7 shows the adsorbance results determined by LSC. The adsorbance decreases with increasing propylene sulfide block size. This is consistent with an adsorption in which the propylene sulfide block (the "sticky" part of the copolymer) strongly adheres and covers up the gold surface: The longer the propylene sulfide block, the fewer chains adsorb. This configuration was suggested[9] for styrene–2-vinylpyridine copolymers adsorbed on mica.

Conclusions

Polystyrene containing a terminal thiol group (PS_X-SH (M_n = 1000–200 000) adsorbs to gold under conditions that polystyrene does not. At higher molecular weight (M_n = 500 000) adsorption does not occur. Film thickness varies with molecular weight, concentration, and solvent property in a fashion similar to the way polystyrene film thickness varies when unmodified polystyrene adsorbs from a poor solvent. Styrene–propylene sulfide block copolymer (PS_A–PPS_B) samples adsorb to gold, and the thickness of the adsorbed polymer layer can be controlled by the length of the propylene sulfide block.

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Registry No. (S)(PS) (block copolymer), 113568-91-5; Au, 7440-57-5.

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Poly([1.1.1]propellane).[1] A Novel Rigid-Rod Polymer Obtained by Ring-Opening Polymerization Breaking a Carbon–Carbon σ-Bond

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ABSTRACT: Treatment of the [1.1.1]propellane **1** with lithium organic initiators such as *tert*-butyllithium and phenyllithium leads to anionically induced ring-opening polymerization of **1**. In the course of the polymerization only the central σ-bond in monomer **1** was opened, leading to an entirely new rigid-rod structure—the poly([1.1.1]propellane) **2**, whose degree of polymerization was determined to be greater than 20. The rigidity of polymer **2** is due to constraints inherently associated with its multicyclic structure. The structure of the poly([1.1.1]propellane) **2** was proved by means of solid-state NMR spectroscopy and was further confirmed by an investigation of soluble, oligomeric material having analogous constitution.

In the late sixties the first report of a ring-opening polymerization involving the central bond of a bicyclobutane derivative appeared in the patent literature.[2] In the following years this singular observation of breaking carbon–carbon σ-bonds in polymerization reactions has been developed to a fruitful field of research mainly by Hall and his co-workers.[3] They showed that, for several bicyclic systems, efficient polymerization occurs only if the strain in the monomer is sufficient to activate the bond in question. In the past few years small-ring propellanes have been established as a new class of highly strained organic molecules.[4] The most intriguing feature of their structures is bridgehead carbon atoms exhibiting "inverted geometry"[5] of the four substituents. This rather unusual bonding situation in propellanes has drawn the attention of both theoreticians and experimentalists toward electron distribution in, and reactivity of, such species.[4,6] The reactivity is reflected in that the central bond, though being a σ-bond formally, is highly prone to radical attack.[4,7] The question arises whether the reactivity of the central bond in small-ring propellanes is high enough to be utilized in ring-opening polymerization reactions. Such a polymerization would result in the formation of a new type of rigid polymer **2**, which is structurally completely different from

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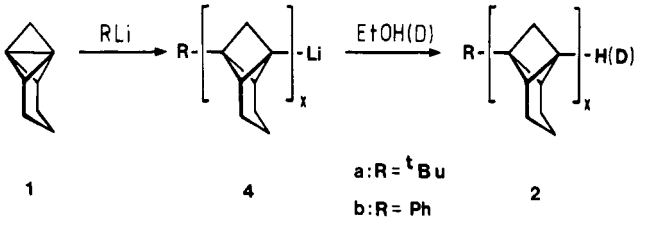
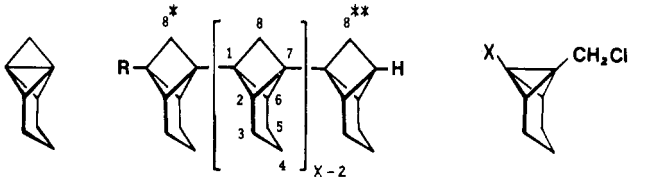
Scheme I



the well-established rigid-chain aromatic polyesters and polyamides.[8] These polymers are rigid due to mesomerically hindered rotation of the ester or amide function, whereas polymer **2** would be a rigid rod per se.



Polymerization of [n.1.1]propellanes ($n > 1$) has been occasionally reported and has been rationalized in terms of a radical reaction;[9] however, to the best of our knowledge, no thorough investigation of the synthesis of a polypropellane nor elucidation of its structure has been published previously.[10] We now report the first anionically induced polymerization of the [1.1.1]propellane **1**[11] leading to formation of the entirely new rigid-rod polymer **2**. We also present a determination of the polymer constitution, especially addressing the questions of whether or not the polymerization of **1** proceeds exclusively by breaking of the central bond and the degree of polymerization (DP) attained in **2**. Some insights into the polymerization mechanism are also provided.

Results and Discussion

The first efficient synthesis of a small-ring propellane was published by Szeimies and co-workers in 1985.[11] The final step of their sequence involves bromolithium exchange from **3a** to **3b**, followed by an intramolecular nucleophilic displacement of the chlorine atom. We have improved Szeimies' synthesis of **1** and are now able to produce compound **3a** in 70-g batches in an overall yield of 32–50% from tricyclo[4.1.0.$0^{2,7}$]heptane.[12] The conversion of **3a** to **1** takes place in a yield of 50–70%, as reported.

We have investigated the reactivity of **1** toward lithium organic compounds such as *tert*-butyllithium and phenyllithium. In fact, monomer **1** reacts violently with 0.15 equiv of lithium organic initiator in hydrocarbon solvents at room temperature with precipitation of a white powdery solid, to which we ascribe the structure **4** (Scheme I; see Experimental Section). After having quenched the reaction mixture with ethanol, the recovered solid material was washed thoroughly to remove both oligomeric material and inorganic residues and was dried to constant weight in high vacuum (10^{-6} mmHg) at 100 °C. The total mass recovery of insoluble and soluble material (ca. 1:1) was greater than 95%, based on the amount of monomer and initiator used. Our main objective was to investigate the polymer structure. The ^{13}C CPMAS NMR spectrum of phenyllithium initiated polymer **2b** is shown in Figure 1a. The spectrum reveals the expected set of five lines between 20 and 60 ppm and one signal of low intensity at 128 ppm. Parts b–d of Figure 1 show a series of special pulse sequences, which

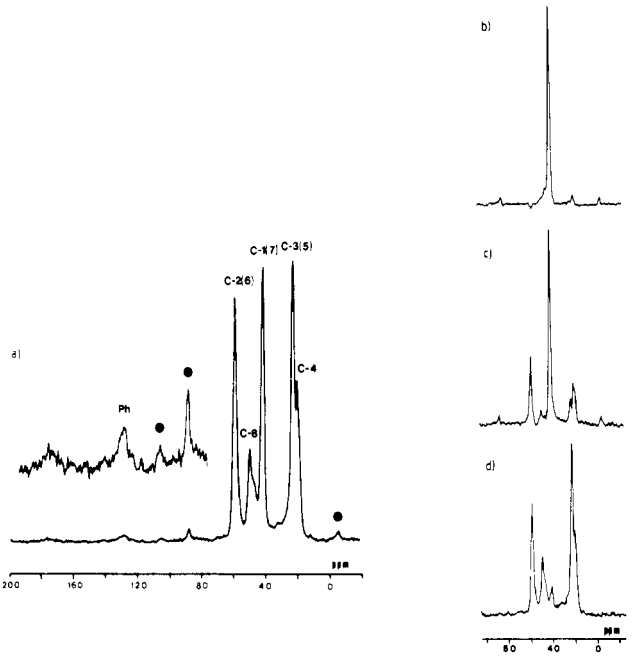


Figure 1. ^{13}C CPMAS NMR of polymer **2b** (spinning frequency 3.516 kHz): (a) full spectrum with a blowup of the downfield part, the spinning side bands being marked (●) (cross-polarization (cp) time 3 ms) (the signal at ca. 175 ppm could not be assigned yet); (b) all hydrogen bearing carbons are suppressed (gated decoupling); (c) quarternary carbons, and those attached to one hydrogen atom only, are favored (gated decoupling); (d) all quarternary carbons are suppressed (cp time 50 μs).

allow an unambiguous identification of carbon atoms depending on the number of hydrogens attached to them. In Figure 1b all hydrogen bearing carbons of polymer **2b** are suppressed; Figure 1d reveals just the opposite—all quarternary carbons are suppressed, and, finally, Figure 1c shows an intermediate state, favoring quarternary carbons and those bonded to one hydrogen only. On the basis of these experiments the carbon atoms of polymer **2b** are tentatively assigned as shown in Figure 1a. The signal at 128 ppm stems from the five tertiary carbons of the phenyl end group. We also recorded the solid-state NMR spectrum of polymer **2a**. This polymer had an identical spectrum except for the aromatic signal; no trace of olefinic carbons could be detected. This is good evidence that the signal of polymer **2b** at 128 ppm is actually caused by the aromatic end group and is also consistent with the hypothesis that only the central σ-bond breaks during the course of the polymerization. Almost all other ring-opening processes (either thermal or catalyzed by traces of transition metals) would result in the generation of vinylic carbons.

So far we have assigned the carbon spectra of the polymers **2a** and **2b** only on the basis of number of lines and connectivity of carbon to hydrogen atoms. The final structure proof was obtained by analyzing the ^{1}H and ^{13}C NMR spectra of the soluble, oligomeric material **2a** (x = 1, ..., 12). Though we did not succeed in completely separating the oligomers, neither on a preparative nor on an analytical scale, the monomeric **2a(x=1)**[11] and the dimeric compound **2a(x=2)** could be enriched up to about 90% by vacuum distillation. In addition a high oligomer fraction of **2a(x~11)** could be obtained by utilizing the decreasing solubility of the oligomers in THF with growing values of x.

The 300-MHz ^{1}H spectrum of dimer **2a(x=2)** is rather informative. The two repeat units give rise to well-separated sets of lines for the hydrogens attached to the respective bicyclopentane moieties. The hydrogens at pos-

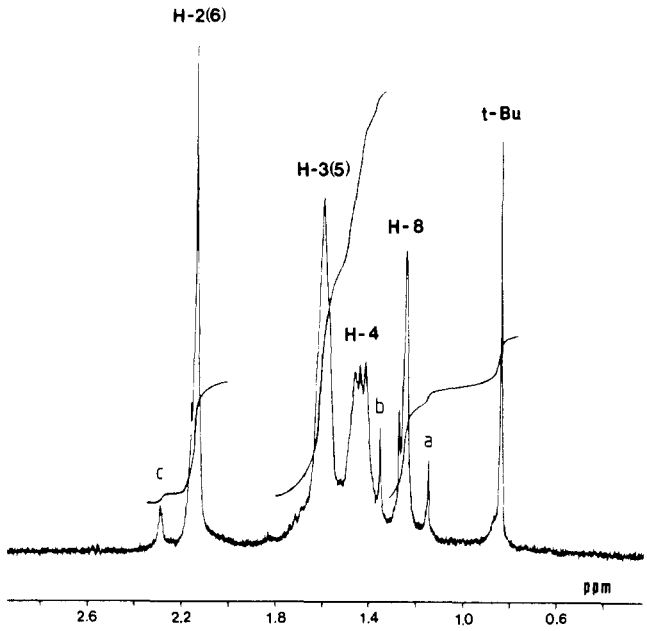


Figure 2. Integrated ^{1}H NMR spectrum of the oligomer **2a-(x~11)**. The signals marked with a, b, and c at 1.15, 1.35, and 2.29 ppm, respectively, are caused by hydrogens at the terminal repeat units and are assigned as follows: a, H-8* or H-8**; b, H-8** or H-8*; c, H-2*(6*) or H-2**(6**).

itions 2*(6*) and 2**(6**) appear as poorly resolved triplets at 2.19 and 2.29 ppm (or vice versa) and the hydrogens at position 8* and 8** as singlets at 1.18 and 1.37 ppm (or vice versa), respectively. Both the *tert*-butyl group at 0.85 ppm and the bridgehead hydrogen (position 7**) at 2.18 ppm appear as singlets. These ^{1}H NMR data are, as are all ^{13}C NMR data as well, in full agreement with those of the known monomeric species **2a(x=1)**[11] and therefore confirm the proposed structure of the dimer.

Figure 2 shows the proton spectrum of the oligomeric material **2a(x~11)**. On the one hand, this spectrum provides evidence for the structure of the oligomers, and, on the other hand, it allows an assessment of a lower limit of the DP. The signals in Figure 2 can easily be assigned, by analogy with the spectrum of dimer **2a(x=2)**. The five different groups of signals are exactly in the expected shift and intensity range. Of particular interest are the signals at 2.29, 1.35, and 1.15 ppm because they represent the hydrogen atoms of the two terminating repeat units. They are assigned as indicated in Figure 2. The ^{13}C NMR spectrum of this fraction of oligomers turned out to be a very interesting link to the solid-state NMR polymer **2**, in that it shows the same number of signals with identical or very similar chemical shifts (see Experimental Section). In addition to these signals one can find a resonance of low intensity caused by the *tert*-butyl end group. From these observations one can conclude that the oligomers **2a(x~11)** do have the same type of structure as the dimeric species and, even more important, as the insoluble polymer.

From the intensities of the *tert*-butyl end group at 0.85 ppm and the one of H-2*(6*) at 2.29 ppm the degree of oligomerization was calculated as x = 11–12. These oligomers are completely soluble in warm chloroform. Therefore, this value represents a lower threshold for the DP of the insoluble polymer **2a**. To get direct information on the DP of solid **2a** the lithiated precursor **4a** was analyzed for lithium by atomic absorption spectroscopy. A minimum,[13] average DP of 17 can be derived from this elemental analysis (Li, 0.38%). This analysis, the surprisingly high DP of soluble oligomeric material, and the rather low intensity of the phenyl end group in the ^{13}C CPMAS NMR spectrum of **2b** (see blowup in Figure 1a) provide sufficient justification for assuming that the DP of insoluble **2a** is higher than 20.

Finally some mechanistic studies that we undertook should be mentioned. The scheme shows the formation of oligomeric/polymeric species **4b**, being the typical product of an anionic initiated chain polymerization. It has not yet been proved possible to obtain an analysis of the distribution of quenched product **2a**, which would help to prove this mechanistic assumption. Hence, we looked for a different way to get insight into the reaction mechanism. With the assumption of an anionic mechanism, the species 4 ought to have two different termini: the *tert*-butyl or phenyl group on one and a lithium atom at the other end. This hypothesis could be verified for the oligomeric molecules. Monomer 1 was reacted with 2 equiv of *tert*-butyllithium at −20 °C, and the reaction mixture was quenched with deuteriomethanol (99% D). Predominantly compound **2a(x=1)** and some dimer **2a(x=2)** could be isolated in an overall yield of 59%. The ^{1}H NMR spectra of both compounds revealed that deuterium had been incorporated at the bridgehead positions, assumed to be the lithiated chain carriers, to more than 96%. Additional evidence for the anionic mechanism stems from the inspection of the proton NMR spectrum of compound **2a(x~11)** as depicted in Figure 2. One can see two different signals for the protons in positions 8* and 8**, respectively, which are in the proper integration ratio to the signal of the *tert*-butyl group. This observation justifies the assumption of two different end groups, necessary for the proposed mechanism.

Conclusion

This work presents the synthesis and structure elucidation of poly([1.1.1]propellane) **2**. It is shown that monomer 1 undergoes anionically induced ring-opening polymerization, breaking the central σ-bond in 1 only. The attainable DP in **2** is greater than 20. Polypropellane **2** represents an entirely novel type of rigid rod polymer, the rigidity of which is due to the connectivity in the molecule and not to mesomeric effects, as it is in polyesters and polyamides. The properties of **2** will be published in subsequent papers.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1430 spectrometer. ^{1}H NMR, ^{13}C NMR, and ^{13}C CPMAS NMR spectra were obtained on Bruker AC 300 (300 MHz) and MSL 300 (300 MHz) instruments. Chemical shifts are given downfield from internal (and external, respectively) tetramethylsilane. Abbreviations used for the NMR data are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were recorded on Varian MAT CH 7A mass spectrometer. *tert*-Butyllithium (1.4 m solution in pentane) and phenyllithium (2.0 m solution in benzene/ether, 70/30) were purchased from Fluka. Tricyclo[4.1.0.0^{2,7}]heptane was prepared on a 150-g scale, as described,[12] starting from cyclohexene. All solvents were kept under nitrogen over sodium/benzophenone and distilled as required. All manipulations with monomer 1 or with lithiated species were carried out either with use of high vacuum/Schlenk techniques or under the inert atmosphere of a high quality glovebox, in which the concentrations of oxygen and water were continuously monitored and proved to be less than 1 ppm. Due to the sensitivity of polymer **2** toward oxygen, it was usually stored under nitrogen.

Improvement of the Synthesis of 3a. The synthesis of **3a** was reported on the gram scale only, giving material of low purity in an overall yield of 25–37%.[11] The reaction can be scaled up at each steps, the time demand can be decreased by a factor of 2, and the yield can be improved to 32–50% (the figures refer to materials of comparable purity), by avoiding distillation wherever possible. A short description of the improved procedure

is as follows. To a solution of tricyclo[4.1.0.0^{2,7}]heptane (94 g, 1 mol) in 200 mL of diethyl ether at room temperature was added *n*-butyllithium (BuLi) (64 g, 1 mol) dissolved in 100 mL of ether. After the solution was stirred for 2 days, paraformaldehyde (30 g, 1 mol) was added in small portions. The mixture was allowed to stand for 3 h, followed by the addition of another portion of BuLi (64 g, 1 mol) in 250 mL of ether. This mixture was stirred for 10 h at room temperature, before solid tosyl bromide (230 g, 1 mol) was added slowly. After the solution was stirred for 1 h, aqueous workup yielded a yellow, oily residue which was dissolved in 1200 mL of carbon tetrachloride. Triphenylphosphine (320 g, 1.2 mol) was added and the solution refluxed for 2 h. After the solvent had been removed, the material was taken up in 600 mL of low boiling petroleum ether (40/60), cooled to −78 °C, and filtered under suction to remove the triphenylphosphine oxide. A short-path distillation under high vacuum (10^{-6} mmHg) yielded 110 g (50%) of crude product which was then fractionated through a 20-cm Vigreux column. The fraction at 42–45 °C (10^{-6} mmMg) contained 70 g (32%) of colorless, almost pure product **3a**.

1*-*tert*-Butyl-poly(tetracyclo[5.1.0.0^{1,6}.0^{2,7}]octane) (2a) and Oligomeric 2a(x∼11). To a stirred solution of 1 (0.50 g, 4.7 mmol) in 3 mL of hexane was added dropwise 0.50 mL of a 1.4 m solution of *t*-BuLi in pentane (0.70 mmol) over a period of 25 min. The color of the solution turned slightly yellow, and the white powdery **4a** started to precipitate. After being stirred for additional 15 min, the mixture was quenched with 2 mL of deoxygenated ethanol and filtered under suction. The remaining solid was thoroughly washed with hot water, methanol, and warm chloroform and, finally, dried under high vacuum (10^{-6} mmHg) at 100 °C. White, powdery polymeric **2a**: yield 269 mg (50%); IR (KBr) 2960–2840 (s), 1460 (m), 1440 (m), 1372 (w), 1351 (w), 1321 (m), 1310 (w), 1270 (m), 1190 (s), 1140 (w), 1040 (w) cm^{-1}; ^{13}C CPMAS NMR (KBr) δ 20 (C-4), 23 (C-3, C-5), 28 (CH_3, very weak), 41 (C-1, C-7), 49 (C-8), 58.5 (C-2, C-6). From the filtrate of polymer **2a** oligomeric material was extracted with chloroform. This solution was dried over magnesium sulfate, and the solvent was evaporated in vacuo at room temperature. The remaining residue of oligomeric **2a** (247 mg, 46%) partially dissolved in THF at room temperature. The insoluble part (7 mg) contained oligomer **2a(x∼11)** and was dried under high vacuum (10^{-6} mmHg) at 20 °C: ^{1}H NMR ($CDCl_3$, 50 °C) δ 0.84 (s, CH_3), 1.15 (s, H-8** or H-8*), 1.24 and 1.27 (s, H-8), 1.35 (s, H-8* or H-8**), 1.43 (m, H-4, H-4*, H-4**), 1.59 (m, H-3(5), H-3*(5*), H-3**(5**)), 2.16 (unresolved t, H-2(6), H-2*(6*), or H-2**(6**)), 2.29 (unresolved t, H-2**(6**) or H-2*(6*)); ^{13}C NMR ($CDCl_3$, 50 °C) δ 17.92 (t, C-4), 22.56 (t, C-3, C-5), 27.76 (q, CH_3), 41.12 (s, C-1, C-7), 47.30 (t, C-8), 57.75 (d, C-2, C-6).

1*-*tert*-Butyl-7-lithio-poly(tetracyclo[5.1.0.0^{1,6}.0^{2,7}]octane) (4a).** This compound was prepared as described above. The white powder of **4a** was washed with two portions of pentane, 10-mL each, and dried in high vacuum (10^{-6} mmHg) at 40 °C. Anal. Calcd for $(CH_3)_3C(C_8H_{10})_{17}Li$: C, 90.20; H, 9.65; Li, 0.37. Found: C, 88.08; H, 10.10; Li, 0.38; O 1.06.

1*-Phenyl-poly(tetracyclo[5.1.0.0^{1,6}.0^{2,7}]octane) (2b). Compound **2b** was prepared similar to polymer **2a**. The solvent of 0.7 mL of a 2.0 m solution of phenyllithium in benzene/ether, 70/30 (1.4 mmol), was removed in vacuo and replaced by 0.1 mL of ether. To this stirred solution was added 1 g (9.4 mmol) of neat monomer 1. This mixture was allowed to stand for 5 h at room temperature, before it was quenched with 2 mL of deoxygenated ethanol. Subsequent workup followed the procedure described for polymer **2a**. **2b**: yield 338 mg (34%); ^{13}C CPMAS NMR (KBr) δ 20 (C-4), 23 (C-3, C-5), 41 (C-1, C-7), 49 (C-8), 58.5 (C-2, C-6), 128 (Ph, very weak). Anal. Calcd for $(C_8H_{10})_x$: C, 90.50; H, 9.49. Found: C, 89.42; H, 9.41. The oligomeric material obtainable from the washing layers was not investigated.

Low Oligomers 2a(x=1,2). To a well-stirred solution of monomer 1 (1 g, 9.4 mmol) in 10 mL of ether was added 12.8 mL of a 1.4 m solution of *t*-BuLi in pentane (17.9 mmol) at −20 °C. The cooling bath was removed and the mixture allowed to warm up to 0 °C in 30 min. Then 2 mL of ethanol was added. Aqueous workup yielded 940 mg of raw material, which was distilled by using a short-path distillation apparatus under vacuum (10^{-2} mmHg). Compound **2a(x=1)**[11] distilled as the first fraction at 20 °C (bath); yield 660 mg (43%). Almost pure dimer **2a(x=2)** distilled as the second fraction at 50 °C (bath): yield 200 mg (16%); ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 9 H, CH_3), 1.17 (s, 2 H, H-8* or H-8**), 1.36 (s, 2 H, H-8** or H-8*), 1,40–1.80 (m, 12 H, H-3*(5*), H-3**(5**), H-4*, H-4**), 2.18 (m, 3 H, H-7**, H-2*(6*)); ^{13}C NMR δ 16.13 (t, C-4* or C-4**), 18.80 (t, C-4** or C-4*), 21.07 (t, C-3*(5*) or (C-3**(5**)), 22.51 (t, C-3**(5**) or C-3*(5*), 27.77 (q, CH_3), 31.41 (s, CCH_3), 31.56 (d, C-7**), 38.65 (s), 44.62 (t, C-8* or C-8**), 45.57 (t, C-8** or C-8*), 46.02 (s), 48.58 (s), 55.09 (d, C-2*(6*) or C-2**(6**)), 57.35 (d, C-2**(6**) or C-2*(6*)); mass spectrum, *m/e* (relative intensity) 255 ($M^+ - CH_3$, 2), 213 ($M^+ - C(CH_3)_3$), 39). A small amount (80 mg) of higher oligomers was obtained in the residue of the distillation.

Deuteriation of 4a(x=1,2). The experiment was carried out in the same way as the synthesis of **2a(x=1,2)**, except that deuterioethanol (99% D), instead of ethanol, was used to quench the lithiated species. The degree of deuteriation attained in species **2a(x=1)** and **2a(x=2)**, respectively, was determined by ^{1}H NMR integration. The intensity of the signal of compound **2a(x=1)** at 2.29 ppm (position 7*) and that of compound **2a(x=2)** at 2.18 ppm (position 7**) had decreased by about 96%. This experiment was repeated twice, giving degrees of deuteriation of 95 and 98%.

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Registry No. 1, 35634-10-7; 1 (homopolymer), 113451-95-9.

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(13) We assume that part of the initiator, *tert*-butyllithium, is involved in the formation of mixed aggregates with species **4a** of varying chain length. We also expect compound **4a** to contain a small amount of lithium hydroxide, due to partial hydrolysis of the initiator. Both these effects result in the dp calculated from percent lithium being a pessimistic estimate of the true dp.