Synthesis of 1,3-Dehydroadamantanes Possessing Alkyl, Phenyl, and Alkoxy Substituents by Intramolecular Wurtz-Type Coupling Reaction of 1,3-Dibromoadamantanes

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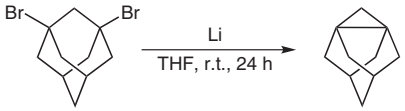
Abstract: A series of highly strained [3.3.1]propellane derivatives, 1,3-dehydroadamantanes (DHAs) possessing alkyl, phenyl, and alkoxy substituents, such as 5-butyl, 5-hexyl, 5-octyl, 5-phenyl, 5-methoxy, 5-butoxy, 5,7-dimethyl, 5-ethyl-7-hexyl, 5,7-dibutyl-, 5-butyl-7-isobutyl, 5-butyl-7-hexyl, 5-butyl-7-phenyl, 5-butyl-7-methoxy, and 5-butoxy-7-butyl, were synthesized in several gram amounts. The 1,3-dibromoadamantanes carrying alkyl, phenyl, and alkoxy substituents were converted into the corresponding DHAs via the intramolecular Wurtz-type coupling reactions with lithium metal in THF in 21–81% yields.

Key words: 1,3-dehydroadamantanes, 1,3-dibromoadamantanes, Wurtz coupling reaction, [3.3.1]propellanes

Introduction

1,3-Dehydroadamantane (**1a**)[1–3] is a typical highly strained [3.3.1]propellane derivative that can be synthesized by the intramolecular Wurtz-type coupling reaction of 1,3-dibromoadamantane (**2a**) with lithium metal in THF, as shown in Scheme 1. It is well known that small-ring propellanes, such as the [1.1.1]-,[4] [2.2.2]-,[5] [2.2.1]-,[6] and [3.3.1]propellanes,[7] show high reactivities toward various chemical reagents due to the high strains in their unique structures.[8] Their reactivity, stability, strain, and structure have attracted significant attention not only from organic chemists, but also from polymer chemists, since these propellanes often exhibit a ring-opening polymerizability to form a polymeric product in addition to the simple ring-opening reaction.[9,10]



Scheme 1 General synthetic scheme of DHAs via intramolecular Wurtz-type coupling reaction

Similar to other small-ring propellanes, **1a** shows a high reactivity derived from its inverted tetrahedral geometry at the bridgehead carbon. The inverted 1,3-carbon–carbon σ-bond of **1a** readily undergoes electrophilic and free-radical ring-opening reactions with acetic acid, bromine, and oxygen to form the corresponding 1,3-disubstituted adamantanes (Scheme 2),[1,2] while no reaction occurred with nucleophilic reagents such as *n*-butyllithium or phenylmagnesium chloride. These results clearly indicate the high electron density of the cyclopropane ring in **1a**. Interestingly, a thermally stable insoluble polymeric product was obtained by heating **1a** at 160 °C, indicating its thermal polymerizability.[2] On the other hand, the cationic or radical ring-opening polymerization of **1a** also proceeded with a catalytic amount of trifluoromethanesulfonic acid (TfOH) or α,α′-azobisisobutyronitrile (AIBN) to give an insoluble polymer in quantitative yield.[11,12] More interestingly, we have found the spontaneous copolymerizability of **1a** with electron-deficient vinyl monomers, such as acrylonitrile or methyl acrylate, to give soluble copolymers with predominantly alternating sequences.[13] The resulting copolymers derived from **1a** showed a high thermal stability and high glass transition temperature (T_g) due to the introduction of a bulky and rigid adamantane-1,3-diyl framework into the main chain.

In order to expand the range of polymerizable cyclic monomers and to increase the solubility of the resulting polymers, we have synthesized a series of alkyl-substituted 1,3-dehydroadamantanes (DHAs) and attempted their homopolymerization under various conditions.[11,12,14] Since the resulting alkyl-substituted polymers showed sufficient solubility in organic solvents, such as THF or $CHCl_3$, as well as an excellent thermal stability, various characterizations, such as NMR and size exclusion chromatography (SEC) measurements, were possible to clarify the unique structure of the poly(1,3-adamantane)s consisting of adamantane-1,3-diyl linkages. Thus, DHAs including **1a** can be positioned as an attractive cyclic monomer or a rigid building unit that affects the thermal property or solubility of the resulting polymers. However, the synthesis of DHA derivatives carrying other substituents is usually difficult and still challenging, because the construction of the highly strained cyclopropane ring is required in the presence of the substituents. In our laboratory, several grams of the DHA compounds are needed in order to examine their ring-opening polymerizability and to characterize the structures, molecular weights, and properties of the resulting poly(1,3-adamantane)s. In this

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paper, we report typical synthetic procedures of DHAs carrying alkyl,[11,12,14] phenyl,[15] and alkoxy substituents[15] in gram-scale experiments and discuss the practical aspects of their preparations.

Scope and Limitations

Pincock and Torupka first succeeded in the synthesis of **1a** by the intramolecular Wurtz-type coupling reaction of **2a** using the Na/K alloy in *n*-heptane under reflux.[1] A similar reaction of **2a** with the Na/K alloy in diethyl ether containing HMPA at room temperature gave **1a** in 77%

Biographical Sketches

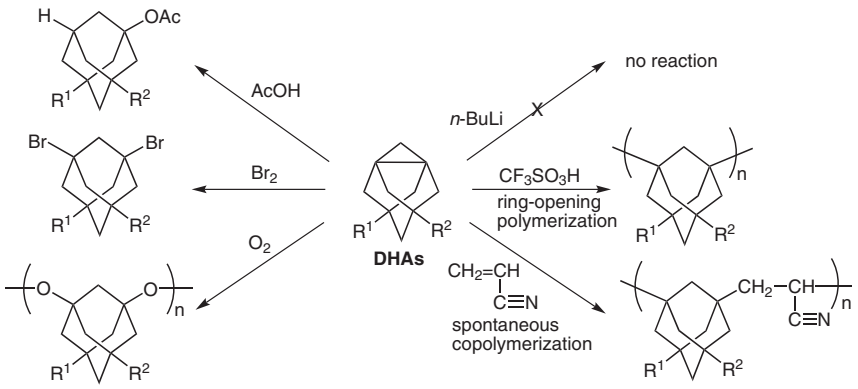
Sotaro Inomata was born in Tokyo, Japan, in 1986. He received a bachelor's degree in polymer chemistry from Tokyo Institute of Technology in 2008 and a master's degree from the same institution in 2010. He obtained a Ph.D. degree on the synthesis of polymers containing adamantane skeletons in the main chain under the supervision of Professor Takashi Ishizone in the same institution in 2013. In 2011, he performed acyclic diene metathesis polymerization in the group of Professor Kenneth B. Wagener at the University of Florida as a visiting student for 6 months. He is currently working in FUJIFILM Corporation in Kanagawa, Japan.

Yusuke Harada was born in Miyazaki, Japan, in 1988. He received a bachelor's degree in polymer chemistry from Tokyo Institute of Technology in 2010. He completed a master's degree on ring-opening polymerization of 1,3-dehydroadamantanes carrying alkoxy groups under the supervision of Professor Takashi Ishizone in the same institution in 2012. He is currently working in SHOWA DENKO K. K. in Hyogo, Japan.

Yuya Nakamura was born in Saitama, Japan, in 1989. He received a bachelor's degree in polymer chemistry from Tokyo Institute of Technology in 2012. He is currently conducting his master course research on ring-opening polymerization of 1,3-dehydroadamantanes carrying trialkylsilyl groups under the supervision of Professor Takashi Ishizone.

Taisuke Nakamura was born in Shizuoka, Japan, in 1989. He received a bachelor's degree in polymer chemistry from Tokyo Institute of Technology in 2013. He is currently conducting his master research on spontaneous copolymerization of 1,3-dehydroadamantanes with electron-deficient monomers under the supervision of Professor Takashi Ishizone.

Takashi Ishizone was born in Saitama, Japan, in 1963. He received a master's degree in polymer chemistry from Tokyo Institute of Technology in 1988 under the supervision of Professors Seiichi Nakahama and Akira Hirao and started his academic career as an assistant professor in the same institution from 1989. After receiving a doctorate degree in 1994, he studied organic chemistry as a visiting scientist at The University of Chicago in the group of Professor P. E. Eaton from 1995 to 1996. Since 2000 he is an Associate Professor in the Department of Organic and Polymeric Materials at Tokyo Institute of Technology. His main research areas center on the synthesis of novel thermally stable polymers possessing adamantane skeletons and the synthesis of novel functional polymers showing water-solubility and thermoresponsive properties by means of living anionic polymerization.



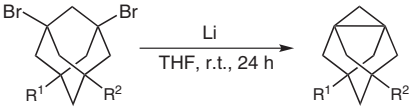
Scheme 2 Ring-opening reactions of DHAs

yield.[2] Adcock and Clark synthesized **1a** in 67% yield by treating **2a** with lithium in diethyl ether under reflux.[16] In these cases of using alkali metals as strong reducing reagents, the intramolecular ring-closing reaction of **2a** produced a highly strained cyclopropane ring in the adamantane framework. When we employed magnesium to react with 5-butyl-1,3-dibromoadamantane (**2b**) in THF, 5-butyl-1,3-dehydroadamantane (**1b**) was similarly obtained in 50% yield. It should be noted that a significant amount (7%) of a reduced by-product, 1-butyladamantane, formed along with **1b** in the reaction using magnesium. Interestingly, 5-bromo-1,3-dehydroadamantane could be prepared by the reaction of 1,3,5-tribromoadamantane with *n*-BuLi at –35 °C in a mixture of diethyl ether and HMPA.[17]

Among these synthetic procedures for the DHAs, the Wurtz-type reaction of the 1,3-dibromoadamantanes with lithium in THF (Scheme 1) is very attractive from the standpoint of yield and safety, since the lithium metal was easy to handle compared to the Na/K alloy in the reaction. This reaction can be performed in hydrocarbons, such as *n*-heptane, or ethereal solvents, such as diethyl ether, THF, and tetra(ethylene glycol) dimethyl ether (tetraglyme). In addition, the starting compounds, a series of 1,3-dibromoadamantanes carrying various substituents, such as alkyl, phenyl, and alkoxy groups, are available via several synthetic pathways as previously reported.[11,12,14] There are several precautions required for the preparation of DHAs from the 1,3-dibromoadamantanes and lithium metal in THF. The substituents in the 1,3-dibromoadamantanes must be stable to lithium during the formation of the DHAs. In addition, the substituents must coexist with the highly reactive DHA frameworks after the reaction.

A series of 1,3-dibromoadamantanes, **2a**–**o**, were converted into the corresponding DHAs **1a**–**o** in 21–81% yields by treating with lithium (3–5 equiv) in THF under argon at room temperature (Table 1). Under argon, the surface of lithium showed a metallic luster and the reaction mixture turned black as the reaction proceeded. The starting compounds, the 1,3-dibromoadamantanes, were always completely consumed and converted into the DHAs within 24 hours, and even the 1-bromoadamantanes were not detected in the reaction mixture. The resulting suspensions were transferred to an all-glass apparatus with

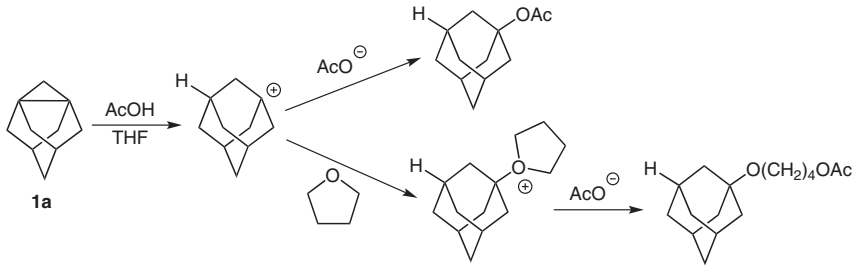
Table 1 Synthesis of 1,3-Dehydroadamantanes[a]



2 **1**

DHA	R^1	R^2	Yield (%)
1a	H	H	81
1a[b]	H	H	46
1b	H	Bu	79
1b[c]	H	Bu	50
1c	H	C_6H_{13}	64
1d	H	C_8H_{17}	73
1e	H	Ph	47
1f	H	OMe	58
1g	H	OBu	57
1h	Me	Me	86
1h[b]	Me	Me	67
1i	Et	C_6H_{13}	38
1j	Bu	Bu	57
1k	Bu	*i*-Bu	67
1l	Bu	C_6H_{13}	54
1m	Bu	Ph	21
1n	Bu	OMe	60
1o	Bu	OBu	62

[a] Unless otherwise indicated, reactions were conducted with Li in THF at r.t. for 24 h.
[b] In tetraglyme at 60 °C for 3 d.
[c] With Mg in THF at reflux for 24 h.



Scheme 3 Reaction of **1a** with AcOH in the presence of THF

break-seals on a vacuum line to remove the excess amount of lithium.[18] Repeated vacuum distillations of the mixture were performed in order to thoroughly remove the lithium bromide and THF from the resulting DHAs. In most cases, except for **1e**, **1i**, and **1m**, the DHAs with sufficient purity could be isolated in over 50% yield after these workup processes. However, it should be noted that the formation of a reduced product, the corresponding strain-free adamantane derivative, was confirmed by NMR and GLC analyses as previously reported by Pincock.[1,2] In most cases, the adamantanes were formed in 1–3% yields in the reaction mixture as side products along with the DHAs. The removal of such adamantanes from the resulting DHAs was very difficult by fractional distillations, since the molecular weights of DHAs and the corresponding adamantanes were very similar and both compounds possessed similar polarities. Therefore, we performed the ring-opening reactions or ring-opening polymerizations of DHAs in the presence of trace amounts of the reduced adamantanes. As expected, the adamantanes were found to be intact during the ring-opening reactions and ring-opening polymerizations of the DHAs.

On the other hand, the complete removal of THF from the DHAs was strongly required in selected cases. For example, the reaction of **1a** with AcOH in the presence of THF unexpectedly gave a mixture of 1-acetoxyadamantane and 1-(4-acetoxybutoxy)adamantane (Figure 1), as shown in Scheme 3. Although **1a** was intact in THF, the 1-adamantyl cation was readily produced via the protonation of **1a** with AcOH. The resulting 1-adamantyl cation was captured by the nucleophilic THF to form a cyclic oxonium species. The subsequent ring-opening reaction of the THF moiety in the oxonium salt occurred with a nucleophilic acetate anion resulting in the formation of 1-(4-acetoxybutoxy)adamantane.[19] For the cationic ring-opening polymerization of DHAs with strong Brønsted acids, such as TfOH, the trace amount of THF certainly hindered the polymerization by formation of the oxonium ion reacting with the 1-adamantyl cation. Thus, the removal of nucleophilic ethereal solvents, such as THF, is essential for the following ring-opening reaction of the DHAs under the cationic conditions. On the other hand, THF did not hinder the spontaneous copolymerization of **1a** with acrylonitrile to afford the copolymer with alternating sequences.[13] We now consider that this copolymerization smoothly proceeds in THF via a radical mechanism. In practice, for most DHAs with high molecular weights, **1b**–**g** and **1i**–**o**, the complete removal of THF was attained after repeated vacuum distillations. On the other hand, for the DHAs having relatively low boiling points, **1a** and **1h**, tetraglyme (bp 95 °C/3.0 mmHg) was often employed as the solvent instead of THF for the reactions of **2a** and **2h** with lithium (Scheme 4). In these cases, the ether-free DHAs could be isolated by vacuum distillation due to the higher boiling point of tetraglyme.

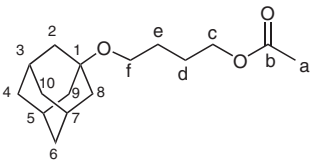
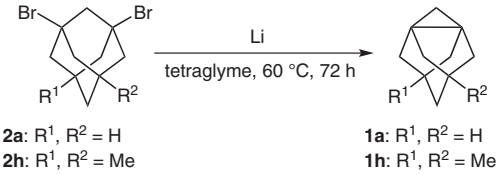


Figure 1 1-(4-Acetoxybutoxy)adamantane



Scheme 4 Synthesis of **1a** and **1h** in tetraglyme

Another significant impurity, which hinders the reaction, is oxygen. Oxygen deactivated the lithium metal during the ring-closing reaction using the 1,3-dibromoadamantanes, and it spontaneously reacted with the DHAs to form an alternating polymer, poly(DHA-*alt*-oxygen), containing peroxide linkages between the adamantane-1,3-diyl moieties (Scheme 2), as previously reported.[1,2] The formation of such alternating copolymers was confirmed by the formation of the 1,3-dihydroxyadamantanes by the reduction reaction of the copolymer with lithium aluminum hydride. Therefore, it is necessary to treat the DHAs in an inert atmosphere, such as argon or nitrogen, not only during the formation process, but also when stored. In practice, the NMR measurements of the DHAs were possible to characterize the chemical structure, if the isolated DHAs were diluted with inert deuterated solvents under an inert atmosphere. On the other hand, elemental analysis and mass spectroscopic measurement of the DHAs were difficult using the normal procedures.

It is noteworthy that the isolated DHAs often underwent spontaneous polymerization in the bulk even under a low

temperature condition, indicating their high reactivities. Therefore, we immediately diluted the isolated DHAs with appropriate inert solvents, such as *n*-heptane, benzene, dichloromethane, and THF, to prevent the spontaneous polymerization. In fact, we could store the DHAs without any polymerization and/or degradation under diluted conditions in the above-mentioned solvents. For example, the DHAs proved to be stable in deuterated benzene, C_6D_6, *for at least several years in sealed glass tubes*. This stability of the DHAs, [3.3.1]propellane, is noteworthy when compared to the relatively short half life of other propellane derivatives.[8] For example, the half life of [2.2.2]propellane was reported to be only 28 minutes at 25 °C.[5]

On the other hand, the DHAs readily underwent ring-opening reactions with acidic reagents, such as AcOH and methanesulfonic acid (MsOH), and the polymers of DHAs were obtained when using the stronger Brønsted acids, such as TfOH and trifluoromethanesulfonimide $[(CF_3SO_2)_2NH]$.[11,12,14] Interestingly, even in methanol, the DHAs were slowly consumed to give exclusively the ring-opening products, 1-methoxyadamantanes. For example, the reaction of **1b** with methanol proceeded to yield 1-butyl-3-methoxyadamantane.[15] The conversion of **1b** could be monitored by NMR and GLC measurements as 8, 48, 85, and 100% after 10 minutes, 1.5, 6, and 30 hours, respectively. On the other hand, all the DHAs rapidly reacted with methanol to form the corresponding 1-methoxyadamantanes in the presence of a catalytic amount of MsOH. These results clearly indicated the high electron density of the cyclopropane rings in the DHAs as well as their intolerance toward acidic reagents. Since an adamantane molecule has a pseudotetrahedral symmetry, an adamantane derivative possessing four different substituents on the four bridgehead carbons should have a stereogenic center.[20] In fact, the ring-opening reactions of DHAs possessing two different substituents on the 5- and 7-positions, **1i** and **1k**–**o**, with suitable acidic reagents, such as AcOH, afforded multi-substituted adamantanes bearing a stereogenic center.[15] Thus, DHAs are regarded as an attractive precursor of chiral adamantane derivatives.

The substituent effect in the DHA framework should be mentioned for estimating the electronic environment and the relative reactivity. Table 2 summarizes the selected ^{13}C NMR chemical shifts and $J_{C,H}$ coupling constants of the DHAs. For the monosubstituted DHAs, carbon signals for C1, C2, C3, and part of the cyclopropane ring were observed in a high-field region compared to the unsubstituted **1a**. In particular, the alkoxy-substituted DHAs **1f** and **1g** showed significant high-field shifts (ca. 7.0 ppm for C1 and C3, and ca. 5.0 ppm for C2) compared to **1a**, while those DHAs exhibited reactivities similar to **1a**. The 5-substituted alkoxy groups presumably affect the electron density of the cyclopropane ring apart from the alkoxy groups through the σ-bond framework without π-conjugation. The ^{13}C NMR chemical shifts of the 5,7-disubstituted DHAs also tended to shift to a higher field region than

Table 2 ^{13}C NMR Chemical Shifts and $J_{C,H}$ Constants of DHAs[a]

DHA	R^1	R^2	Position (ppm)				$J_{C,H}$ (Hz)[b]
			1,3	2	5	7	
1a	H	H	37.3	49.6	54.5	54.5	156
1b	H	Bu	36.0	48.0	64.3	53.5	155
1c	H	C_6H_{13}	36.1	48.1	64.4	53.5	157
1d	H	C_8H_{17}	36.0	48.0	64.4	53.5	154
1e	H	Ph	35.4	47.9	67.4	53.8	156
1f	H	OMe	30.3	44.2	91.6	52.9	160
1g	H	OBu	30.4	44.2	91.3	52.9	161
1h	Me	Me	36.5	46.4	59.6	59.6	156
1i	Me	C_6H_{13}	34.7	46.4	63.5	63.9	159
1j	Bu	Bu	34.8	46.5	63.5	63.5	155
1k	Bu	*i*-Bu	34.8	46,5	63.5	63.5	155
1l	Bu	C_6H_{13}	34.3	46.4	63.6	63.6	156
1m	Bu	Ph	34.3	46.4	66.7	63.9	156
1n	Bu	OMe	28.9	42.7	91.2	63.9	155
1o	Bu	OBu	29.1	42.7	90.9	64.0	154

[a] Measured in C_6D_6.
[b] $J_{C,H}$ coupling constants of C2 carbon.

the corresponding monosubstituted DHAs. We next compared the $J_{C,H}$ coupling constant of the C2 methylene group in the DHA framework in order to estimate the orbital hybridization,[21] since no proton was present on the C1 and C3 carbons. The $J_{C,H}$ values of the DHAs are observed between 154 and 161 Hz, indicating their similar electronic environments. In fact, these $J_{C,H}$ values are comparable to the typical compounds showing an sp^2 orbital hybridization, such as ethylene (156 Hz), cyclopropane (161 Hz), and [1.1.1]propellane (164 Hz), but are very different when compared to the values of ethane (125 Hz, sp^3), adamantane (131 Hz, sp^3), and acetylene (249 Hz, sp).

Finally, we would like to describe the practical synthetic aspects. Due to the high reactivity of the DHAs, it is often difficult to estimate the yields of the produced DHAs in gravimetric terms, while the conversion of the starting 1,3-dibromoadamantanes could be checked by GLC or NMR measurements. Therefore, an aliquot of the reaction mixture was taken under nitrogen to estimate the yields of the DHAs by gravimetric means and/or by NMR spectroscopy. The conversion of the 1,3-dibromoadamantanes and the yield of the DHAs were often estimated by the NMR measurements after converting the DHAs into the corresponding 1-acetoxyadamantanes by quenching with AcOH. In our laboratory, the preparations of the DHAs were usually performed using 1,3-dibromoadamantanes in 3–30 gram amounts. This means that 1–15 grams of the DHAs will be theoretically obtained after isolation. In fact, the reaction mixture was transferred to an all-glass apparatus on the vacuum line to effectively isolate the DHAs and remove THF and lithium bromide.[18] The experiments under high vacuum conditions (10^{-6} Torr) using an all-glass hand-made apparatus equipped with break-seals were very effective for producing reproducible and reliable results. For the DHAs with high boiling points, the thermal polymerizations often lowered the isolated yields of the DHAs during the vacuum distillations, in particular, for the large-scale preparation.

In summary, we have developed practical synthetic procedures for a series of DHAs carrying alkyl, phenyl, and alkoxy substituents in several gram amounts. The highly strained [3.3.1]propellane frameworks in the DHAs can be constructed in 21–81% yields by the reaction of the 1,3-dibromoadamantane derivatives with lithium in THF. The resulting DHAs show similar high ring-opening reactivities and polymerizabilities toward various chemical reagents, which are not the subjects of this report. The resulting asymmetrical 5,7-disubstituted DHAs were revealed to be precursors of multi-substituted adamantane derivatives bearing a stereogenic center. From the viewpoint of polymer chemists, DHAs are promising novel cyclic monomers for constructing a rigid building unit, adamantane-1,3-diyl, via the ring-opening polymerization.

1,3-Dibromoadamantane (**2a**), Li (wire), Na, Mg, AcOH, MsOH, MeOH, and $LiAlH_4$ were used as received. Other 1,3-dibromoadamantanes, **2b–o**, were synthesized according to our previous report.[15] Tetraglyme was distilled over $LiAlH_4$ in vacuo. THF was refluxed over sodium wire for 3 h, and distilled over $LiAlH_4$ under N_2.

^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, either in $CDCl_3$ or C_6D_6. The chemical shifts were reported in ppm downfield relative to $CHCl_3$ (δ = 7.26) or C_6H_6 (δ = 7.16) for ^{1}H NMR and $CDCl_3$ (δ = 77.1) or C_6D_6 (δ = 128.0) for ^{13}C NMR as standards. In the ^{1}H NMR spectral data, the marking of the 5-substituent group of **1** is provided to distinguish them from the ring CH_2 groups, wherever necessary. IR spectra were recorded on a FT-IR instrument by ATR or NaCl disk method. High-resolution mass spectra (HRMS) were obtained on an electrospray ionization (ESI) mass spectrometer.

Preparation of DHAs in THF; 5-Butyl-1,3-dehydroadamantane (1b); Typical Procedure A

A mixture of 1,3-dibromo-5-butyladamantane (**2b**; 11.1 g, 31.7 mmol) and Li (1.00 g, 144 mmol) in anhydrous THF (50 mL) was reacted at r.t. for 24 h under argon. The resulting suspension was transferred into a round-bottomed flask equipped with a break-seal to remove residual Li, and THF was removed from the suspension in vacuo. The residue was sealed off under high vacuum conditions (10^{-6} Torr) on a vacuum line.[18] After first vacuum distillation in an all-glass apparatus, **1b** was isolated from LiBr. Repeating vacuum distillations in the all-glass apparatus gave **1b** as a colorless liquid (4.76 g, 25.0 mmol, 79%). For the cationic polymerization, the distilled DHAs were rapidly diluted with anhydrous CH_2Cl_2 or anhydrous *n*-heptane in an ampoule equipped with a break-seal, and the solution was stored at –30 °C. For the NMR measurement, the distilled DHAs were rapidly diluted with C_6D_6 and sealed in an NMR tube.

Marking of the butyl group: $C^dH_2C^cH_2C^bH_2C^aH_3$.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.89 (t, J = 7.1 Hz, C^aH_3, 3 H), 1.09–1.29 (m, 10 H, $C^dH_2C^cH_2C^bH_2$, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.63 (s, 2 H, C^6H_2), 1.73 (d, J = 10 Hz, 2 H, one of C^4H_2, one of C^9H_2), 1.86 (d, J = 10 Hz, 2 H, one of C^8H_2, one of $C^{10}H_2$), 1.97–2.05 (m, 2 H, C^2H_2), 2.81 (s, 1 H, C^7H).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.4 (C^a), 24.2 (C^b), 27.8 (C^c), 36.1 (C^1, C^3), 37.8 (C^d), 42.6 (C^6), 45.3 (C^8, C^{10}), 48.1 (C^2), 49.8 (C^4, C^9), 53.5 (C^7), 64.4 (C^5).

In the large-scale preparation of DHA, the reaction was similarly conducted using **2b** (31.3 g, 89.4 mmol) to yield 13.2 g of **1b** (67.9 mmol, 76%). It is also noteworthy that isolation of DHAs was possible by the vacuum distillation using usual laboratory glassware, although the experimental procedure using vacuum line seemed more effective for achieving reproducible and reliable results. For example, **1b** (1 g scale with sufficient purity) was obtained in 60% yield after vacuum distillation using usual laboratory glassware, when **1b** was carefully treated to prevent contact with air.

5-Hexyl-1,3-dehydroadamantane (1c)

The reaction was performed following typical procedure A, starting from 5-hexyl-1,3-dibromoadamantane (**2c**; 11.7 g, 30.9 mmol) to yield **1c** (4.32 g, 19.8 mmol, 64%) as a colorless oil.

Marking of the hexyl group: $C^fH_2C^eH_2C^dH_2C^cH_2C^bH_2C^aH_3$.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.89–0.93 (t, J = 6.5 Hz, 3 H, C^aH_3), 1.10–1.40 (m, 14 H, C^bH_2, C^cH_2, C^dH_2, C^eH_2, C^fH_2, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.64 (s, 2 H, C^6H_2), 1.73–1.76 (d, J = 10 Hz, 2 H, one of C^4H_2, one of C^9H_2), 1.85–1.88 (d, J = 10 Hz, 2 H, one of C^8H_2, one of $C^{10}H_2$), 1.98–2.06 (m, 2 H, C^2H_2), 2.82 (br s, 1 H, C^7H).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.5 (C^a), 23.2 (C^b), 25.6 (C^c), 30.8 (C^d), 32.3 (C^e), 36.1 (C^1, C^3), 38.1 (C^f), 42.6 (C^6), 45.3 (C^8, C^{10}), 48.1 (C^2), 49.9 (C^4, C^9), 53.5 (C^7), 64.4 (C^5).

5-Octyl-1,3-dehydroadamantane (1d)
The reaction was performed following typical procedure A, starting from 5-octyl-1,3-dibromoadamantane (**2d**; 4.93 g, 12.1 mmol) to yield **1d** (2.17 g, 8.82 mmol, 73%) as a colorless oil.

Marking of the octyl group: $C^hH_2C^gH_2C^fH_2C^eH_2C^dH_2C^cH_2C^bH_2C^aH_3$.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.89–0.93 (t, *J* = 6.4 Hz, 3 H, C^aH_3), 1.11–1.40 (m, 18 H, C^bH_2, C^cH_2, C^dH_2, C^eH_2, C^fH_2, C^gH_2, C^hH_2, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.65 (s, 2 H, C^6H_2), 1.73–1.77 (d, *J* = 10 Hz, 2 H, one of C^4H_2, one of C^9H_2), 1.85–1.88 (d, *J* = 10 Hz, one of C^8H_2, one of $C^{10}H_2$), 1.95–2.05 (m, 2 H, C^2H_2), 2.82 (s, 1 H, C^7H).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.4 (C^a), 23.2 (C^b), 25.6 (C^c), 29.9 and 30.1 (C^d, C^e), 31.2 (C^f), 32.4 (C^g), 36.0 (C^1, C^3), 38.1 (C^h), 42.6 (C^6), 45.3 (C^8, C^{10}), 48.0 (C^2), 49.8 (C^4, C^9), 53.5 (C^7), 64.4 (C^5).

5-Phenyl-1,3-dehydroadamantane (1e)
The reaction was performed following typical procedure A, starting from 5-phenyl-1,3-dibromoadamantane (**2e**; 7.90 g, 21.3 mmol) to yield **1e** (2.10 g, 10.0 mmol, 47%) as a white solid.

^{1}H NMR (300 MHz, C_6D_6): δ = 1.10–1.14 (d, *J* = 11 Hz, 2 H, one of C^8H_2, one of $C^{10}H_2$), 1.43–1.47 (d, *J* = 11 Hz, 2 H, one of C^4H_2, one of C^9H_2), 1.87–2.03 (m, 6 H, C^2H_2, C^6H_2, one of C^8H_2, one of $C^{10}H_2$), 2.18–2.23 (m, 2 H, one of C^4H_2, one of C^9H), 2.79 (s, 1 H, C^7H), 7.05–7.20 (m, 5 H, C_6H_5).

^{13}C NMR (75 MHz, C_6D_6): δ = 35.4 (C^1, C^3), 44.9 (C^8, C^{10}), 45.1 (C^6), 47.9 (C^2), 50.1 (C^4, C^9), 53.8 (C^7), 67.4 (C^5), 126.1 (C_m), 126.5 (C_p), 128.4 (C_o), 146.7 (C_i).

5-Methoxy-1,3-dehydroadamantane (1f)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5-methoxyadamantane (**2f**; 4.37 g, 13.5 mmol) to yield **1f** (1.28 g, 7.80 mmol, 58%) as a colorless oil.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.90–0.94 (d, *J* = 11 Hz, 2 H, one of C^8H_2, one of $C^{10}H_2$), 1.39–1.42 (d, *J* = 10 Hz, 2 H, one of C^4H_2, one of C^9H_2), 1.62–1.67 (m, 3 H, one of C^2H_2, one of C^8H_2, one of $C^{10}H_2$), 1.76–1.78 (m, 1 H, one of C^2H_2), 1.83–1.88 (m, 4 H, C^6H_2, one of C^4H_2, one of C^9H_2), 2.69 (br s, 1 H, C^7H), 3.09 (s, 3 H, OCH_3).

^{13}C NMR (75 MHz, C_6D_6): δ = 30.3 (C^1, C^3), 41.7 (C^6), 44.2 (C^2), 44.3 (C^8, C^{10}), 46.0 (C^4, C^9), 51.0 (OCH_3), 52.9 (C^7), 91.6 (C^5).

5-Butoxy-1,3-dehydroadamantane (1g)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5-butoxyadamantane (**2g**; 7.21 g, 19.7 mmol) to yield **1g** (2.31 g, 11.2 mmol, 57%) as a colorless oil.

Marking of the butoxy group: $OC^dH_2C^cH_2C^bH_2C^aH_3$.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.85–0.96 (m, 5 H, C^aH_3, one of C^8H_2, one of $C^{10}H_2$), 1.36–1.58 (m, 6 H, C^bH_2, C^cH_2, one of C^4H_2, one of C^9H_2), 1.66–1.69 (m, 3 H, one of C^2H_2, one of C^8H_2, one of $C^{10}H_2$), 1.78–1.80 (m, 1 H, one of C^2H_2), 1.90–1.93 (C^6H_2, one of C^4H_2, one of C^9H_2), 2.72 (br s, 1 H, C^7H), 3.28–3.32 (t, *J* = 6.3 Hz, 2 H, C^dH_2).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.2 (C^a), 19.8 (C^b), 30.4 (C^1, C^3), 33.1 (C^c), 42.1 (C^6), 44.2 (C^2), 44.3 (C^8, C^{10}), 46.8 (C^4, C^9), 52.9 (C^7), 63.0 (C^d), 91.3 (C^5).

5-Ethyl-7-hexyl-1,3-dehydroadamantane (1i)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5-ethyl-7-hexyladamantane (**2i**; 6.68 g, 16.4 mmol) to yield **1i** (1.54 g, 6.26 mmol, 38%) as a colorless oil.

Marking of the ethyl and hexyl groups: $C^bH_2C^aH_3$; $C^cH_2C^dH_2C^eH_2C^fH_2C^gH_2C^hH_3$.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.82–0.87 (t, *J* = 7.5 Hz, 3 H, C^aH_3), 0.91–0.95 (t, *J* = 6.4 Hz, 3 H, C^hH_3), 1.06–1.14 (m, 4 H, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.26–1.43 (m, 12 H, C^bH_2, C^cH_2, C^dH_2, C^eH_2, C^fH_2, C^gH_2), 1.59 (s, 2 H, C^6H_2), 1.64–1.70 (m, 4 H, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.93 (s, 2 H, C^2H_2).

^{13}C NMR (75 MHz, C_6D_6): δ = 9.8 (C^a), 14.5 (C^h), 23.2, 25.7, 30.0, 30.9, 32.9, and 37.9 (C^b, C^c, C^d, C^e, C^f, C^g), 34.7 (C^1, C^3), 46.5 (C^2), 47.3 (C^6), 48.5 and 49.1 (C^4, C^8, C^9, C^{10}), 63.5 and 63.9 (C^5, C^7).

5,7-Dibutyl-1,3-dehydroadamantane (1j)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5,7-dibutyladamantane (**2j**; 15.3 g, 37.7 mmol) to yield **1j** (5.30 g, 21.5 mmol, 57%) as a colorless oil.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.92 (t, *J* = 6.7 Hz, 6 H, C^aH_3), 1.05–1.08 (d, *J* = 10 Hz, 4 H, one of C^4H_2, one of C^8H_2, one of C^9H_2, and one of $C^{10}H_2$), 1.16–1.29 (m, 12 H, C^bH_2, C^cH_2, C^dH_2), 1.57 (s, 2 H, C^6H_2), 1.65–1.68 (d, *J* = 10 Hz, 4 H, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.94 (s, 2 H, C^2H_2).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.4 (C^a), 24.2 (C^b), 27.9 (C^c), 34.8 (C^1, C^3), 37.6 (C^d), 46.5 (C^2), 47.8 (C^6), 49.1 (C^4, C^8, C^9, C^{10}).

5-Butyl-7-isobutyl-1,3-dehydroadamantane (1k)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5-butyl-7-isobutyladamantane (**2k**; 8.35 g, 20.6 mmol) to yield **1k** (3.41 g, 13.9 mmol, 67%) as a colorless oil.

Marking of the butyl and isobutyl groups: $C^dH_2C^cH_2C^bH_2C^aH_3$; $C^eH_2C^fH(C^gH_3)_2$.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.89–0.95 (m, 9 H, C^aH_3, C^gH_3), 1.01–1.10 (m, 4 H, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.20–1.29 (m, 8 H, C^bH_2, C^cH_2, C^dH_2, C^eH_2), 1.58 (s, 2 H, C^6H_2), 1.63–1.72 (m, 5 H, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$, C^fH), 1.93 (br s, 2 H, C^2H_2).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.4 (C^a), 24.2 (C^b), 25.0 (C^f), 25.3 (C^g), 27.9 (C^c), 34.8 (C^1, C^3), 37.6 (C^d), 46.5 (C^2), 47.0 (C^e), 48.1 (C^6), 49.0 and 50.0 (C^4, C^8, C^9, C^{10}), 63.5 (C^5, C^7).

5-Butyl-7-hexyl-1,3-dehydroadamantane (1l)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5-butyl-7-hexyladamantane (**2l**; 4.47 g, 10.3 mmol) to yield **1l** (1.52 g, 5.55 mmol, 54%) as a colorless oil.

Marking of the butyl and hexyl groups : $C^dH_2C^cH_2C^bH_2C^aH_3$; $C^eH_2C^fH_2C^gH_2C^hH_2C^iH_2C^jH_3$.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.89–0.93 (m, 6 H, C^aH_3, C^jH_3), 1.04–1.14 (m, 4 H, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.20–1.35 (m, 16 H, C^bH_2, C^cH_2, C^dH_2, C^eH_2, C^fH_2, C^gH_2, C^hH_2, C^iH_2), 1.60 (s, 2 H, C^6H_2), 1.66–1.70 (m, 4 H, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$), 1.95 (s, 2 H, C^2H_2).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.5 (C^a, C^j), 23.2, 24.2, 25.7, and 27.9 (C^b, C^g, C^h, C^i), 31.0 and 32.4 (C^c, C^f), 34.8 (C^1, C^3), 37.6 and 37.9 (C^d, C^e), 46.6 (C^2), 47.9 (C^6), 49.2 (C^4, C^8, C^9, C^{10}), 63.6 (C^5, C^7).

5-Butyl-7-phenyl-1,3-dehydroadamantane (1m)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5-butyl-7-phenyladamantane (**2m**; 6.44 g, 15.1 mmol) to yield **1m** (830 mg, 3.12 mmol, 21%) as a colorless oil.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.87–0.91 (t, *J* = 6.7 Hz, 3 H, C^aH_3), 1.06–1.10 (d, *J* = 10 Hz, 2 H, one of C^4H_2, one of C^9H_2), 1.18–1.24 (m, 6 H, C^bH_2, C^cH_2, C^dH_2), 1.40–1.44 (d, *J* = 10 Hz, 2 H, one of C^8H_2, one of $C^{10}H_2$), 1.71 (m, 2 H, one of C^4H_2, one of C^9H_2), 1.86 (s, 2 H, C^6H_2), 1.94 (s, 2 H, C^2H_2), 2.16 (m, 2 H, one of C^8H_2, one of $C^{10}H_2$), 7.10–7.20 (m, 5 H, C_6H_5).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.4 (C^a), 24.1 (C^b), 27.8 (C^c), 34.3 (C^1, C^3), 37.4 (C^d), 46.4 (C^2), 48.8 (C^4, C^9), 49.3 (C^8, C^{10}), 50.4 (C^6), 63.9 (C^5), 66.7 (C^7), 126.2 (C_m), 126.7 (C_p) 128.4 (C_o) 146.8 (C_i).

5-Butyl-7-methoxy-1,3-dehydroadamantane (1n)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5-butyl-7-methoxyadamantane (**2n**; 6.51 g, 17.1 mmol) to yield **1n** (2.26 g, 10.3 mmol, 60%) as a colorless oil.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.85–0.94 (m, 5 H, C^aH_3, one of C^8H_2, and one of $C^{10}H_2$), 1.12–1.24 (m, 6 H, C^bH_2, C^cH_2, C^dH_2), 1.36–1.39 (d, *J* = 10 Hz, one of C^4H_2, one of C^9H_2), 1.51–1.57 (m, 3 H, one of C^2H_2, one of C^8H_2, one of $C^{10}H_2$) 1.73–1.86 (m, 5 H, one of C^2H_2, C^6H_2, one of C^4H_2, one of C^9H_2), 3.14 (s, 3 H, OCH_3).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.4 (C^a), 24.1 (C^b), 27.9 (C^c), 28.9 (C^1, C^3), 36.6 (C^d), 42.7 (C^2), 45.3 (C^8, C^{10}), 46.7 (C^6), 48.3 (C^4, C^9), 51.2 (OCH_3), 63.9 (C^5), 91.2 (C^7).

5-Butoxy-7-butyl-1,3-dehydroadamantane (1o)
The reaction was performed following typical procedure A, starting from 1,3-dibromo-5-butoxy-7-butyladamantane (**2o**; 2.33 g, 5.52 mmol) to yield **1o** (904 mg, 3.45 mmol, 62%) as a colorless oil.

Marking of the butyl and butoxy groups: $C^dH_2C^cH_2C^bH_2C^aH_3$; $OC^hH_2C^gH_2C^fH_2C^eH_3$.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.87–0.95 (m, 8 H, C^aH_3, C^eH_3, one of C^8H_2, one of $C^{10}H_2$), 1.16–1.22 (m, 6 H, C^bH_2, C^cH_2, C^dH_2), 1.36–1.59 (m, 9 H, one of C^2H_2, one of C^4H_2, one of C^8H_2, one of C^9H_2, one of $C^{10}H_2$, C^fH_2, C^gH_2), 1.74–1.77 (m, 1 H, one of C^2H_2), 1.83–1.86 (m, 4 H, C^6H_2, one of C^4H_2, one of C^9H_2), 3.31–3.35 (t, *J* = 6.3 Hz, 2 H, C^hH_2).

^{13}C NMR (75 MHz, C_6D_6): δ = 14.3 (C^e), 14.4 (C^a), 19.9 (C^f), 24.1 (C^b), 28.0 (C^c), 29.1 (C^1, C^3), 33.2 (C^g), 36.7 (C^d), 42.7 (C^2), 46.0 (C^4, C^9), 47.1 (C^6), 48.4 (C^8, C^{10}), 63.1 (C^h), 64.0 (C^5), 90.9 (C^7).

Preparation of 1a and 1h in Tetraglyme; 1,3-Dehydroadamantane (1a); Typical Procedure B
A mixture of 1,3-dibromoadamantane (**2a**; 9.96 g, 39.1 mmol) and Li (1.20 g, 173 mmol) in anhydrous tetraglyme (80 mL) was reacted at 60 °C for 3 days under argon. Complete consumption of **2a** was confirmed by GLC. The resulting suspension was transferred into a round-bottomed flask equipped with a break-seal and then sealed off under high vacuum conditions. Vacuum distillations in the all-glass apparatus gave **1a** as a white solid (2.41 g, 18.0 mmol, 46%). The resulting DHAs were diluted with CH_2Cl_2 or *n*-heptane and used for the cationic polymerization.

^{1}H NMR (300 MHz, C_6D_6): δ = 1.26–1.30 (d, *J* = 11 Hz, 4 H, C^4H_2, C^8H_2, C^9H_2, $C^{10}H_2$), 1.84 (br s, 2 H, C^6H_2), 2.02–2.06 (d, *J* = 11 Hz, 4 H, C^4H_2, C^8H_2, C^9H_2, $C^{10}H_2$), 2.19 (s, 2 H, C^2H_2), 2.90 (br s, 2 H, C^5H, C^7H).

^{13}C NMR (75 MHz, C_6D_6): δ = 37.8 (C^1, C^3), 38.1 (C^6), 46.6 (C^4, C^8, C^9, C^{10}), 50.1 (C^2), 55.0 (C^5, C^7).

5,7-Dimethyl-1,3-dehydroadamantane (1h)
The reaction was performed following typical procedure B, starting from 1,3-dibromo-5,7-dimethyladamantane (**2h**; 11.6 g, 35.9 mmol) to yield **1h** (3.90 g, 24.1 mmol, 67%) as a white solid.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.90 (s, 6 H, CH_3), 0.99–1.02 (d, *J* = 10 Hz, 4 H, C^4H_2, C^8H_2, C^9H_2, $C^{10}H_2$), 1.47 (br s, 2 H, C^6H_2), 1.57–1.61 (d, *J* = 10 Hz, 4 H, C^4H_2, C^8H_2, C^9H_2, $C^{10}H_2$), 1.91 (s, 2 H, C^2H_2).

^{13}C NMR (75 MHz, C_6D_6): δ = 22.6 (CH_3), 36.5 (C^1, C^3), 46.4 (C^2), 50.9 (C^4, C^8, C^9, C^{10}), 52.1 (C^6), 59.6 (C^5, C^7).

Preparation of 1,3-Dehydroadamantane (1a) in THF; Typical Procedure C
A mixture of **2a** (17.1 g, 68.5 mmol) and Li (1.70 g, 245 mmol) in anhydrous THF (50 mL) was reacted at r.t. for 24 h under argon. The resulting suspension was transferred into a round-bottomed flask equipped with a break-seal and then sealed off under high vacuum conditions. Repeating vacuum distillations in the all-glass apparatus gave **1a** as a white solid (7.45 g, 55.5 mmol, 81%). Then, **1a** was diluted with THF (40 mL) and stored in an ampoule equipped with a break-seal at –30 °C. The resulting THF solution of **1a** was used for the copolymerization reaction with acrylonitrile or methyl acrylate.[13]

5,7-Dimethyl-1,3-dehydroadamantane (1h)
Similarly following typical procedure C, **1h** was obtained in 86% (4.15 g, 25.6 mmol) yield by the reaction of **2h** (9.60 g, 29.8 mmol) and Li (1.50 g, 217 mmol) in THF (55 mL).

Synthesis of 1b Using Magnesium
A mixture of **2b** (2.75 g, 7.86 mmol) and Mg (0.71 g, 29.6 mmol) in anhydrous THF (28 mL) was refluxed for 24 h under argon. Then, the resulting black solution was transferred into a distillation flask to remove residual Mg by vacuum distillation to give **1b** (0.75 g, 3.92 mmol, 50%) as a colorless oil. The distilled products contained 7% of reduced 1-butyladamantane along with **1b**.

Reaction of 1b with Oxygen in the Bulk
Liquid of **1b** (0.70 g, 3.66 mmol) was stirred in the air in the bulk at r.t. After 24 h, the resulting viscous liquid was diluted with THF (5 mL) and poured into MeOH (100 mL) to afford white powdery solid (0.38 g, 54%). The resulting powder was identified as an alternating copolymer of **1b** with oxygen, poly(**1b**-*alt*-O_2), by ^{1}H and ^{13}C NMR measurements.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (br s, 3 H, C^aH_3), 1.21 (br s, 6 H, C^bH_2, C^cH_2, C^dH_2), 1.27 (br s, 2 H, C^6H_2), 1.41–1.50 (br m, 4 H, C^4H_2, C^9H_2), 1.59–1.72 (br m, 4 H, C^8H_2, $C^{10}H_2$), 1.78–1.85 (br m, 2 H, C^2H_2), 2.31 (br s, 1 H, C^7H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (C^a), 23.5 (C^b), 25.2 (C^c), 30.5 (C^7), 37.2 (C^5), 39.4 (C^8, C^{10}), 40.7 (C^6), 42.9 (C^d), 43.4 (C^2), 44.6 (C^4, C^9).

The resulting polymer possessed M_n = 6000 g/mol and M_w/M_n = 2.60, measured by size exclusion chromatography in THF calibrated with polystyrene standards.

Reaction of Poly(1b-*alt*-O_2) with $LiAlH_4$
Poly(**1b**-*alt*-O_2) [0.12 g, 0.54 mmol (number of repeating units)] was treated with $LiAlH_4$ (2.18 g, 57.4 mmol) in THF (20 mL) at reflux for 72 h. After quenching with *i*-PrOH (2 mL), MeOH (2 mL), H_2O (5 mL), and aq HCl (10 mL), the resulting mixture was extracted with $CHCl_3$ (4 × 30 mL), and the combined organic layers were dried ($MgSO_4$). After removal of the solvent in vacuo, the major product (0.14 g, quant) was identified as 1-butyl-3,5-dihydroxyadamantane; viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86–0.91 (t, *J* = 6.4 Hz, 3 H, C^aH_3), 1.22 (br s, 6 H, C^bH_2, C^cH_2, C^dH_2), 1.28 (m, 2 H, C^6H_2), 1.40 (s, 4 H, C^4H_2, C^9H_2), 1.53–1.64 (2 d, *J* = 12.2 Hz, 4 H, C^8H_2, $C^{10}H_2$), 1.69 (s, 2 H, C^2H_2), 2.30 (m, 1 H, C^7H), 2.66 (br s, 2 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (C^a), 23.5 (C^b), 25.2 (C^c), 30.9 (C^7), 37.7 (C^1), 39.9 (C^8), 42.4 (C^d), 43.5 (C^6, C^{10}), 48.9 (C^2, C^9), 52.4 (C^4), 70.9 (C^3, C^5).

Reaction of 1a with MeOH in the Presence of MsOH
A methanolic solution of MsOH (0.145 M, 0.145 mmol, 1 mL) was added to a solution of **1a** (372 mg, 2.77 mmol) in CH_2Cl_2 (4.5 mL) and then the mixture was stirred at r.t. under N_2 atmosphere for 3.5 h. After removal of solvent in vacuo, 1-methoxyadamantane (383 mg, 2.31 mmol, 83%, bp 37–39 °C/4.0 mmHg) was obtained as a colorless oil.

IR (film): 2903, 2850, 1451, 1354, 1177, 1115, 1089, 1051, 893 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53–1.66 (m, 6 H, C^4H_2), 1.71 (s, 6 H, C^2H_2), 2.13 (s, 3 H, C^3H), 3.21 (s, 3 H, OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.6 (C^3), 36.6 (C^4), 41.1 (C^2), 47.9 (OCH_3), 72.0 (C^1).

Reaction of 1b with MeOH in the Absence of Acid

A mixture of **1b** (190 mg, 1.0 mmol), CH_2Cl_2 (1.6 mL), and MeOH (1.0 mL) was stirred at r.t. under argon. The substrate **1b** was slowly consumed, and 1-butyl-3-methoxyadamantane was newly formed in the mixture. The conversion of **1b** was monitored by NMR and GLC measurements as 8, 48, 85, and, 100% after 10 min, 1.5 h, 6 h, and 30 h, respectively. Finally, 1-butyl-3-methoxyadamantane was obtained as the only product after 30 h.[15]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, C^aH_3), 1.13–1.25 (m, 6 H, C^bH_2, C^cH_2, C^dH_2), 1.37 (br s, 4 H, C^8H_2, C^9H_2), 1.43 (s, 2 H, C^6H_2), 1.53 (br s, 2 H, C^2H_2), 1.64–1.68 (m, 4 H, C^4H_2, $C^{10}H_2$), 2.18 (br s, 2 H, C^5H, C^7H), 3.22 (s, 3 H, OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (C^a), 23.7 (C^b), 25.1 (C^c), 30.7 (C^5, C^7), 35.8 (C^1), 36.3 (C^6), 40.7 (C^8, C^9), 41.6 (C^4, C^{10}), 43.8 (C^2), 45.9 (C^d), 48.0 (OCH_3), 73.0 (C^3).

Reaction of 1b with AcOH

AcOH (1 mL, 17.5 mmol) was added to a solution of **1b** (698 mg, 3.67 mmol) in CH_2Cl_2 (7.7 mL) and stirred for 5 min under N_2. After removal of solvent in vacuo, 1-acetoxy-3-butyladamantane (910 mg, 99%) was obtained as a colorless oil.

IR (film): 2960, 2855, 1731, 1455, 1365, 1238, 1139, 1024, 864, 606 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86–0.90 (t, *J* = 6.6 Hz, 3 H, C^aH_3), 1.12–1.54 (m, 12 H, C^bH_2, C^cH_2, C^dH_2, C^4H_2, C^6H_2, $C^{10}H_2$), 1.81 (s, 2 H, C^2H_2), 1.96 (s, 3 H, $COCH_3$), 2.01–2.09 (m, 4 H, C^8H_2, C^9H_2), 2.18–2.19 (br s, 2 H, C^5H, C^7H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (C^a), 22.8 ($COCH_3$), 23.6 (C^b), 24.9 (C^c), 30.9 (C^5, C^7), 35.9 (C^6), 36.2 (C^3), 40.9 (C^8, C^9), 41.2 (C^4, C^{10}), 43.4 (C^d), 45.9 (C^2), 81.3 (C^1), 170.4 (C=O).

HRMS (ESI-TOF): *m*/*z* calcd for $C_{16}H_{26}O_2$ + Na $[M + Na]^+$: 273.1825; found: 273.1820.

Reaction of 1a with AcOH in THF

AcOH (0.83 mL, 13.2 mmol) was added to a solution of **1a** (379 mg, 2.83 mmol) in THF (9.0 mL) and stirred for 15 min under argon. After removal of solvent in vacuo, a mixture (760 mg) of 1-acetoxyadamantane (~22%) and 1-(4-acetoxybutoxy)adamantane (~78%) was obtained as a viscous liquid. Column chromatography (SiO_2; hexane–EtOAc, 9:1) of the mixture gave 1-acetoxyadamantane (119 mg, 0.613 mmol, 22%, colorless oil) and 1-(4-acetoxybutoxy)adamantane (496 mg, 1.86 mmol, 66%, colorless oil), respectively.

Selected data for 1-(4-acetoxybutoxy)adamantane:

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48–1.70 (m, 9 H, C^3H, C^4H_2, C^5H, C^6H_2, C^7H, $C^{10}H_2$), 1.70–1.81 (m, 6 H, C^2H_2, C^8H_2, C^9H_2), 2.01–2.09 (s, 3 H, C^aH_3), 2.09–2.11 (br, 4 H, C^dH_2, C^eH_2), 3.87–3.48 (t, *J* = 6.3 Hz, 2 H, C^fH_2), 4.02–4.13 (t, *J* = 6.6 Hz, 2 H, C^cH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (C^a), 25.7 (C^e), 27.1 (C^d), 30.6 (C^3, C^5, C^7), 36.6 (C^4, C^6, C^{10}), 41.7 (C^2, C^8, C^9), 59.2 (C^f), 64.6 (C^c), 71.9 (C^1), 171.3 (C^b).

HRMS (ESI-TOF): *m*/*z* calcd for $C_{16}H_{26}O_3$ + Na $[M + Na]^+$: 289.1780; found: 289.1778.

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