A [1.1.1]Propellane with a Protected Functional Group in the Side Chain and Its Homopolymer

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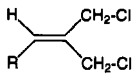
[1.1.1]Propellanes[1] represent a new class of highly reactive monomers. They polymerize regiospecifically with breaking of the central CC σ-bond furnishing homo- and copolymers with the rigid bicyclo[1.1.1]pentane fragment as part of the backbone.[2] To avoid problems due to the insolubility of unsubstituted homopolymers, monomers with flexible alkyl and methoxyalkyl chains were used. This caused the pentyl substituted homopolymer to turn into a soluble and processable material.[3]

The most efficient protocol for the synthesis of [1.1.1]-propellanes involves carbene additions and halogen/lithium exchange reactions.[4,5] The introduction of substituents other than alkyl or methoxyalkyl is therefore a somewhat tricky matter. In spite of this synthetic obstacle, it would be desirable to make rigid-rod polypropellanes available which have functional groups attached to the backbone. This way not only the solution and packing behavior could be modified as required but, alternatively, the functional groups could be used for chemical modifications aiming at, e.g., new types of polyelectrolytes or, by the attachment of dendritic fragments, cylindrically shaped dendritic structures.[6] In this paper we report on (a) the synthesis of a [1.1.1]propellane that carries an acetal protected hydroxy function with a short methylene spacer between the functional group and the strained hydrocarbon moiety, (b) its purification to polymerization grade monomer, and (c) its radically initiated homopolymerization to the corresponding structurally perfect and high-molecular weight poly([1.1.1]propellane).

Results and Discussion

Propellane **3**, which carries a methoxymethyl (MOM)-protected alcohol function, was selected as target monomer because MOM (a) ought to withstand the reaction conditions during synthesis as well as the polymerization, (b) does not increase the monomers' molecular weight much and, thus, does not make the purification of the sensitive[7] propellane (by distillation) difficult, and (c) should be easily cleaved off the polymer. It was synthesized from olefin **1** in analogy to the Szeimies route to propellanes.[4a,8] This olefin was obtained on the 50-g scale using Wittig chemistry with 1,3-dichloroacetone as the carbonyl compound. Dibromocarbene addition to **1** gave the cyclopropane derivative **2** from which monomer **3** was obtained by bromo/lithium exchange and nucleophilic displacement reactions as a colorless liquid on the 3-g scale. The purity of the material obtained was approximately 95% (by ^{1}H NMR). This was not acceptable because the impurities, which are mostly of an olefinic nature,[9] were at least partially incorporated into the backbone during polymerization. Further purification of gram quantities of this monomer was easily achieved by a rapid high-vacuum transfer (see Experimental Section) which afforded **3** in a purity exceeding 98%. The loss of material associated with this procedure only amounted to some 10–15%. The purity was determined by comparing the intensity of the ^{13}C-satellites of the $-OCH_2O-$ signal in the ^{1}H NMR spectrum of **3** with that of the impurities.[10] Monomer **3** was characterized by ^{1}H- and ^{13}C-NMR and IR spectroscopy. The spectra exhibit all the features typical for propellanes. Specifically informative are the chemical shift of the bridgehead carbons (δ = 5.4 ppm) and the IR stretch of the central propellane bond at 607 cm^{-1}. Monomer **3** is, like other substituted [1.1.1]-propellanes,[8] sensitive toward traces of electrophiles, but can be stored under exclusion of oxygen at –78 °C for months. At room temperature highly purified monomer slowly polymerizes spontaneously.



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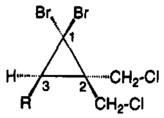

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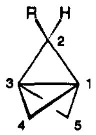

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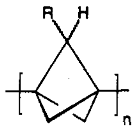

4

R = $-CH_2-CH_2-O-MOM$

In a typical polymerization, a mixture of 1 g of purified **3** and azoisobutyronitrile (AIBN) in a quartz ampule was irradiated with a high-pressure mercury lamp for 20 h. After 0.5–1 h the mixture had already solidified. Standard workup including lyophilization with benzene furnished 500–600 mg of polymer **4** (yield 50–60%). Both the ^{1}H- and the ^{13}C NMR spectra of **4** show no indication of structural irregularities (see supplementary material), which confirms that only the central bond breaks in the course of the polymerization. The methylene signal at δ = 44 ppm shows a splitting due to tacticity (atactic). The molecular weights are in the following ranges: $15\,000 < M_n < 20\,000$ ($100 < P_n < 130$); $45\,000 < M_w < 55\,000$ ($290 < P_w < 360$); $3 < D < 3.5$ (SEC in THF versus polystyrene, 20 °C). A fractionated sample with M_n = 17 000 and M_w = 38 000 (D = 2.2) has the Staudinger index [η_{inh}] = 0.48 dL/g in THF at 20 °C, a value which is in good agreement

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[2] Schlüter, A.-D.; Bothe, H.; Gosau, J.-M. *Makromol. Chem.* **1991**, *192*, 2497–2519.

[3] Opitz, K.; Schlüter, A.-D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 456. (b) Bothe, H.; Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 440.

[4] (a) Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410. (b) Belzner, J.; Bunz, U.; Semmler, K.; Szeimies, G.; Opitz, K.; Schlüter, A.-D. *Chem. Ber.* **1989**, *122*, 397.

[5] For the synthesis of the first [1.1.1]propellane see: Walker, F. H.; Wiberg, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 5239.

[6] Freudenberger, R.; Claussen, W.; Schlüter, A.-D.; Wallmeier, H. *Polymer*, in press.

[7] [1.1.1]Propellanes tend to decompose to olefinic compounds in normal glassware readily upon standing at room temperature (under nitrogen), presumably because of a sensitivity toward traces of electrophiles.

[8] Schlüter, A.-D.; Bothe, H. *Chem. Ber.* **1991**, *124*, 587.

[9] The nature of the impurities has partially been disclosed. See ref 8.

[10] We assume that each signal of an impurity resembles one proton.

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with other polypropellanes.[3] Polymer 4 forms transparent freely standing and flexible films from solution. The differential scanning calorimetry curve shows no phase transition up to 308 °C where exothermic decomposition occurs (heating rate 20 K/min, under nitrogen).

The thermogravimetric analysis (heating rate 10 K/min, under nitrogen) shows that there is almost no weight loss up to 280 °C (4.4 %). From 280 to 400 °C polymer 4 loses 30% of its mass and from 400 to 460 °C 37% of its mass. Its deprotection and the use of the deprotected polyalcohol in the synthesis of dendritic structures is reported elsewhere.[6] Polymer 4 is the first polypropellane carrying substituents amenable to further chemical modification.[11]

Experimental Section

General. All chemicals were purchased from Fluka or Aldrich and used without further purification. Diethyl ether and THF were distilled from sodium/benzophenone. Monomer 3 was handled under nitrogen and in glassware that had been rinsed with triethylamine before use.

1-Chloro-2-(chloromethyl)-5-[(methyloxy)methoxy-2-pentene (1). (a) Synthesis of the Ylide. A mixture of 3-bromo-1-propanol (146 g, 1.06 mol), dimethoxymethane (403 g, 5.3 mol), and P_4O_{10} (2.5 g) was stirred for 3 d and then treated with a saturated Na_2CO_3 solution. The layers were separated, the aqueous layer was washed with ether, and the combined organic layers were dried over $MgSO_4$. After removal of the solvent, vacuum distillation (0.1 mbar) yielded 148 g (77%) of MOM-protected 3-bromopropanol. This compound (96 g, 524 mmol) and triphenylphosphine (138 g; 526 mmol) were refluxed in *tert*-butyl methyl ether (100 mL) for approximately 7 d. The white percipitate that formed during this process was removed regularly by filtration. Yield of phosphonium bromide: 208 g (89%). **(b) Wittig Reaction.** To a solution of the phosphonium bromide (150 g, 338 mmol) in THF (450 mL) was slowly added 211 mL of a 1.6 N solution of methyllithium in ether. The resultant red mixture was stirred for 2 h and then cooled to −70 °C. A solution of dichloroacetone (43 g, 338 mmol) in THF (100 mL) was added so that the temperature did not exceed −60 °C. The mixture was then allowed to warm to room temperature and poured into n-hexane (300 mL). The precipitate was recovered by filtration. After removal of the solvent in vacuo, the crude product was chromatographed through silica (eluent: hexane). High-vacuum distillation yielded 50 g (70%) of colorless 1: bp 75 °C; ^{1}H-NMR ($CDCl_3$) δ 5.78 (t, 1H), 4.55 (s, 2 H), 4.19 (s, 2 H), 4.14 (s, 2 H), 3.53 (t, 2 H), 3.29 (s, 3 H), 2.40 (dt, 2 H); ^{13}C-NMR ($CDCl_3$) δ 134.2 (s), 132.4 (d), 96.2 (t), 66.0 (t), 55.1 (q), 47.1 (t), 38.8 (t), 28.4 (t).

1,1-Dibromo-2,2-bis(chloromethyl)-3-[[(methyloxy)methoxy]ethyl]cyclopropane (2). A mixture of 1 (60 g, 282 mmol), bromoform (150 g, 600 mmol), and hexane (200 mL) was cooled to −30 °C, and KO^{t}Bu was added so that the temperature remained below −15 °C. The mixture was allowed to slowly warm to room temperature. Standard workup afforded a yellowish oil which contained unreacted 1 and product 2 (^{1}H NMR). High vacuum distillation afforded 42 g of the starting material in the first fraction, which was used in subsequent carbene additions, and 25 g of 2 in the second fraction (bp 95–105 °C) (yield 23%) as a colorless, viscous oil: ^{1}H-NMR ($CDCl_3$) δ 4.63 (s, 2 H), 4.01–3.75 (m, 4 H), 3.64 (t, 2 H), 3.36 (s, 3 H), 1.84 (m, 3 H); ^{13}C-NMR ($CDCl_3$) δ 96.5 (t), 65.2 (q), 55.3 (t), 49.4 (t), 44.0 (t), 39.3 (s), 38.3 (d), 36.6 (s), 28.0 (t). Anal. Calcd for $C_9H_{14}Br_2Cl_2O_2$ (381.9): C, 28.28; H, 3.69. Found: C, 28.29; H, 3.40.

[[(Methyloxy)methoxy]ethyl][1.1.1]propellane (3). To a cooled, well-stirred solution (−78 °C) of 2 (21 g, 55 mmol) in diethyl ether (50 mL) was added 69 mL a 1.6 N solution of methyllithium in ether drop by drop. The resultant brownish-red mixture was allowed to warm to room temperature for 2 h, whereupon stirring was continued for another 2 h. Aqueous workup under nitrogen using deoxygenated water, after careful drying of the organic layer ($MgSO_4$) and removal of the solvent in vacuo, afforded a slightly yellowish oil. Two successive high vacuum, room temperature transfer cycles into cooled Schlenk tubes (−78 °C) gave 2.4–2.8 g of 3 as a colorless oil (yield 30%). ^{1}H-NMR (benzene-d_6) δ 4.43 (s, 2 H), 3.37 (t, 2 H), 3.13 (s, 3 H), 2.58 (dt,1 H), 2.46 (dd, 1 H), 1.92 (dd, 1 H), 1.57–1.46 (m, 4 H); ^{13}C-NMR (benzene-d_6) δ 96.5 (t), 87.6 (d), 72.0 (t), 69.5 (t), 67.4 (t), 54.9 (q), 25.3 (t), 5.4 (s); IR ν 607 cm^{-1}; EIMS *m/z* (rel intensity) 154 (M^+, 2.3), 139 ($M^+ - CH_3$, 5.1), 123 ($M^+ - OCH_3$, 8.7), 109 ($M^+ - CH_2OCH_3$, 13.1), 45 (100).

Poly[[[(methyloxy)methoxy]ethyl][1.1.1]propellane] (4). A quartz glass vessel with Rotaflo stopper was charged with propellane 3 (1.0 g, 6.5 mmol) and AIBN (4.2 mg, 0.4 mol %), cooled to 0 °C, and irradiated with a high-pressure mercury lamp (300 W) for 20 h. The resultant polymer 4 was dissolved in toluene, precipitated into methanol, recovered by filtration, and lyophilized with benzene: yield 0.58 g (58%); ^{1}H-NMR ($CDCl_3$) δ 4.59 (s, 2 H), 3.45 (t, 2 H), 3.33 (s, 3 H), 2.23–0.39 (m, 7 H); ^{13}C-NMR ($CDCl_3$) δ 96.2 (t), 67.8 (t), 57.3 (d), 55.1 (q), 48.5 (t), 44.2, 44.0, 43.6 (3t), 41.1 (s), 25.4 (t). Anal. Calcd for $C_9H_{14}O_2$ (154.10): C, 70.09; H, 9.16. Found: C, 69.01; H, 8.72

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Supplementary Material Available: ^{1}H- and ^{13}C-NMR spectra of 3 and 4 (4 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[11] Hamrock, S. J.; Michl, J. *J. Org. Chem.* **1992**, *57*, 5027.