three times with 20% aqueous LiCl, and the LiCl solutions were extracted twice with ether. The solvent of the combined organic layers was removed under reduced pressure to give a solid that was dried overnight at 100 °C under reduced pressure.

Preparation of 1-LiC(BMe)$_{11}^-$ and $CH_2=CH(CH_2)_{n-2}$-C(BMe)$_{11}^-$ Cs$^+$ ([*n*]2), Procedure P2 (Table 2). At −78 °C under argon, **4** or **5** (1 equiv) in 50 mL of THF or toluene was treated with 1.6 M *n*-BuLi (1.6 M solution in hexanes, 2.2 equiv) and stirred for 15 min at that temperature. The resulting solution was cannulated into a solution of $CH_2=CH(CH_2)_nBr$ (2.5 equiv) in THF or toluene at −20 °C and then kept either at room temperature or at reflux at 50 °C. About 15−72 h later, the reaction was quenched by the addition of water. The solvent was evaporated, and **[*n*]2** was extracted into diethyl ether (3 × 20 mL), followed by extraction with 20% aqueous CsCl (3 × 15 mL). After evaporation of the solvent, the resulting solid was purified by reverse-phase column chromatography using a buffered water/methanol eluent (50% methanol, 50% water, each containing 0.7% of Et_3N and 1% AcOH).

Preparation of Br(CH$_2$)$_n$C(BMe)$_{11}^-$ Cs$^+$ ([*n*]7), Procedure P3 (Table 3). At −78 °C under argon, **4** or **5** (1 equiv) in 50 mL of THF or toluene was treated with *n*-BuLi (1.6 M solution in hexanes, 2.5 equiv) and stirred for 15 min at that temperature. The resulting solution was cannulated into a solution of $Br(CH_2)_nBr$ (2.5 equiv) in THF or toluene at −20 °C and then kept at room temperature. After 6−18 h, the reaction was quenched by the addition of water. The solvent was evaporated, and the product was extracted into diethyl ether (3 × 20 mL), followed by extraction with 20% aqueous CsCl (3 × 15 mL). After evaporation of the solvent, the resulting solid was purified by reverse-phase column chromatography using buffered water/methanol eluent (50% methanol, 50% water, each containing 0.7% of Et_3N and 1% AcOH).

Table 3. Yields of Products **[*n*]7** in General Procedure P3

n	**4** (g, mmol)	*t*-BuLi (mL, mmol)	$Br-(CH_2)_n-Br$ (g, mmol)	time (h)	**[*n*]7** (g, %)
3	0.150, 0.27	0.45, 0.68	0.140, 0.68	6	0.112, 75
4	0.500, 0.90	1.50, 2.25	0.500, 2.25	9.5	0.410, 81
5	0.500, 0.90	1.50, 2.25	0.520, 2.25	15	0.340, 65
6	0.220, 0.40	0.65, 1.00	0.250, 1.00	12	0.200, 85
7	0.100, 0.18	0.25, 0.40	0.110, 0.40	18	0.086, 79

Table 4. Yields of Products **[*n*]2** in General Procedure P4

n	**[*n*]7** (g, mmol)	LiTMP (g, mmol)	**[*n*]2** (g, %)
3	0.250, 0.45	0.34, 2.25	0.200, 93
4	0.340, 0.60	0.45, 3.00	0.280, 96
5	0.100, 0.17	0.13, 0.85	0.078, 91
6	0.100, 0.18	0.14, 0.90	0.075, 87
7	0.390, 0.64	0.48, 3.20	0.330, 98

Table 5. Yields of Products **[*n*]2** in General Procedure P5

n	**4** (g, mmol)	*t*-BuLi (mL, mmol)	$CH_2=CH-(CH_2)_{n-2}-OTos$ (g, mmol)	time (h)	**[*n*]2** (g, %)
3	0.075, 0.13	0.20, 0.29	0.070, 0.33	10	0.060, 95
4	0.050, 0.09	0.15, 0.20	0.052, 0.23	12	0.041, 92
5	0.100, 0.18	0.25, 0.40	0.108, 0.45	15	0.088, 98
6	0.100, 0.18	0.25, 0.40	0.115, 0.46	9	0.082, 89
7	0.050, 0.09	0.15, 0.20	0.062, 0.23	6	0.043, 91

Preparation of Cs$^+$ [*n*]2 from [*n*]7, Procedure P4 (Table 4). At 0 °C, 1.6 M *n*-BuLi (23.2 mL, 37.2 mmol) was added dropwise to TMP (6.31 mL, 37.2 mmol) in 20 mL of benzene. After 5 min, the resulting LiTMP solution (5.0 equiv) was cannulated to a stirred solution of Cs$^+$ **[*n*]7** (1 equiv) in benzene at 50 °C. The reaction was quenched after 45 min with 100 mL of 25% CsCl (aqueous) and THF. Solvent was evaporated under reduced pressure. The crude product was extracted from the resulting aqueous mixture with 3 × 100 mL of EtOEt and concentrated under reduced pressure. It was purified by chromatography and further recrystallized from acetone (100 mL) and water (30 mL) to give **[*n*]7** as white crystals.

Preparation of Cs$^+$ [*n*]2 Using Alkenyl Tosylates, Procedure P5 (Table 5). At −78 °C under argon, **4** or **5** (1 equiv) in 50 mL of THF or toluene was treated with 1.6 M *n*-BuLi (1.6 M solution in hexanes, 2.2 equiv) and stirred for 15 min at that temperature. The resulting solution was cannulated into a solution of $CH_2=CH$-$(CH_2)_nOTos$ (2.5 equiv) in THF or toluene at −20 °C and then kept at room temperature. About 10−15 h later, the reaction was quenched by the addition of water. The solvent was evaporated, and **[*n*]2** was extracted into diethyl ether (3 × 20 mL), followed by extraction with 20% aqueous CsCl (3 × 15 mL). After evaporation of the solvent, the resulting solid was purified by recrystallization using MeOH/water (1:9).

Radical Polymerization of Li$^+$ Salts of [*n*]2. Either under air in dark or upon UV irradiation, or with triple freeze−pump−thaw degassing, as specified, a ∼10% solution of the Li$^+$ salt of the monomer in benzene (∼15 mL) containing the stated percentage of an initiator by weight was allowed to stand at room temperature for the specified amount of time. The irradiation was done at room temperature in a Rayonet merry-go-round apparatus using a 450-W medium-pressure mercury lamp with a Pyrex filter.

Most of the solvent was evaporated, a small sample for GPC analysis in THF was removed, methanol (∼5 mL) was added, and the precipitated polymer was filtered and dried. The polymers are soluble in THF, benzene, acetonitrile, and acetone. Their ^{1}H and ^{13}C NMR spectra were very similar to those of the monomers, but vinylic resonances were absent.

Polymers from Solid Li$^+$ Salts in Air (Supporting Information). **[5]2**: ^{1}H NMR (300 MHz) δ 2.74−0.90 (m), −0.60−0.20 (m, BCH_3), 3.21 (m); ^{13}C NMR (100 MHz) δ 52.80, 32.51, 27.55, 23.50, −3.26 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.12, −8.23, −10.20; IR (KBr pellet) 566, 668, 730, 764, 832, 871, 900, 1026, 1084, 1103, 1142, 1253, 1268, 1287, 1302, 1379, 1408, 1147, 1631, 2338, 2357, 2827, 2890, 2924 cm^{-1}. **[6]2**: ^{1}H NMR (300 MHz) δ 2.90−0.88 (m), −0.16−0.55 (m, BCH_3), 3.32 (m); ^{13}C NMR (100 MHz) δ 53.01, 35.20, 33.22, 32.91, 27.80, −3.66 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.15, −8.34, −10.39; IR (KBr pellet) 595, 704, 742, 915, 1035, 1149, 1257, 1312, 1377, 1388, 1426, 1480, 1502, 1632, 2360, 2827, 2897, 2924 cm^{-1}. **[7]2**: ^{1}H NMR (300 MHz) δ 3.15−0.92 (m), −0.18−0.49 (m, BCH_3), 3.46 (m); ^{13}C NMR (100 MHz) δ 55.05, 53.09, 51.24, 32.84, 31.25, 28.77, 27.50, 25.39, 22.24, −2.99 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.23, −8.80, −11.25; IR (KBr pellet) 562, 638, 644, 785, 834, 877, 937, 1040, 1122, 1295, 1377, 1458, 1480, 1627, 2349, 2533, 2827, 2859, 2930 cm^{-1}.

Polymers from Benzene Solutions of Li$^+$ Salts in Air (Supporting Information). **[5]2**: ^{1}H NMR (300 MHz) δ 2.90−1.05 (m), −0.50−0.15 (m, BCH_3), 3.35 (m); ^{13}C NMR (100 MHz) δ 53.25, 33.24, 28.09, 23.99, −3.51 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.15, −8.44, −10.15; IR (KBr pellet) 534, 685, 696, 810, 871, 900, 1004, 1056, 1390, 1466, 1487, 1577, 1622, 2550, 2593, 2872, 2897, 2920 cm^{-1}. **[6]2**: ^{1}H NMR (300 MHz) δ 3.05−0.95 (m), −0.10−0.49 (m, BCH_3), 3.44 (m); ^{13}C NMR (100 MHz) δ 51.05, 38.88, 35.80, 33.10, 27.10, −3.10 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.10, −8.10, −10.25; IR (KBr pellet) 754, 923, 1275, 1344, 1409, 1678, 2839, 2950 cm^{-1}. **[7]2**: ^{1}H NMR (300 MHz) δ 3.22−1.05 (m), −0.05−0.50 (m, BCH_3), 3.55 (m); ^{13}C NMR (100 MHz) δ 58.46, 50.25, 36.77, 34.60, 32.11, 28.08, 23.50, −3.55 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.31, −8.55, −11.01; IR (KBr pellet) 698, 723, 762, 1008, 1049, 1160, 1231, 1367, 1404, 1487, 1707, 2541, 2808, 2890 cm^{-1}.

Polymers from Li$^+$ Salts in Benzene with AIBN (Supporting Information). **[5]2**: ^{1}H NMR (300 MHz) δ 3.05−0.1.10 (m), −0.52−0.20 (m, BCH_3); ^{13}C NMR (100 MHz) δ 68.34, 53.45, 32.36, 31.06, 28.49, −2.52 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.12, −9.11, −10.50; IR (KBr pellet) 754, 824, 845, 1155, 1240, 1390, 1603, 2588, 2844, 2960 cm^{-1}. **[6]2** ^{1}H NMR (300 MHz) δ 3.30−1.15 (m), −0.21−0.50 (m, BCH_3); ^{13}C NMR (100 MHz) δ 63.88, 53.55, 35.81, 32.78, 30.66, 27.65, 25.50, −1.90 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.18, −8.66, −11.05; IR (KBr pellet) 480, 546, 625, 709, 758, 814, 1088, 1128, 1247, 1393, 1600, 2601, 2953 cm^{-1}. **[7]2**: ^{1}H NMR (300 MHz) δ 3.40−1.30 (m), −0.40−0.16 (m, BCH_3); ^{13}C NMR (100 MHz) δ 72.34, 55.50, 53.88, 34.10, 33.92, 31.09, 28.32, 27.41, −2.55 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.19, −8.15, −10.56; IR (KBr pellet) 519, 559, 621, 677, 718, 754, 812, 837, 1114, 1249, 2604, 2952 cm^{-1}.

Polymers from Li$^+$ Salts Irradiated in 1,2-Dichloroethane with (*t*-BuO)$_2$ (Supporting Information). **[5]2**: ^{1}H NMR (300 MHz) δ 3.27−1.60 (m), −0.55−0.28 (m, BCH_3); ^{13}C NMR (100 MHz) δ 60.09, 55.65, 52.34, 45.09, 38.22, 24.22, 18.39, −3.08 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.18, −8.80, −10.22; IR (KBr pellet) 492, 503, 557, 660, 725, 883, 910, 1013, 1051, 1089, 1382, 1464, 1600, 2506, 2577, 2859, 2914, 2941 cm^{-1}. **[6]2**: ^{1}H NMR (300 MHz) δ 3.50−1.22 (m), −0.62−0.01 (m, BCH_3); ^{13}C NMR (100 MHz) δ 64.75, 53.20, 50.39, 34.15, 32.10, 28.85, 22.05, −3.85 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.11, −8.70, −10.50; IR (KBr pellet) 611, 736, 780, 921, 970, 1095, 1143, 1301, 1388, 1426, 1627, 2468, 2533, 2827, 2892, 2919 cm^{-1}. **[7]2**: ^{1}H NMR (300 MHz) δ 3.44−1.51 (m), −0.60−0.00 (m, BCH_3); ^{13}C NMR (100 MHz) δ 61.01, 57.83, 53.90, 43.75, 33.58, 31.87, 27.60, 26.40, −3.50 (BCH$_3$); ^{11}B{^{1}H} NMR (96 MHz) δ 0.10, −8.05, −10.20; IR (KBr pellet) 655, 736, 866, 1008, 1138, 1306, 1377, 1594, 1632, 2501, 2827, 2903, 2935 cm^{-1}.

Miscellaneous Polymerization Experiments. To a ∼10% solution of the Li$^+$ salt of **[5]2** in 1,2-dichloroethane (∼15 mL) was added a stoichometric amount of hydroquinone or TEMPO, and the contents were heated to reflux. After 16 h, the samples were analyzed by ^{1}H NMR spectroscopy and GPC, and no polymer was detected. In a similar experiment in THF solvent, even without a radical trap, no polymer was formed.

To a ∼10% solution of the Li$^+$ salt of **[5]2** in 1,2-dichloroethane (∼15 mL) was added a stoichometric amount of 12-crown-4, and the contents were stirred at room temperature for 4 days. No polymer formation was observed by ^{1}H NMR spectroscopy.

A ∼10% solution of the Na$^+$ or Cs$^+$ salt of **[5]2** in benzene was left for 2 days at room temperature, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. No polymer formation was observed.

To a ∼10% solution of the Li$^+$ salt of **[5]2** in benzene (∼15 mL) was added 10% AIBN by weight and 0.1 mL of *t*-BuOLi (1 M solution in hexanes). The contents were heated to reflux, and after 18 h the polymer formed was precipitated from methanol and characterized by ^{1}H NMR spectroscopy. Similar experiments were conducted with 1% CH_3OD and 10% AIBN by weight and with 1% CD_3OD and 10% AIBN by weight at room temperature. Polymers were obtained after 8 and 10 h, respectively, and characterized by NMR spectroscopy.

Nickel-Catalyzed Polymerization of [*n*]2. Under an argon atmosphere, the nickel catalyst **8** (5 mg) was dissolved in anhydrous dichloroethane (40 mL) and stirred for 30 min at room temperature. The Cs$^+$ salt of the monomer **[*n*]2** (100 mg) in dichloroethane (5 mL) was then added, and stirring was continued. After 18 h ($n = 5$) or 2 h ($n = 6$), the reaction was quenched by the addition of water. The organic layer was separated and the solvent removed under reduced pressure. The residue was dissolved in THF and filtered. The THF was removed, and the resulting solid was dried under reduced pressure. The yields were ∼50%, and the molecular weights (M_w) were 1700−1800.

Titanium-Catalyzed Polymerization of [*n*]2. Under an argon atmosphere, the titanium catalyst **9** (7 mg), $B(C_6F_5)_3$ (10 mg), and the Cs$^+$ salt of the monomer **[5]2** (100 mg) were dissolved in anhydrous CH_2Cl_2 (5 mL). The reaction mixture was stirred for either 0.5 or 48 h, with identical results, and then quenched by the addition of a 1 M solution of HCl (3 mL). The mixture was extracted with hexanes, the solvent was removed, and the resulting solid was dried under reduced pressure. Molecular weights (M_w) were 1900−2600. The same process, using 2 mg of **9**, 3 mg of $B(C_6F_5)_3$, 20 mg of the Cs$^+$ salt of **[6]2**, and an 18 h reaction time, yielded an oligomer with $M_w \approx 2400$.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of the polymers (poly **[*n*]2**) prepared with various initiators. This material is available free of charge via the Internet at http://pubs.acs.org.

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