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Regioselective Cyclopolymerization of 1,7-Octadiynes

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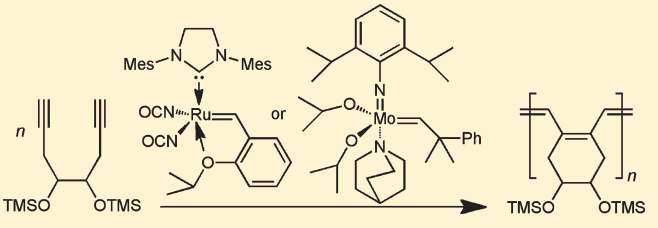
Supporting Information

ABSTRACT: The regioselective cyclopolymerization of two structurally different 1,7-octadiynes, i.e. of 1,4-dihexyloxy-2,3-dipropargylbenzene (**M1**) and (*R*,*R*)/(*S*,*S*)-4,5-bis(trimethylsilyloxy)-1,7-octadiyne (**M2**) has been achieved with the modified Grubbs-Hoveyda-type metathesis initiator $Ru(NCO)_2(IMesH_2)(=CH\text{-}(2\text{-}(2\text{-}PrO)C_6H_4))$ (**I1**, $IMesH_2$ = 1,3-dimesitylimidazolidin-2-ylidene) and with a series of Schrock initiators in the presence of quinuclidine, yielding conjugated polymers consisting virtually exclusively of 1,2-cyclohex-1-enylenvinylene units. In contrast to **I1**, $Mo(N\text{-}2,6\text{-}(2\text{-}Pr)_2C_6H_3)(CHCMe_2Ph)(OCHMe_2)_2$ (**I3**) allows for establishing a living polymerization with **M2** in the presence of quinuclidine. The structure of the polymers, which represent highly soluble and stable poly(acetylene) analogues, was confirmed by comparing the ^{13}C NMR shifts of model compounds with those of the corresponding polymer. Poly(ene)s that are virtually solely based on six-membered repeat units show a bathochromic shift in UV-absorption compared to poly(ene)s based on six- and seven-membered rings.



INTRODUCTION

Centered in the fields of conjugated materials and metathesis, cyclopolymerization has found considerable interest during the last years.[1−3] This is a direct consequence of the shortcomings of other conjugated polymers like poly(acetylene)s, which are either nonprocessable, unstable or display poor effective conjugation lengths.[4−8] The cyclopolymerization of 1,6-heptadiynes has first been accomplished with Ziegler−Natta catalysts, Pd- and Ni-initiators and binary or ternary Mo- and W-catalysts to yield soluble, conjugated poly(acetylene)-type polymers.[9−17] More recently, carefully designed Mo-based Schrock initiators and appropriate reaction conditions allowed for the regioselective and stereoselective cyclopolymerization of various 1,6-heptadiynes to yield polymers consisting exclusively of either cyclopent-1-enylene-1-vinylene- or cyclohex-1-ene-3-methylidenes based repeat units.[18−20] Complementary, modified Grubbs- and Grubbs-Hoveyda catalysts allowed for the regioselective cyclopolymerization of 1,6-heptadiynes to yield poly(ene)s that are exclusively based on five-membered repeat units, i.e., cyclopent-1-enylene-1-vinylenes.[21,22] With these Ru-based initiators, the polarization and thus activation of the ruthenium-carbene by strongly electron withdrawing ligands and electron-rich *N*-heterocyclic carbenes (NHCs) is a prerequisite to render this type of initiator suitable for cyclopolymerization while maintaining high selectivity. Generally, the key to any selective formation of a certain repeat unit is selectivity in α- or β-addition, which in turn depends on the steric demand and electronic situation in both the initiator and the monomer.

Scheme 1 illustrates the changes when moving from 1,6-heptadiynes to 1,7-octadiynes. Thus, with 1,7-octadiynes, α- or β-addition will deliver either six- or seven-membered repeat units instead of five- or six-membered ones. Clearly, the six-membered repeat units resulting from the α-addition of 1,7-octadiynes are thermodynamically favored. We were interested, whether the concept of regioselective cyclopolymerization with modified Grubbs-Hoveyda and with Schrock-type initiators could be extended to 1,7-octadiynes, the more since α-insertion-derived poly(1,7-octadiynes) could serve as soluble progenitors to poly(o-phenylenevinylene)s, which are accessible from the corresponding poly(1,2-cyclohex-1-enylenevinylene)s via oxidation or thermally induced elimination of suitable substituents at the 4,5-position.

MATERIALS AND CHARACTERIZATION

All manipulations where conducted in an N_2-filled glovebox (MBraun Lab Master 130) or standard Schlenk techniques were used. CH_2Cl_2, diethyl ether, toluene, pentane and THF were dried by a solvent purification system (SPS, MBraun). 1,2-Dichloroethane and CCl_4 were stirred over CaH_2 for several hours and then distilled under nitrogen. Starting materials were purchased from Aldrich (Munich, Germany), TCI Europe (Zwijndrecht, Belgium) and ABCR (Karlsruhe, Germany) and used without further purification. All initiators were prepared as described in the literature.[23−26] NMR measurements were recorded on a

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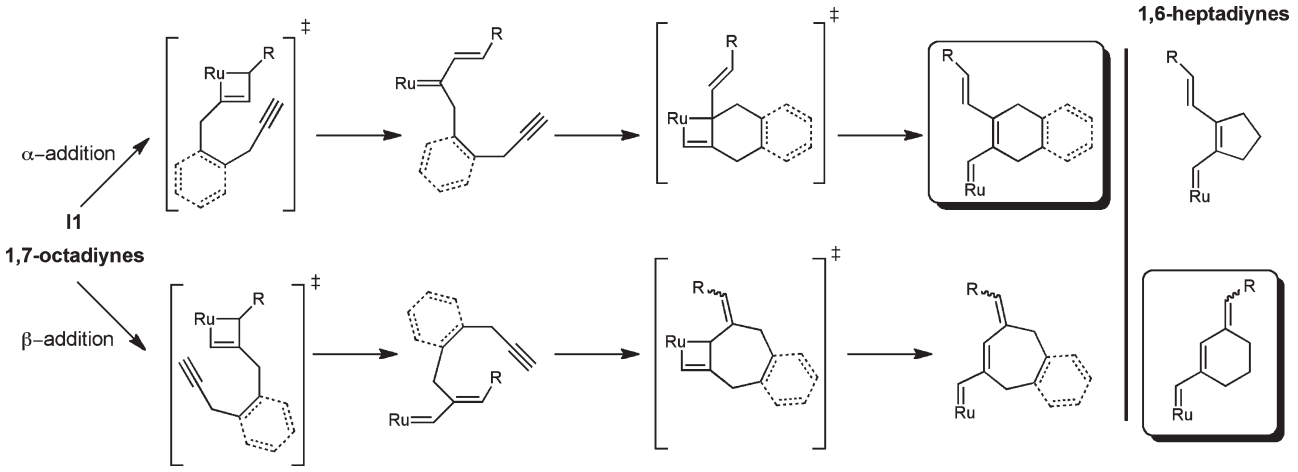
Scheme 1. Two Possible Modes of Insertion Leading to Different Repeat Units[a]



[a] Left: 1,7-octadiynes yielding six- (top) and seven-membered (bottom) ring structures (dashed: aromatic backbone as present in **M1**). Right: Corresponding structures derived from 1,6-heptadiynes.

Bruker Avance 250 or Bruker Avance III 400. IR spectra were measured on an IFS 28 (Bruker) using NaCl cuvettes. UV/vis measurements were carried out in $CHCl_3$ on a Perkin-Elmer Lambda 2. GC−MS data were recorded on an Agilent Technologies device consisting of a 7693 autosampler, a 7890A GC and a 5975C quadrupole MS. Dodecane was used as internal standard. A SPB-5 fused silica column (34.13 m × 0.25 mm × 0.25 μm film thickness) was used. The injection temperature was set to 150 °C. The column temperature ramped from 45 to 250 °C within 8 min, and was then held for further 5 min. The column flow was 1.05 mL per minute. GPC measurements were carried out on a system constituted by a Waters 515 HPLC pump, a Waters 2707 autosampler, PolyPore columns (300 × 7.5 mm, Agilent technologies, Böblingen, Germany), a Waters 2489 UV/vis- and a Waters 2414 refractive index detector.

Synthesis of M1. *1,4-Dihexyloxy-2,3-dimethylbenzene (**2**).* 2,3-Dimethylhydroquinone (**1**, 7.50 g, 54.3 mmol) and 1-hexyl bromide (20.5 g, 130.3 mmol, 2.4 equiv) were dissolved in 80 mL of acetonitrile, K_2CO_3 (48.25 g, 0.35 mol) was added, and the mixture was refluxed for 25 h. The reaction was monitored by GC−MS. The salts were removed by filtration and carefully washed with acetonitrile until colorless. Then, the solvent was removed and the dark brown residue was dissolved in petrol ether. After washing with 1 M NaOH solution, the organic layer was washed with water and saturated NaCl solution and dried over Na_2SO_4. The excess of hexyl bromide was removed in vacuo. The resulting brown liquid was further purified by column chromatography (silica) using petrol ether to yield 7.61 g (24.8 mmol, 46%) of a colorless liquid. ^{1}H NMR ($CDCl_3$, δ): 6.65 (s, 2H); 3.89 (t, ^3J = 6.5 Hz, 4H); 2.18 (s, 6H); 1.79 (quint, ^3J = 6.4 Hz, 4H); 1.41−1.55 (m, 4H); 1.28−1.41 (m, 8H); 0.92 (t, ^3J = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, δ): 151.6, 127.4, 109.6, 69.4, 32.0, 29.9, 26.3, 23.0, 14.5, 12.5. GC−MS (relative intensity): *m*/*z* calcd for $C_{20}H_{34}O_2$, 306.26; found, 306.1 (19%), 222.1 (7%), 138.1 (100%), 123.0 (4%), 107.0 (4%), 55.1 (13%). IR (film, cm^{-1}): 2933 (s), 2860 (s), 1599 (w), 1468 (s), 1381 (m), 1254 (s), 1211 (s), 1107 (s), 1014 (w), 787 (m).

*2,3-Bis(bromomethyl)-1,4-dihexyloxybenzene (**3**).* **2** (560 mg, 1.83 mmol) was dissolved in 15 mL of dry CCl_4 and the solution was heated to reflux. Then, *N*-bromosuccinimide (650 mg, 3.66 mmol, 2 equiv) and AIBN (8 mg, 0.05 mmol) were added simultaneously. After 30 min, the reaction was finished as evidenced by discoloration of the solution and formation of succinimde at the surface. The latter was removed by filtration and the solvent was evaporated to yield 715 mg (1.54 mmol, 84%) of a pale yellow crystalline solid. ^{1}H NMR ($CDCl_3$, δ): 6.80 (s, 2H), 4.76 (s, 4H), 3.97 (t, ^3J = 6.45 Hz, 4H), 1.82 (quint., ^3J = 6.45 Hz, 4H), 1.43−1.59 (br s, 4H), 1.27−1.43 (br s, 8H), 0.92 (t, ^3J = 6.65 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 151.6, 126.8, 113.5, 69.4, 31.9, 29.7, 26.2, 24.6, 23.0, 14.5. GC−MS (relative intensity): *m*/*z* calcd for $C_{20}H_{32}Br_2O_2$, 464.08; found, 464.1 (22%), 383.1 (24%), 304.1 (13%), 216.9 (39%), 135.0 (100%), 83.1 (89%), 55.1 (93%). IR (film, cm^{-1}): 2929 (s), 2870 (m), 1714 (w), 1593 (w), 1487 (m), 1466 (s), 1267 (s), 1068 (w).

*1,4-Dihexyloxy-2,3-bis(3-trimethylsilyl-2-propinyl)benzene (**4**)*[27]. At −78 °C, *n*-BuLi (8.1 mL, 1.6 M in hexane; 12.9 mmol) was added to a solution of trimethylsilylacetylene (1.47 g, 15 mmol) in 20 mL of dry THF. The cooling bath was removed and the mixture was stirred for a further 50 min. **3** (1.00 g, 2.15 mmol) was dissolved in 5 mL of THF and added to this solution at −78 °C. The mixture was warmed to room temperature and stirred overnight. After heating to 50 °C for 8 h, the reaction was stopped with saturated NaCl solution. The phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and saturated NaCl solution and dried over Na_2SO_4. After removal of the solvent, a dark reddish oil was isolated. Purification by column chromatography (silica, petrol ether: ethyl acetate = 50:1) yielded an orange colored solid (660 mg, 1.32 mmol, 61%). ^{1}H NMR ($CDCl_3$, δ): 6.73 (s, 2H), 3.93 (t, ^3J = 6.45 Hz, 4H), 3.79 (s, 4H), 1.69−1.87 (m, 4H), 1.20−1.58 (m, 12H), 0.92 (br s, 6H), 0.11 (s, 18H). ^{13}C NMR ($CDCl_3$, δ): 152.2, 126.6, 111.9, 105.2, 83.9, 69.9, 32.0, 29.8, 27.3, 23.0, 17.1, 14.5, 0.5. GC−MS (relative intensity): *m*/*z* calcd for $C_{30}H_{50}Si_2O_2$, 498.33; found, 498.3 (4%), 413.2 (3%), 329.1 (22%), 308.9 (31%), 278.8 (9%), 241.0 (10%), 216.9 (5%), 84.0 (44%), 55.0 (100%). IR (film, cm^{-1}): 2929 (s), 2858 (m), 2173 (s), 1466 (s), 1250 (s), 1074 (m), 1020 (m), 843 (s), 760 (m).

*1,4-Dihexyloxy-2,3-dipropargylbenzene (**M1**)*[28]. **4** (300 mg, 0.60 mmol) was dissolved in a mixture of CH_2Cl_2, acetone and water (7:4:1). Under exclusion of light, $AgNO_3$ (450 mg, 2.60 mmol) was added. After stirring for 45 min at room temperature, 5 mL of water and 4 mL of 12.5 N hydrochloric acid were added. After stirring for another hour, the phases were separated and the aqueous part was extracted twice with CH_2Cl_2. The combined organic phases were washed with water and saturated NaCl solution and dried over Na_2SO_4. The solvent was removed *in vacuo* to yield a red-brown oil. It was purified by column chromatography (silica, petrol ether:ethyl acetate=200:3). 185 mg (0.52 mmol, 87%) of a yellow oil were obtained. ^{1}H NMR ($CDCl_3$, δ): 6.74

(s, 2H), 3.93 (t, ^3J = 6.45 Hz, 4H), 3.74 (d, ^3J = 2.70 Hz, 4H), 1.94 (t, ^3J = 2.70 Hz, 2H), 1.79 (quint, ^3J = 6.45 Hz, 4H), 1.19−1.58 (m, 12H), 0.91 (br s, 6H). ^{13}C NMR ($CDCl_3$, δ): 151.1, 125.9, 111.8, 82.7, 69.6, 68.1, 32.0, 29.8, 26.2, 23.0, 15.7, 14.4. HRMS (ESI): m/z calcd for $C_{24}H_{34}O_2$, 354.2559; found, 354.2560. IR (film, cm^{-1}): 3311 (s), 2931 (s), 2870 (m), 2117 (w), 1630 (m), 1597 (w), 1466 (s), 1261 (s), 1080 (s), 796 (m), 633 (m).

Synthesis of M2. *(R,R),(S,S)-4,5-Dihydroxy-1,7-octadiyne (**7**)*[31]. Lithium acetylide (2.9 g, 32.1 mmol) was dissolved in 80 mL of THF/DMSO (3:1), diastereomeric diepoxybutane (1.3 g, 16 mmol) was added dropwise at 0 °C and the mixture was stirred for 3 h at 0 °C. After stirring overnight at room temperature, the reaction was stopped by adding 5 mL of a saturated NH_4Cl solution. The THF was removed *in vacuo* and the mixture was extracted with CH_2Cl_2. The combined organic phases were washed with saturated NaCl solution and dried over Na_2SO_4. After removal of the solvent, a white solid remained. Purification by column chromatography (silica, ethyl acetate:pentane = 3:1) yielded **7** (718 mg, 5.20 mmol, 38%, *ee* = 4%). The enantiomers were separated by chiral GC-chromatography on a Carlo Erba Strumentazione HRGC-5300 Mega Series instrument using an Ambidex B column (20 m x 0.3 mm x 0.25 μm; based on 21 mol % valinbornylamid, 5 mol % permethyl-β-cyclodextrin). The injection temperature was 40 °C, the temperature was then increased to 200 °C with a heating rate of 2.5 °C/min. ^{1}H NMR (CD_3OD, δ): 4.78 (s, 2H, OH), 3.67 (m, 2H, CH), 2.31 (m, 4H, CH_2), 2.17 (t, 2H, C≡H). ^{13}C NMR (CD_3OD, δ): 82.32, 72.31, 71.48, 24.61. GC−MS (EI, 70 eV): m/z calcd for $C_8H_{10}O_2$, 138.07; found, 138 ($M^{\bullet+}$). Elem. Anal. calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.53, H, 7.37. IR (cm^{-1}): 3286 (s), 2928 (s), 2891 (s), 2114 (m), 2170 (w), 2170 (w), 1469 (w), 1430 (w), 1331 (w), 1258 (w), 1219 (w), 1155 (w), 1124 (w), 1012 (s), 862 (w), 893 (w), 831 (w) cm^{-1}.

*(R,R)/(S,S)-4,5-Bis(trimethylsilyloxy)-1,7-octadiyne (**M2**).* Triethylamine (0.80 mL, 5.6 mmol) and trimethylchlorosilane (0.7 mL, 0.5 mmol) were added to a solution of **7** (309 mg, 2.2 mmol) in 60 mL of CH_2Cl_2. After stirring for 5 h at room temperature, the reaction was stopped by addition of 5 mL of saturated NH_4Cl solution. The phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with water and saturated NaCl solution and dried over Na_2SO_4. After removal of the solvent, a crystalline, white solid (512 mg, 1.8 mmol, 80%) was isolated. ^{1}H NMR ($CDCl_3$, δ): 3.92−2.83 (m, 2H, CH−OTMS), 2.47 (ddd, ^2J = 16.6 Hz, ^3J = 6.1 Hz, ^4J = 2.7 Hz, 2H, CH_2), 0.2.24 (ddd, ^2J = 16.6 Hz, ^3J = 6.5 Hz, ^4J = 2.7 Hz, 2H, CH_2) 1.95 (q, ^4J = 2.7 Hz, 2H, C≡CH), 0.19 (s, 18H, $OSi(CH_3)_3$. ^{13}C NMR ($CDCl_3$, δ): 82.23, 72.12, 70.46, 23.29, 0.81. Elem. Anal. Calcd for $C_{14}H_{26}O_2Si_2$: C, 59.52; H, 9.82. Found: C, 59.60, H 9.85. IR (cm^{-1}): 3277 (m), 3254 (m), 2959 (m), 2921 (w), 2908 (w), 2888 (vw), 1429 (w), 1371 (m), 1253 (s), 1204 (w), 1127 (m), 1038 (s), 1002 (m), 968 (s), 947 (m), 843 (s), 751 (s), 685 (s).

Synthesis of Model Compounds A and B. *6,7-Dimethyltetrahydro-4a,5,8,8a-1,4-naphtoquinone (**5**).* Benzoquinone (2.00 g, 18.5 mmol) was dissolved in 18 mL of acetic acid. Two portions of 2,3-dimethyl-1,3-butadiene (each portion 675 mg; 9.25 mmol) were added slowly to this solution. After stirring at room temperature overnight, the crystalline needles that had formed were removed by filtration and washed with water to yield **5** (630 mg, 3.3 mmol, 22%). ^{1}H NMR ($CDCl_3$, δ): 6.63 (s, 2H), 3.17 (m, 2H), 2.37 (m, 2H), 2.04 (m, 2H), 1.60 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 200.7, 139.7, 47.4, 30.8, 19.2. IR (film, cm^{-1}): 2925 (m), 1687 (s), 1267 (m), 1090 (m), 847 (w).

*6,7-Dimethyl-5,8-dihydronaphthaline-1,4-diol (**6**)*[29]. **5** (325 mg, 1.71 mmol) was dissolved in 4 mL of acetic acid and the mixture was heated to 80 °C under stirring. The oil bath was removed and one drop of hydrobromic acid (32% in acetic acid) was added. The reaction solution immediately solidified. The resulting white solid was then washed with water to yield 280 mg (1.47 mmol, 86%) of **6**. ^{1}H NMR (DMSO-d_6, δ): 8.53 (s, 2H), 6.45 (s, 2H), 3.07 (s, 4H), 1.75 (s, 6H). ^{13}C NMR (DMSO-d_6, δ): 147.5, 123.2, 123.0, 112.3, 32.2, 19.5. IR (film, cm^{-1}): 3230 (br), 2856 (w), 1600 (w), 1423 (m), 1335 (s), 1244 (s), 1119 (m), 968 (m), 804 (s), 741 (m).

*5,8-Dihexyloxy-2,3-dimethyl-1,4-dihydronaphthaline (**A**).* **6** (270 mg, 1.42 mmol), 1-hexyl bromide (700 mg, 4.26 mmol, 3 equiv), and K_2CO_3 (1.17 g, 8.46 mmol) were added to 20 mL of acetone and refluxed for 2 days. The reaction was monitored by GC−MS. The suspension was filtered to remove all salts and vacuum distilled to remove any excess of hexyl bromide. Column purification (silica, petrol ether:ethyl acetate = 100:0 to 50:1) yielded 100 mg (0.28 mmol, 20%) of a greenish solid. ^{1}H NMR ($CDCl_3$, δ): 6.61 (s, 2H), 3.92 (t, ^3J = 6.5 Hz, 4H), 3.23 (s, 4H), 1.81 (m, 4H), 1.29−1.59 (m, 12H), 0.94 (t, ^3J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 150.4, 125.7, 122.9, 108.2, 68.7, 32.0, 31.6, 29.8, 26.3, 23.1, 19.1, 14.5; GC−MS (relative intensity): m/z calcd for $C_{24}H_{38}O_2$, 358.29; found, 358.3 (51%), 343.1 (1%), 274.1 (7%), 201.0 (4%), 187.0 (100%), 173.0 (71%), 159.1 (12%), 145.0 (15%), 115.0 (12%), 55.0 (46%). IR (film, cm^{-1}): 2937 (s), 2922 (s), 2854 (s), 1610 (s), 1464 (s), 1255 (s), 1128 (s), 1066 (s), 779 (s).

*trans-4,5-Bis(trimethylsilyloxy)-1-cyclohexene (**B**).* *trans*-1-Cyclohexene-4,5-diol (**8**) was prepared as described in the literature.[30] (**8**) (175 mg, 1.53 mmol) and triethylamine (0.60 mL, 3.98 mmol) were dissolved in 40 mL of CH_2Cl_2 and trimethylchlorosilane (0.50 mL, 3.52 mmol) was added at 0 °C. After stirring for 5 h at room temperature, the reaction was stopped by addition of 2 mL of saturated aqueous NH_4Cl-solution. The phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with water and saturated NaCl solution and dried over Na_2SO_4. Column purification (silica, CH_2Cl_2) yielded 127 mg (0.49 mmol, 33%) of a colorless oil. ^{1}H NMR ($CDCl_3$, δ): 5.44−5.33 (m, 2H), 3.60−3.46 (m, 2H), 2.31−2.13 (m, 2H), 1.99−1.80 (m, 2H), 0.00 (s, 18H); ^{13}C NMR ($CDCl_3$, δ): 124.14, 71.32, 33.96, 0.00; GC−MS (EI, 70 eV) m/z calcd for $C_{12}H_{26}O_2Si_2$ = 258.1; found: 258.1 ($M^{\bullet+}$).

Cyclopolymerization with Grubbs (−Hoveyda)-Type Initiators. The monomer was dissolved in 1,2-dichloroethane (ca. 0.12 mmol/mL), the solution was filtered through neutral Al_2O_3 and heated to 45 °C. Under nitrogen, a solution of **I1** in 1,2-dichloroethane was added via syringe. After 150 min, the polymerization was stopped by addition of ethyl vinyl ether. After stirring for another 20 min, the solution was concentrated and precipitated in methanol. The resulting red solid was washed twice with methanol and acetone and dried *in vacuo*.

Poly-M1. ^{1}H NMR ($CDCl_3$, δ): 7.37−7.75 (br s, 1H), 6.39−6.80 (br s, 2H), 3.36−4.23 (br s, 8H), 0.50−1.98 (m, 25 H). ^{13}C NMR ($CDCl_3$, δ): 150.2, 130.8, 125.7, 123.7, 107.3, 68.3, 31.7, 29.5, 26.6, 26.2, 22.8, 14.1. IR (film, cm^{-1}): 2929 (s), 2868 (s), 1603 (m), 1468 (s), 1379 (m), 1257 (s), 1084 (s), 951 (m), 787 (m). UV/vis ($CHCl_3$): λ_{max} = 470 nm.

Poly-M2. ^{1}H NMR ($CDCl_3$, δ): 6.95−6.63 (br,s, 1H), 3.75−3.45 (br s, 3H), 2.77−2.07 (m, 4H), 0.19−0.13 (m, 24). ^{13}C NMR ($CDCl_3$, δ): 131.7, 125.4, 71.5, 34.6, 1.3. IR (film, cm^{-1}): 2960 (m), 2907 (m), 1580 (w), 1443 (w), 1411 (w), 1319 (vw), 1251 (vs), 1097 (vs), 1012 (vs), 917 (m), 885 (m), 837 (s), 795 (vs), 742 (s), 683 (w). UV/vis ($CHCl_3$): λ_{max} = 483 nm.

Cyclopolymerization with Schrock-Type Initiators. The monomer was dissolved in CH_2Cl_2 or THF (c = 0.12 mol/L) and the solution was filtered through neutral Al_2O_3. The initiator was dissolved in the same solvent (1 mL) and added to the one of the monomer. For polymerizations carried out at low temperature, both solutions were first placed into the freezer and cooled to −36 °C. After 90 min, the reaction was stopped by adding ferrocenylaldehyde (10 molequiv. with respect to initiator), and after another 15 min the solution was concentrated and precipitated in acetone. The resulting red solid was washed twice with methanol and acetone or methanol/pentane (3:1) and dried in vacuo.

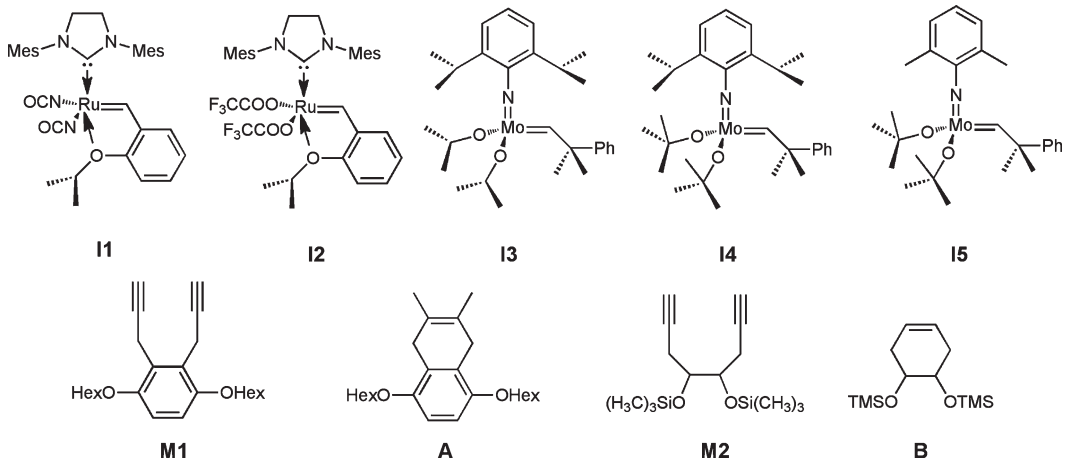
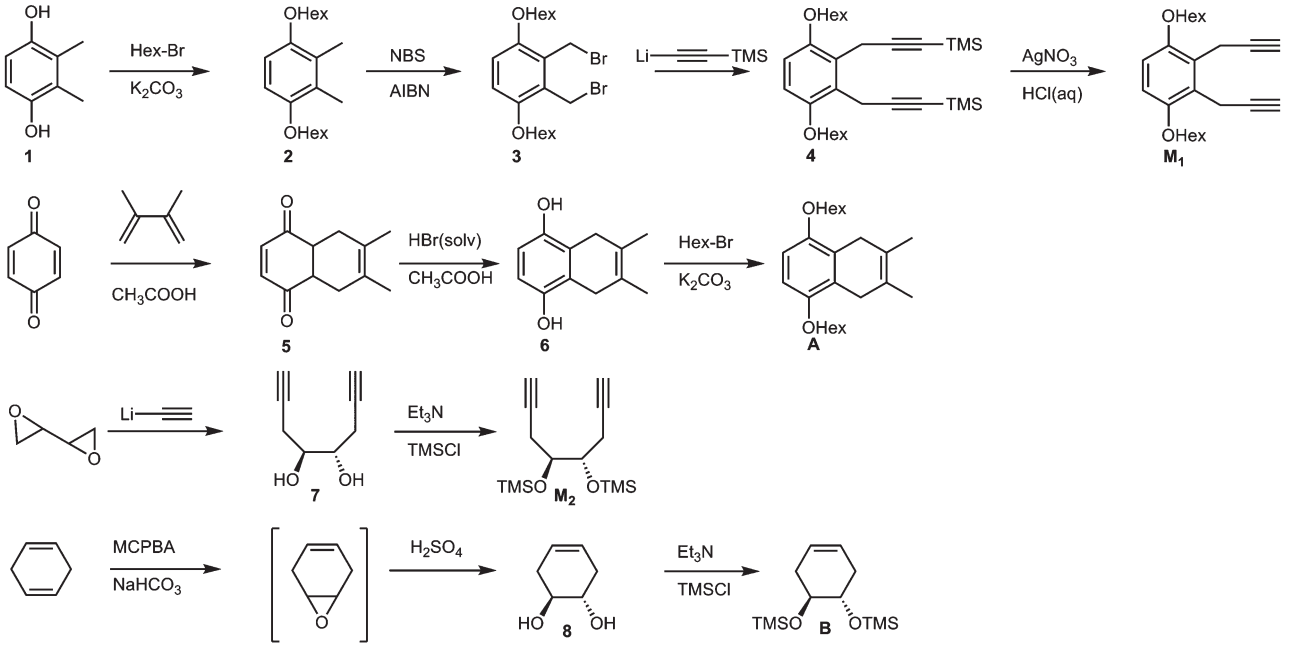


Figure 1. Initiators employed for the cyclopolymerizations of **M1** and **M2** and structure of the model compounds **A** and **B**.

Scheme 2. Synthesis of M1 and M2 and of the Model Compounds A and B



RESULTS AND DISCUSSION

Synthesis of Initiators, Monomers, and Model Compounds. The modified Grubbs-Hoveyda catalysts **I1** and **I2** (Figure 1) as well as the Schrock-type initiators **I3**-**I5** were prepared according to the literature.[23−26]

1,4-Dihexyloxy-2,3-dipropargylbenzene (**M1**) was accessible starting from commercially available 2,3-dimethylhydroquinone via a four-step synthesis (Scheme 2). A simple sequence of etherification, benzylic bromination and nucleophilic substitution yielded trimethylsilyl-protected **M1.** Deprotection proved critical because standard procedures[32,33] resulted in the partial formation of allenes. It was thus necessary to deprotect **M1** with the aid of $AgNO_3$ under acidic conditions.[28]

Model compound **A** was synthesized via the Diels−Alder reaction of benzoquinone with 2,3-dimethylbutadiene, followed by acid-catalyzed aromatization and etherification (Scheme 2).

The synthesis of **M2** was accomplished starting from commercially available diastereomeric butadiene diepoxide via a two-step route (Scheme 2). Nucleophilic ring-opening of the diepoxide with lithium acetylide was followed by standard trimethylsilyl-protection of the resulting diol **7**. Spectroscopic results and the X-ray structure of **M2** provide an argument for the stereoselective ring-opening of only one of the diastereomers, i.e., of the (*R*,*R*)/(*S*,*S*) but not of the (*R*,*S*)/(*S*,*R*) couple, thereby selectively forming diastereomeric (*R*,*R*)/(*S*,*S*)-4,5-bis(trimethylsilyloxy)-1,7-octadiyne (**M2**). Model compound **B** was accessible via epoxidation of 1,4-cyclohexadiene, followed by acid-catalyzed ring-opening of the epoxide to yield the diol **8**. Its etherification with trimethylsilyl chloride in the presence of NEt_3 finally yielded model compound **B** (Scheme 2).

Cyclopolymerizations. The cyclopolymerization of both **M1** and **M2** by the action of **I1** and **I3**−**I5**·**quinuclidine** (Figure 1)

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Table 1. Cyclopolymerization of M1 and M2 by Initiators I1−I5

no.	initiator	monomer	M_n (theor.) (g/mol)	M_n[a] (g/mol)	PDI	λ_{max}[b] (nm)	%[c] α-insertion	yield (%)
1[d]	**I1**	**M1**	17 700	12 000	2.0	470	>98	24
2[e]	**I3**	**M1**	26 600	16 000	1.6	458	90	64
3[e]	**I3·quinuclidine**	**M1**	26 600	25 000	1.9	461	80	48
4[f]	**I4·quinuclidine**	**M1**	26 600	13 000	1.5	454	79	47
5[f]	**I5·quinuclidine**	**M1**	26 600	15 000	1.6	461	83	54
6[d]	**I1**	**M2**	22000	11000	1.7	483	>95	17
7[h]	**I3·quinuclidine**	**M2**	28000	57000	1.3	485	>94	80
8[g]	**I4·quinuclidine**	**M2**	28000	32000	1.2	485	>98	96
9[g]	**I5·quinuclidine**	**M2**	20000	7000	1.2	484	>98	89
10[g]	**I5·quinuclidine**	**M2**	28000	67000	1.3	487	>94	95

[a] Vs PS. [b] In $CHCl_3$. [c] By ^{13}C NMR. [d] $ClCH_2CH_2Cl$, 45 °C. [e] CH_2Cl_2, −36 °C → room temperature. [f] THF, −36 °C → room temperature. [g] CH_2Cl_2, room temperature. [h] THF, room temperature.

resulted in red, film-forming polymers. The materials showed no signs of decomposition even after prolonged storage under air or in solution. Thus, no significant changes in the corresponding NMR and UV spectra or in GPC were observed. Solubility was very good in THF and halogenated solvents such as $CHCl_3$. Acetone could be used for washing **poly-M1**, while **poly-M2** proved to be soluble in acetone at least up to number-average molecular weights of 65 000 g/mol. Some significant differences, however, between **I1**/**I2** and **I3**−**I5·quinuclidine** have to be stated (Table 1). Thus, the cyclopolymerization of **M1** by the ruthenium-based initiator **I1** resulted in yields ≤24% when used in 1,2-dichloroethane at 45 °C. Lowering the reaction temperature to room temperature resulted in yields <5%. Interestingly, initiator **I2** was not able to induce the cyclopolymerization of **M1** at all. This contrasts former investigations regarding various 1,6-heptadiynes, where the use of **I2** allowed for controlled, sometimes living, regioselective cyclopolymerizations[1,21,22,34] and clearly illustrates the low cyclopolymerization propensity of this monomer. Consequently, a more drastic activation of the ruthenium alkylidene as is given in **I1**, where the highly activating isocyanates coordinate to the metal center[23] appears to be necessary for this particular 1,7-octadiyne. Even so, the latter only delivers low yields. Similar accounts for the cyclopolymerization of **M2** by the action of **I1**. GPC traces of both **poly-M1** and **poly-M2** prepared by the action of **I1** were monomodal with 1.7 < PDI < 2.0 and an M_n around 12 000 g/mol (vs polystyrene); however, yields were poor (17%). In no case could a controlled or even living polymerization setup be accomplished.

In contrast to these findings, the more reactive molybdenum-based Schrock initiators **I3**−**I5·quinuclidine** allowed for the complete consumption of both **M1** and **M2**. The quinuclidine adducts of the Schrock initiators were chosen since they sometimes allow for more controlled polymerizations, i.e. lower values of k_p/k_i. As can be seen in Table 1, the Schrock initiators produced the corresponding cyclopolymers in up to 96% isolated yield. In no case, any cross-linking, leading to insoluble polymers or polymers with residual alkyne groups was observed. Values for M_n were between 12 000 and 67 000 g/mol, poldispersity indices ranged from 1.2 to 2.0. It is worth emphasizing that despite the fact that isolated yields were <100%, in most cases the experimentally determined number-average molecular weights were significantly higher than the theoretical ones. This is, on the one hand, attributable to initiation kinetics. Thus, for the polymerization of **M2** by the action of **I3·quinuclidine**, a value of 60 was

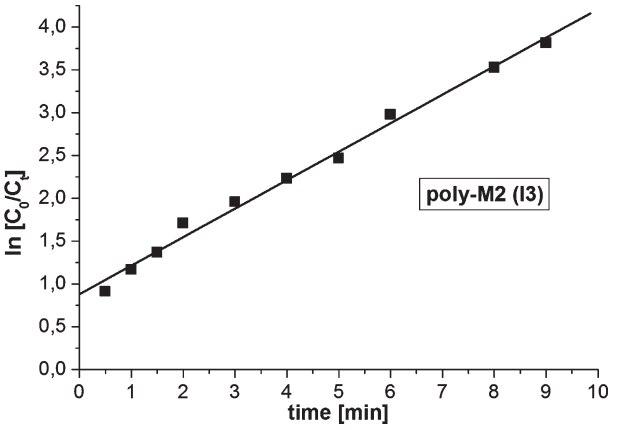

Figure 2. Graph of $\ln(C_0/C_t)$ vs time for the cyclopolymerization of **M2** by the action of **I3·quinuclidine**. C_0 = 44.3 mmol/L, T = 25 °C, THF.

determined for k_p/k_i[35] using a noncoordinating solvent, i.e. C_6D_6. This value also accounts for the positive intercept in Figure 2 (*vide supra*). On the other hand, the rigid nature of the poly(1,7-octadiynes) plays a key role. As found for poly(1,6-heptadiynes),[18] where the rod-like structure leads to apparent number-average molecular weights up to 50% higher than the theoretical ones in case molecular weights are determined vs PS, higher apparent number-average molecular weights must be expected for **poly-M1** and **poly-M2**, too. Changing the solvent from CH_2Cl_2 to THF did not only result in lower PDIs, but also allowed for the polymerization of **M2** by the action of **I3·quinculidine** in a living manner. As can be deduced from Figure 2, a linear plot of $\ln(M_0/M)$ vs time, which supports first-order polymerization kinetics, was obtained.

Microstructure and Optical Spectra. For reasons of symmetry, the ^{13}C NMR spectrum of **poly-M1** based on six-membered repeat units prepared via selective α-addition should show five signals in the aromatic region. This is what was observed in case **I1** was used for polymerization (Figure 3). Three signals that can be assigned to the carbon atoms incorporated in the aromatic ring (A, B, and C) were observed at δ = 150.2, 125.7, and 107.3 ppm. These chemical shifts perfectly fit the ones of model compound **A**, where A*, B*, and C* appear at δ = 150.1, 125.5, and 107.9 ppm. The additional peaks at δ = 130.8 and 123.7 ppm were assigned to the conjugated chain. Interestingly, these signals are comparably sharp, pointing

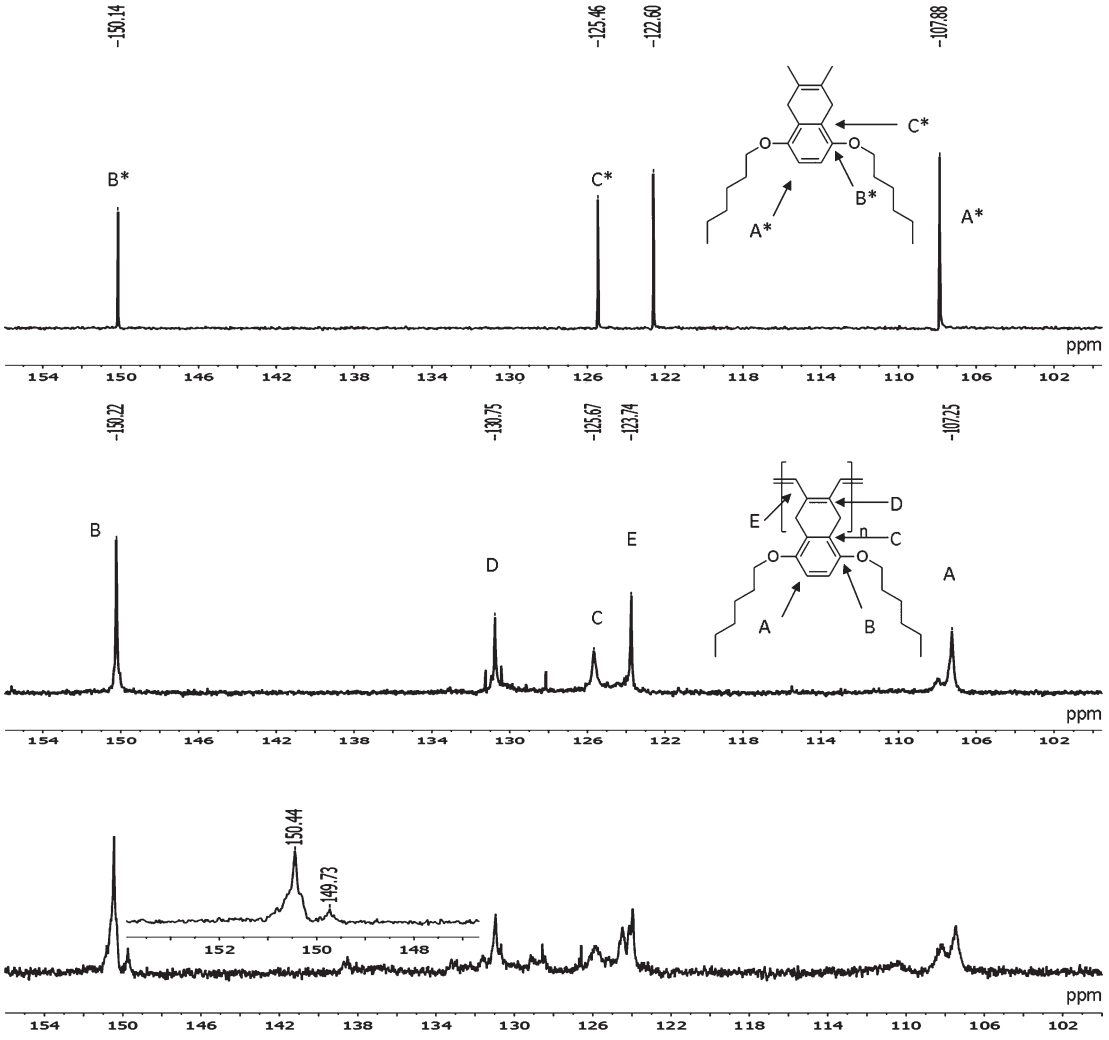

Figure 3. Aromatic region of the ^{13}C NMR spectrum ($CDCl_3$) of model compound **A** (top), **poly-M1** prepared by the action of **I1** (middle) and of **poly-M1** prepared by the action of **I3·quinuclidine** (bottom).

toward a more flexible and most probably predominant all-*trans*-configuration of the polymer, which is also supported by the IR spectrum in which a strong signal at 960 cm^{-1} can be observed for $C{=}C_{trans}$. The chemical shift of the methylene carbon inside the newly formed 6-membered ring of the repeat units overlaps with signals of the alkoxy side chains; tentatively, one peak at δ = 26.6 ppm can be assigned to this atom. These findings clearly indicate that the cyclopolymerization of this 1,7-octadiyne by the modified Grubbs-Hoveyda initiator **I1** proceeds, as observed for 1,6-heptadiynes, via regioselective α-insertion. Most probably, the same arguments for the regioselective α-insertion, i.e. a strong steric interaction between the N-heterocyclic carbene and the second metallacyclobutene ring in β-insertion derived intermediates, apply.[36]

Using the Schrock-type initiators **I3**−**I5**, the ^{13}C NMR of **poly-M1** showed additional signals, irrespective of the catalyst used. The spectra are consistent with a polymer structure containing both α- and β-addition derived repeat units. The arylic C_B next to the oxygen serves as a sensitive probe to calculate the ratio of six-membered units as given in Table 1.[37] Thus, two signals at δ = 150.2 and 149.5 ppm are observed in polymers containing both six- and seven-membered repeat units (Figure 3). Since the carbon atoms are of the same kind, integration can help to calculate the ratio of α− over β-addition (Table 1). The highest content of 6-membered repeat units was obtained with **I3** and **I5·quinuclidine**. As has been found for 4-aza-1,6-heptadiynes,[37] **I4** containing the sterically most demanding ligands displays the lowest regioselectivity in insertion, resulting in only 79% of α-insertion-derived repeat units (Table 1).

In the cyclopolymerization of **M2** by the ruthenium-based initiator **I1**, again a regioselective α-addition occurs as evidenced by the ^{13}C NMR spectrum of **poly-M2**, which displays 5 signals. Two signals (D, E) that can be assigned to the conjugated chain appear at δ = 131.7 and 125.4 ppm. The chemical shift of the methylene carbon of the newly formed 6-membered ring of the repeat unit appears at δ = 34.6 ppm (F), the low field shifted signal for the tertiary carbon (G) and finally the signal of the TMS group (H) can be found at δ = 71.5 and 1.27 ppm, respectively. These values again perfectly fit the chemical shifts of model compound **B**, where E*, F*, G*, and H* appear at δ = 124.1, 71.3, 33.9, and 0.0 ppm. Again, an all-*trans* structure is proposed for **poly-M2** as indicated by the IR-signal at 958 cm^{-1}. In contrast to the ^{13}C NMR spectrum of **poly-M1**, the ones of **poly-M2** prepared by any of the Schrock-type initiators **I3**−**I5·quinuclidine** showed two signals at δ = 71.0 and 70.4 ppm,

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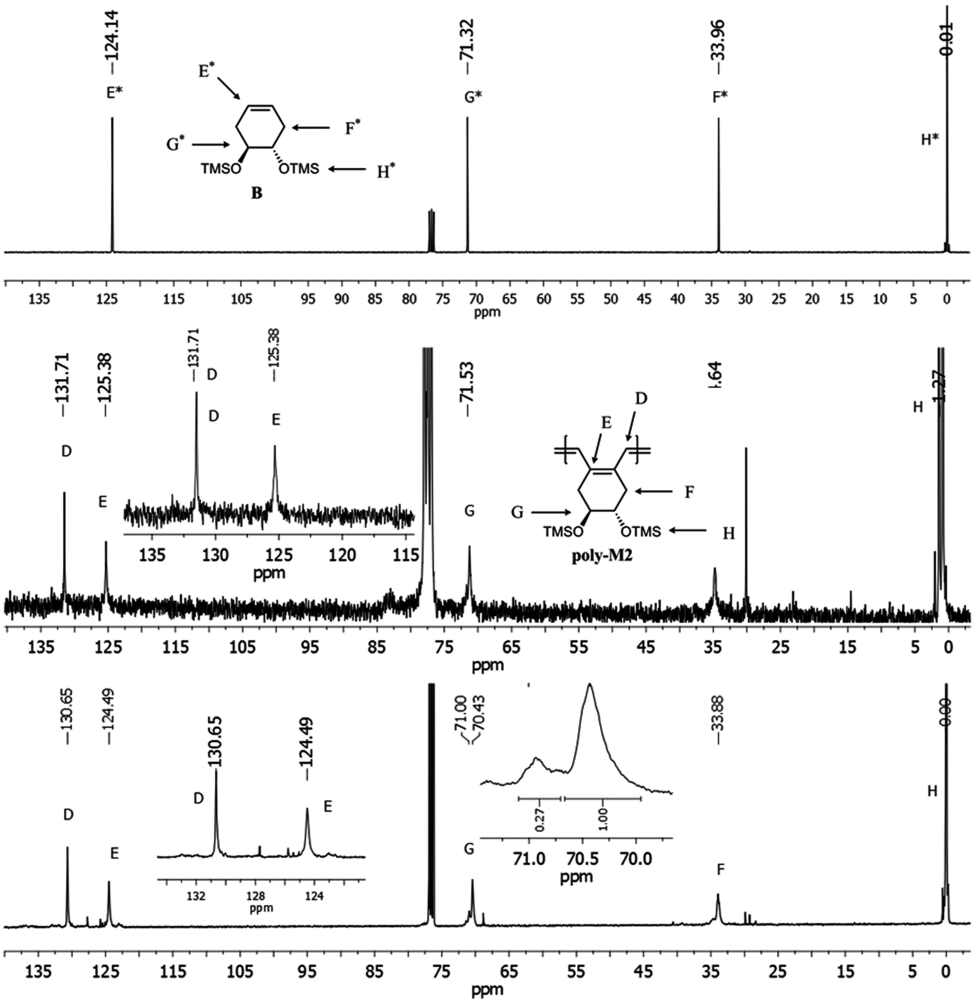

Figure 4. ^{13}C NMR ($CDCl_3$) of model compound **B** (top) and **poly-M2** prepared by the action of **I1** (middle) and **I4·quinuclidine** (bottom).

however, *no additional signals in the olefinic region that would suggest a mixed polymer structure* resulting from both α- and β-addition (Figure 4).

Apparently, in the presence of quinuclidine, all Mo-based initiators, **I3**−**I5**, produce cyclopolymerization-derived **poly-M2** via regioselective α-insertion. From the corresponding ^{13}C NMR spectra, an α-insertion selectivity up to >98% was determined. The signal splitting around δ = 71 and 34.0 ppm is attributed to a poly(ene)s in which an (*R*,*R*)-configured monomer is followed by an (*R*,*R*) or an (*S*,*S*)-configured one. The different regioselectivities in insertion are also reflected by the UV−vis spectra of the corresponding polymers. Thus, UV/vis measurements revealed a maximum in absorption at λ_{max} = 470 nm for **poly-M1** prepared by the action of **I1**. In contrast, lower absorption maxima were found for **poly-M1** prepared by the action of **I3**−**I5·quinuclidine**, which all contain a lower fraction of 6-membered repeat units. Vice versa, **poly-M2** produced by the action of **I1** as well as by **I3**−**I5·quinuclidine** showed virtually identical absorption maxima in the range of 483−487 nm, which further supports the high regioselectivity in insertion.

CONCLUSIONS

A "pseudo-halide"-modified Grubbs−Hoveyda type initiator bearing strongly electron withdrawing groups, i.e., $Ru(NCO)_2(IMesH_2)(=CH-(2\text{-}(2\text{-}PrO)C_6H_4))$ (**I1**) is able to cyclopolymerize 1,4-dihexyloxy-2,3-dipropargylbenzene (**M1**) and (*R*,*R*)/(*S*,*S*)-4,5-bis(trimethylsilyloxy)-1,7-octadiyne (**M2**) exclusively via α-addition to yield unprecedented poly(1,2-cyclohex-1-enylenevinylene)s, albeit in low yields and in a nonliving manner. With **M2**, selected Schrock-type initiators also deliver poly(ene)es based on 6-membered repeat units via regioselective α-insertion. Furthermore, a living polymerization setup can be created with $Mo(N\text{-}2,6\text{-}(2\text{-}Pr)\text{-}C_6H_3)(CHCMe_2Ph)(OCH(CH_3)_2)_2$ in the presence of quinuclidine. Both **poly-M1** and **poly-M2** that are virtually solely based on 6-membered repeat units possess higher absorption maxima than the corresponding polymers containing both 6- and 7-membered repeat units.

ASSOCIATED CONTENT

Supporting Information. ^{13}C NMR spectra of **M1**, **A**, **poly-M1**, and **M2**, ^1H NMR spectrum of **poly-M1**, **M2**, and **B**, IR spectra of **poly-M1** and **poly-M2**, UV−vis spectrum of **poly-M2**, GC chromatogram of **7**, and X-ray structure and crystal data of **M2**. This material is available free of charge via the Internet at http://pubs.acs.org/.

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REFERENCES

(1) Buchmeiser, M. R. *Adv. Polym. Sci.* **2005**, *176*, 89.
(2) Choi, S.-K.; Gal, Y.-S.; Jin, S.-H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645.
(3) Kim, S.-H.; Kim, Y.-H.; Cho, H.-N.; Kwon, S. K.; Kim, H. K.; Choi, S.-K. *Macromolecules* **1996**, *29*, 5422.
(4) Seeger, K.; Gill, W. D. *Colloid Polym. Sci.* **1980**, *258*, 252.
(5) Enkelmann, V.; Lieser, G.; Müller, W.; Wegner, G. *Angew. Makromol. Chem.* **1981**, *94*, 105.
(6) Shirakawa, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2574.
(7) MacDiarmid, A. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2581.
(8) Heeger, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2591.
(9) Stille, J. K.; Frey, D. A. *J. Am. Chem. Soc.* **1961**, *83*, 1697.
(10) Gibson, H. W.; Epstein, A. J.; Rommelmann, H.; Tanner, D. B.; Yang, X. Q.; Pochan, J. M. *J. Phys. Colloq.* **1983**, *C3*, 651.
(11) Gibson, H. W.; Bailey, F. C.; Epstein, A. J.; Rommelmann, H.; Pochan, J. M. *Chem. Commun.* **1980**, 426.
(12) Gibson, H. W.; Bailey, F. C.; Epstein, A. J.; Rommelmann, H.; Kaplan, S.; Harbour, J.; Yang, X. Q.; Pochan, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 4417.
(13) Aso, C.; Kunitake, T.; Saiki, K. *Makromol. Chem.* **1972**, *151*, 265.
(14) Hubert, A. J.; Dale, J. *J. Chem. Soc.* **1990**, 3160.
(15) Harrell, K. J. S.; Nguyen, S. T. *Abstr. Pap. Chem. Soc.* **1999**, *217*, 121.
(16) Sivakumar, C.; Vasudevan, T.; Gopalan, A.; Wen, T.-C. *Polymer* **2002**, *43*, 1781.
(17) Colthoup, E. C.; Meriwether, L. S. *J. Org. Chem.* **1961**, *26*, 5169.
(18) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 4044.
(19) Buchmeiser, M. R.; Anders, U.; Nuyken, O.; Wurst, K. *Macromolecules* **2002**, *35*, 9029.
(20) Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3295.
(21) Buchmeiser, M. R.; Krause, J. O.; Zarka, T. M.; Anders, U.; Weberskirch, R.; Nuyken, O. *Angew. Chem., Int. Ed.* **2003**, *42*, 5965.
(22) Krause, J. O.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. *Chem.—Eur. J.* **2004**, *10*, 777.
(23) Kumar, S. P.; Wurst, K.; Buchmeiser, M. R. *Chem. Asian J.* **2009**, *4*, 1275.
(24) Halbach, T. S.; Mix, S.; Fischer, D.; Maechling, S.; Krause, J. O.; Sievers, C.; Blechert, S.; Nuyken, O.; Buchmeiser, M. R. *J. Org. Chem.* **2005**, *12*, 4687.
(25) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; ÓDell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.
(26) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Macromolecules* **2002**, *35*, 9029.
(27) Eskildsen, J.; Reenberg, T.; Christensen, J. *Eur. J. Org. Chem.* **2000**, 1637.
(28) Orsini, A.; Vitérsi, A.; Bodlenner, A.; Weibel, J.-M.; Pale, P. *Tetrahedron Lett.* **2005**, *46*, 2259.
(29) Tririya, G.; Zanger, M. *Synth. Commun.* **2004**, *17*, 3047.
(30) Suemune, H.; Hizuka, M.; Kamashita, T.; Sakai, K. *Chem. Pharm. Bull.* **1989**, *37*, 1379.
(31) Quayle, P.; Rahman, S. *Tetrahedron Lett.* **1995**, *36*, 8087.
(32) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K.-I. *J. Org. Chem.* **2006**, *71*, 7967.
(33) Trachsel, D. *Helv. Chim. Acta* **2003**, 2754.
(34) Halbach, T. S.; Krause, J. O.; Nuyken, O.; Buchmeiser, M. R. *Macromol. Rapid Commun.* **2005**, *26*, 784.
(35) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; ÓRegan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
(36) Kumar, P. S.; Wurst, K.; Buchmeiser, M. R. *J. Am. Chem. Soc.* **2009**, *131*, 387.
(37) Schmidt, C.; Buchmeiser, M. R.; Wang, D. *Macromol. Chem. Phys.* **2011**, *212*, 1999.