Ring-Opening Olefin Metathesis Polymerization of Spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane)

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ABSTRACT: Spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) was polymerized by ring-opening olefin metathesis polymerization (ROMP) to produce poly[2,1′-spirocyclopropane-1,3-cyclopentylenevinylene]. The polymerization reactions were carried out with conventional metathesis catalysts based on W and Ru. The steric bulk of the three-membered ring was not sufficient to prevent the approach of the catalytically active transition metal carbene species to the exo face of the monomer. However, steric hindrance had an important influence on the microstructure of the polymers formed. The resulting polymers contained a high proportion of trans carbon–carbon double bonds and a slight excess of racemic dyads. Models based on steric repulsion are proposed to describe trans/cis and racemic/meso selectivity. Hydrogenation of the double bonds resulted in the formation of partially crystalline poly[2,1′-spirocyclopropane-1,3-cyclopentyleneethylene].

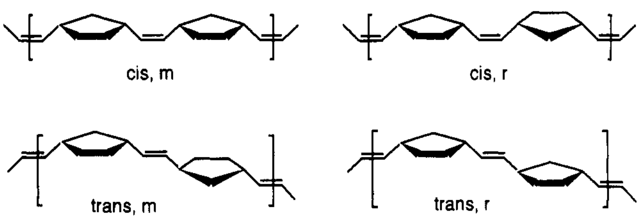
Introduction

Ring-opening olefin metathesis polymerization (ROMP) of cyclic olefins is an important application of the olefin metathesis reaction.[1] Commercial polymers are currently produced from norbornene, cyclooctene, and dicyclopentadiene.[2] The large ring strain of the bicyclic olefin structure[3] (approximately 25 kcal/mol) makes norbornene and norbornene derivatives suitable monomers for living polymerization reactions initiated by well-defined catalysts based on Ti,[4] Ta,[5] Mo,[6] and W.[7]

In earlier studies, Rooney and Ivin et al.[8] have pioneered microstructure analysis of polynorbornene and polynorbornene derivatives by ^{13}C NMR spectroscopy. Monomers in their investigations included 1-, 5-, and 7-monosubstituted and 5,5- and 5,6-disubstituted norbornene derivatives. The stereochemical configuration of polynorbornenes[8] (Chart I) can differ due to (a) double bond isomerism, i.e., cis or trans configuration of the carbon–carbon double bonds; (b) regiochemistry of monomer addition, i.e., head-to-tail (HT), head-to-head (HH), or tail-to-tail (TT) sequences in polymers based on norbornene derivatives with C_1 symmetry; or (c) tacticity, i.e., meso (m) or racemic (r) dyads within the polymer structure. Polymers containing exclusively m dyads are isotactic; macromolecules consisting entirely of r dyads are syndiotactic. A random distribution of m and r dyads represents an atactic polymer.

The syn isomer of 7-methylnorbornene initially resisted homopolymerization by conventional metathesis catalysts because the methyl substituent hinders the approach of the catalytically active transition metal carbene species to the exo face of the monomer.[8a] Only a highly reactive catalyst derived from (mesitylene)W(CO)$_3$/EtAlCl$_2$/norbornene epoxide affected the copolymerization of *syn*-7-methylnorbornene with *anti*-7-methylnorbornene or norbornene.[8a] In recent studies, Kress, Ivin et al.[9] and Feast, Gibson, Ivin et al.[10] obtained block copolymers when they reacted mixtures of *syn*- and *anti*-7-methylnorbornene with $\{W[C(CH_2)_3CH_2](OCH_2CMe_3)_2Br\}^+\{GaBr_4\}^-$ (plus GaBr$_3$) and Schrock's catalyst Mo(CHCMe$_3$)(NC$_6$H$_3$-2,6-*i*-Pr$_2$)(OCMe$_3$)$_2$,[7] respectively. These results reflect the large difference in the polymerization rates of the syn and the anti isomers. In most of these polymerizations, the degree of polymerization of the second polymer block based on *syn*-7-methylnorbornene remained relatively small (P_n < 100) even after extended reaction times of several days.

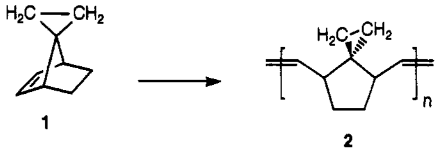
Chart I. Structures of Polynorbornene Diads



The present report describes our investigations on the polymerization behavior of spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane), a norbornene derivative containing a spiro-linked cyclopropane ring attached to carbon atom C^7. We expected steric hindrance to be lower, when the methyl group of *syn*-7-methylnorbornene was replaced by a spiro-linked three-membered ring.

Results and Discussion

Spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) (1) underwent ring-opening olefin metathesis polymerization (ROMP) upon treatment with the conventional catalyst systems RuCl$_3$-hydrate and WCl$_6$/tetraphenyltin (molar ratio = 1/2) (eq 1).[11] High molecular weight samples



(1)

of poly[2,1′-spirocyclopropane-1,3-cyclopentylenevinylene] (2) with M_n = 73 000 and 150 000 (calibration with polystyrene) were obtained (Table I).

Relatively moderate reaction conditions, i.e., 4 h at 75 °C for the Ru-catalyzed and 15 h at 20 °C for the W-catalyzed polymerization, were sufficient to produce polymer yields of 96%. Thus, the spiro-linked three-membered ring of 1 reduced the rate of polymerization to a smaller extent than the methyl substituent of *syn*-7-methylnorbornene.[8a]

A remarkable feature is the high proportion of trans olefin units (85%) in polymer 2 prepared with the W-based catalyst (Table I).[12] For comparison, a trans/cis olefin ratio of 48/52 was reported for the polymer of *anti*-7-

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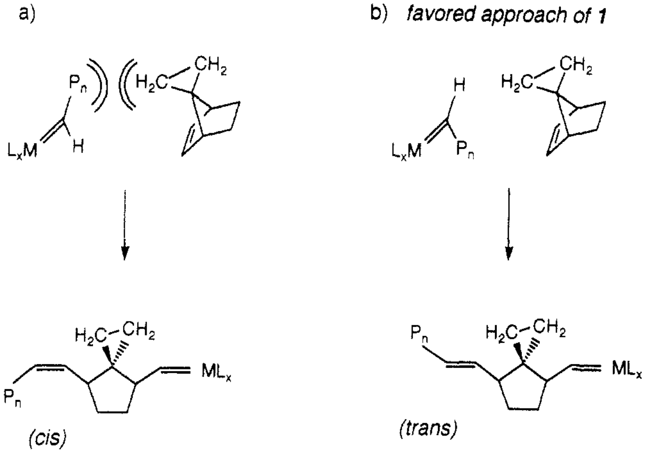
Table I. Olefin Metathesis Polymerization of Spiro(bicyclo[2.2.1]hept-2-ene-7,1'-cyclopropane)

cat.[a]	M_n[b]	M_w/M_n[b]	trans/cis[c]	T_g/°C[d]	yield/%
$RuCl_3$–hydrate	73 000	2.0	95/5	50	96
WCl_6/Ph_4Sn	150 000	2.7	85/15	57	96
$ReCl_5$	e	e			4

[a] Reaction conditions: ($RuCl_3$-hydrate) [M]/[I] (molar ratio of monomer to catalyst) = 250/1, solvent = toluene/ethanol (12/1), 4 h at 75 °C; (WCl_6/Ph_4Sn) [M]/[I] = 50/1 in toluene, 15 h at 20 °C; ($ReCl_5$) [M]/[I] = 50/1 in toluene, 18 h at 75 °C. [b] M_n = number average molecular weight determined by GPC calibrated with polystyrene standards, eluent = chlorobenzene; M_w/M_n = polydispersity index. [c] Ratio of trans/cis C=C double bonds, determined by NMR. [d] Glass transition temperature determined by differential scanning calorimetry. [e] Only a trace of oligomeric material was obtained.

Scheme I. Preferred Formation of trans Olefin Units Due to Steric Hindrance



methylnorbornene synthesized with WCl_6/Bu_4Sn.[8a] Steric effects caused by the cyclopropane ring seemed to be an important factor in the preferential formation of trans olefin linkages. The approach of spiro-monomer 1 with the three-membered ring pointing away from the α-substituent of the transition metal carbene appeared to be less hindered (Scheme Ib).[13]

Furthermore, only a minor amount of oligomeric product could be obtained by reacting spiro-monomer 1 with $ReCl_5$ (Table I), a catalyst known for the production of metathesis polymers containing predominantly cis olefin structures.[8]

It was possible to distinguish trans and cis olefin units and racemic and meso dyads by ^1H NMR spectroscopy (Figure 1a–c). Figure 1a shows the ^1H NMR spectrum of spiro-polymer 2 prepared with WCl_6/Ph_4Sn; Figure 1b (trans/cis olefin ratio = 85/15) and Figure 1c (trans/cis = 95/5) present expanded regions of the olefin and cyclopropane ^1H NMR signals of metathesis polymer 2 prepared with the W- and Ru-based catalyst, respectively. Signals at δ 5.02 ($H^{2,3}$ in Figure 1a–c) and 2.71 ($H^{1,4}$ in Figure 1a) correspond to olefin and allylic hydrogens of units containing cis –C=C– structures; multiplets at δ 4.95, 4.91 ($H^{2,3}$ in Figure 1a–c), and 2.37 ($H^{1,4}$ in Figure 1a) were assigned to olefin and allylic H of trans –C=C– linked monomer units, respectively. The signals at δ 4.95 and 4.91 correspond to trans-meso and trans-racemic dyads, respectively. In addition, trans m units are characterized by a multiplet of the cyclopropane protons at δ 0.22, whereas the cyclopropane protons of trans r dyads gave rise to a multiplet at δ 0.19 (Figure 1b,c).[14]

^{13}C NMR spectroscopy provides a more detailed sequence analysis of poly[2,1'-spirocyclopropane-1,3-cyclopentylenevinylene] (2) (Figure 2a,b). Figure 2a shows the ^{13}C NMR signals of the cyclopentylene carbons of 2 prepared with the W-based catalyst. The weaker signals correspond to monomer units with cis –C=C– structures.[15] Resonances for the allylic carbon atoms ($C^{1,4}$ in Figure 2a) appeared at δ 48.62 (trans–cis triad, r), 48.37 (trans–cis, m), 48.10 (trans–trans, rm), 47.93 (trans–trans, rr), 47.83 (trans–trans, mm), 47.67 (trans–trans, mr), 42.53 and 42.43 (cis–cis triads), 41.92 (cis–trans, r), and 41.78 (cis–trans, m). These assignments were made on the basis of data published about the polymer of *anti*-7-methylnorbornene by Ivin, Rooney et al.[8a,16] In addition, signals corresponding to mm, rm (=mr) and rr triads were resolved for the cyclopropane carbons C^7, C^8, and C^9 of repeating units with trans olefin structures (Figure 2b).

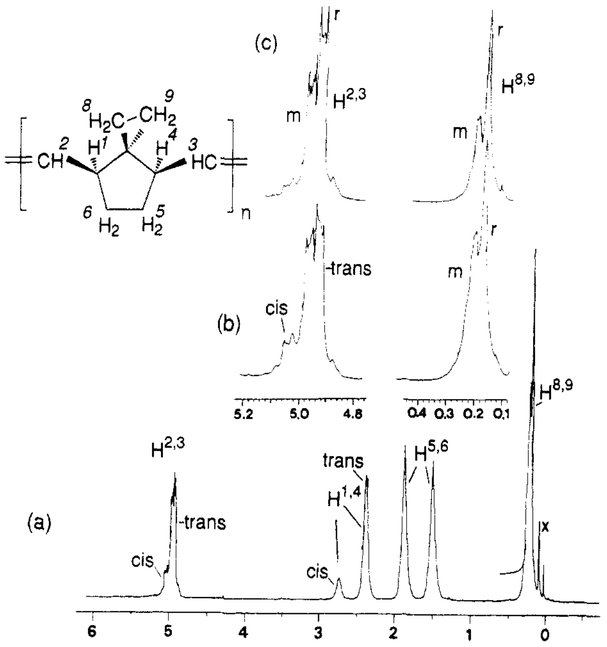
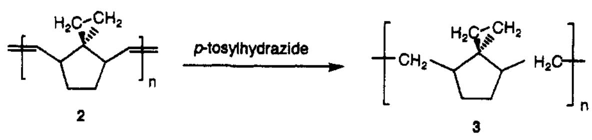


Figure 1. (a) ^1H NMR spectrum of poly[2,1'-spirocyclopropane-1,3-cyclopentylenevinylene (2) (in $CDCl_3$), prepared with WCl_6/Ph_4Sn (1/2); x = impurities. (b) Expanded region of the signals corresponding to the olefin and cyclopropyl protons, $H^{2,3}$ and $H^{8,9}$, respectively; r = racemic, m = meso dyads. (c) Expanded region of the signals of $H^{2,3}$ and $H^{8,9}$, polymer prepared with $RuCl_3$–hydrate.

A slight excess of racemic dyads, r/m = 56/44, was observed for monomer units linked by trans olefin structures. This result contrasts with the observation that trans units are often associated with an excess of meso dyads.[8] By comparison, a small excess of meso dyads has been reported for trans –C=C– linked units of the polymer of *anti*-7-methylnorbornene prepared with WCl_6/Bu_4Sn.[8a]

Polymerization by $RuCl_3$ produced spiropolynorbornene 2 with an even larger r/m ratio of 62/38. A model, again based on steric repulsion, is proposed to account for the preferred formation of racemic dyads. Backside approach of monomer 1 is sterically favored over the frontside approach (Scheme II).

Spiropolynorbornene derivative 2 was hydrogenated by treatment with an excess of *p*-tosylhydrazine (eq 2). The reduced polymer, poly[2,1'-spirocyclopropane-1,3-cyclopentyleneethylene] (3), is partially crystalline with a melt transition at 172 °C.[17] The presence of two different stereochemical configurations, meso and racemic, does not prevent polymer chains of 3 from packing in a regular



(2)

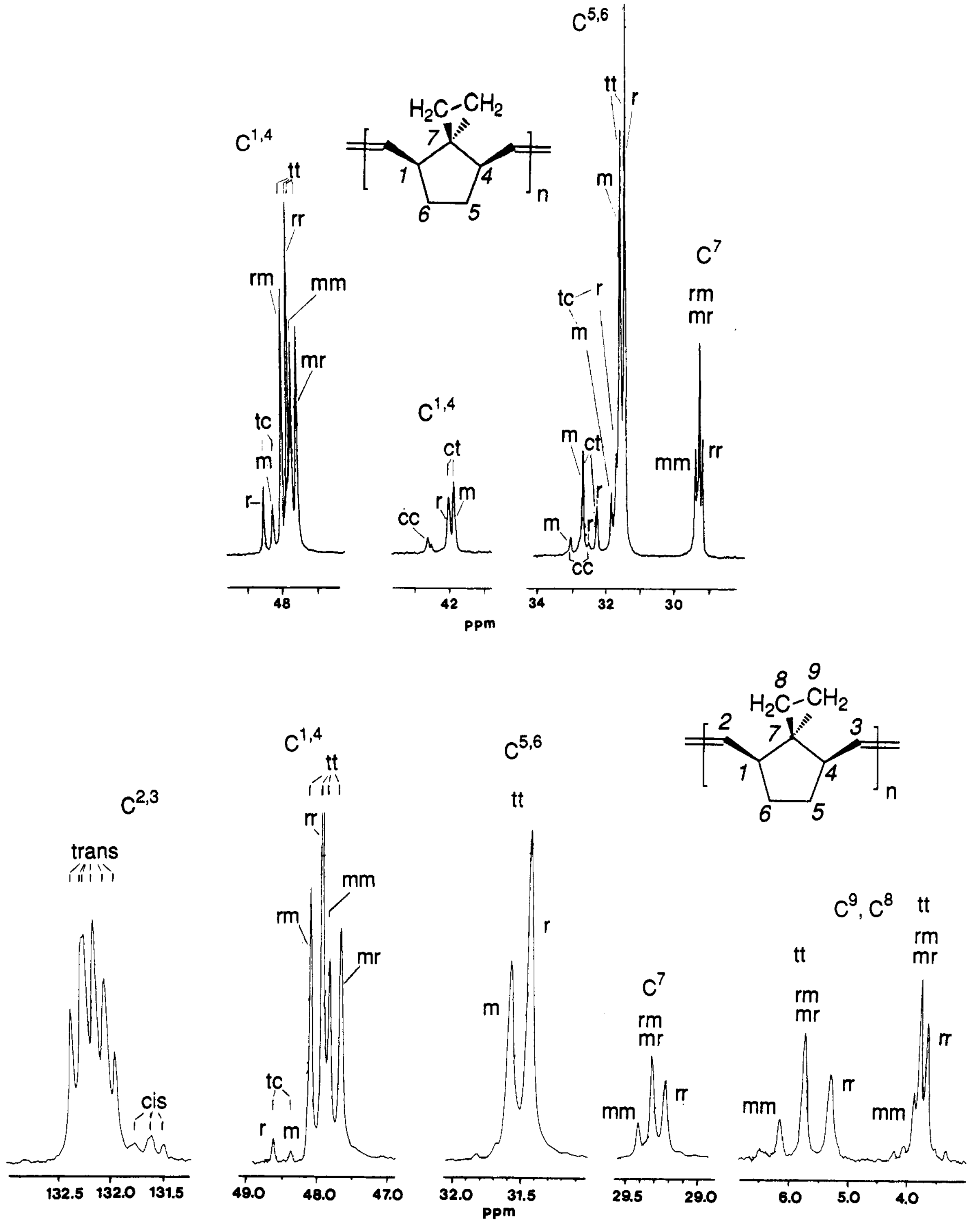
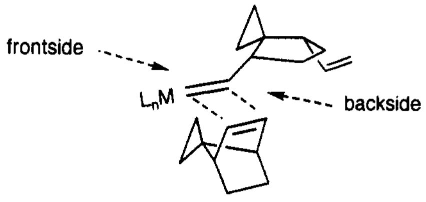


Figure 2. (a, Top) ^{13}C NMR signals of the cyclopentylene unit of poly[2,1′-spirocyclopropane-1,3-cyclopentylenevinylene] (**2**) (in CDCl$_3$), prepared with WCl$_6$/Ph$_4$Sn (1/2). (b, Bottom) ^{13}C NMR spectrum of poly[2,1′-spirocyclopropane-1,3-cyclopentylenevinylene] (**2**) (in CDCl$_3$), prepared with RuCl$_3$–hydrate (r = racemic, m = meso dyads; rm = racemic–meso, rr = racemic–racemic, mm = meso–meso, mr = meso–racemic triads; tc = trans–cis, tt = trans–trans, cc = cis,cis, ct = cis–trans triads).

fashion. By contrast, metathesis polymer **2** is amorphous with a glass transition temperature T_g of 57 °C (polymer with 85% trans –C=C– units and M_n of 150 000, Table I).

Scheme II. Proposed Model[a]



[a] Backside approach leading to trans-meso diads is sterically preferred.

The hydrogenated polymer **3** was considerably less soluble in organic solvents than **2** due to its crystallinity (insoluble in THF, toluene, chloroform; soluble in chlorobenzene and bromobenzene above 70 °C). A ^{13}C NMR spectrum of polymer **3** was recorded in bromobenzene-d_5 at 70 °C (Figure 3). Upon hydrogenation of the double bonds of **2**, the fine structure of $C^{1,4}$ carbons simplified to two signals at δ 45.49 and 44.77 corresponding to meso and racemic dyads, respectively. Only one resonance at δ 4.40 could be observed for carbon C^8 of **3** (Figure 3). ^{1}H

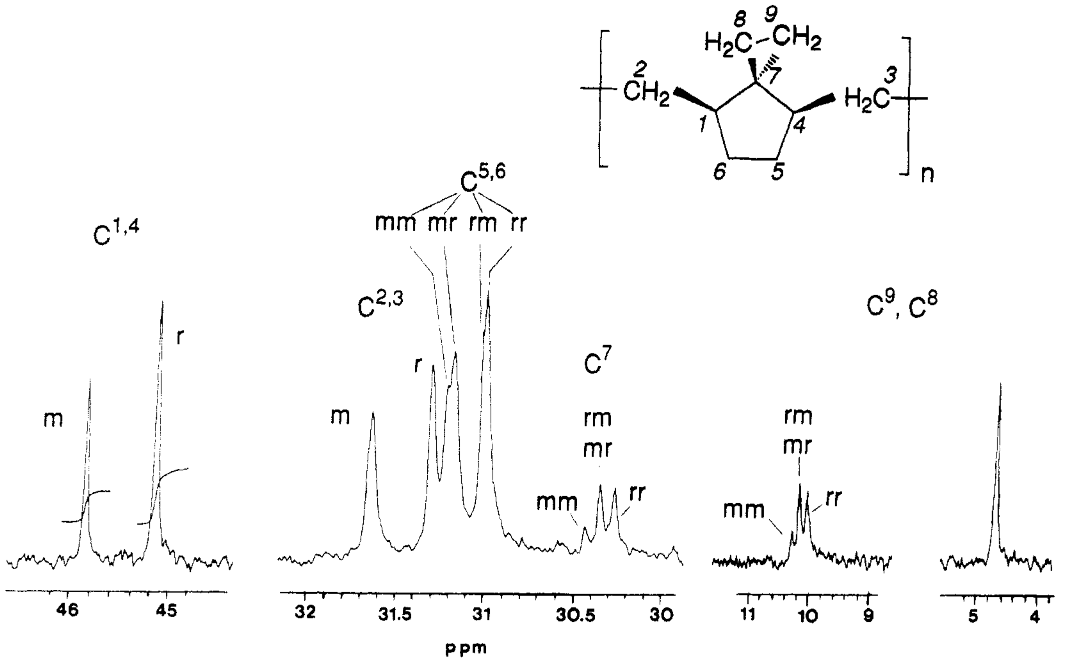


Figure 3. ^{13}C NMR spectrum of poly[2,1′-spirocyclopropane-1,3-cyclopentyleneethylene] (3) (in bromobenzene-d_5, 70 °C) (m = meso, r = racemic dyads; mm = meso–meso, mr = meso–racemic, rm = racemic–meso and rr = racemic–racemic triads).

NMR spectroscopy indicated more than 95% of hydrogenation of the double bonds of 2.

Conclusions

Spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) was polymerized by conventional olefin metathesis catalysts based on W and Ru. Steric hindrance caused by the three-membered ring slightly reduced the rate of polymerization but did not prevent the formation of high molecular weight polymers in excellent yields. Preferential formation of trans olefin units and racemic dyads appeared to be affected by steric repulsion caused by the cyclopropane ring.

Experimental Section

General Procedures and Materials. All work involving air- and/or moisture-sensitive compounds was carried out by using standard high-vacuum Schlenk or drybox (M. Braun) techniques. NMR spectra were recorded on Bruker AC 300 (300.133 MHz), Bruker WH 400 (400.132 MHz), and Bruker AMX 500 (500.137 MHz) instruments. Differential scanning calorimetry was performed on a Mettler DSC 20 (TC 10A processor). Gel permeation chromatographic (GPC) analysis utilized two Polymer Standards Service columns (10-μm gel, SDV linear, 60 cm) and a Knauer differential refractometer (R 2025). Calibration was based on seven polystyrene standards ranging from M_n = 1700 to 560 000. Tungsten hexachloride (99.9%), tetraphenyltin, rhenium pentachloride, and ruthenium trichloride hydrate was used as obtained (Alrich). Toluene was vacuum transferred from sodium benzophenone ketyl and stored under argon. Spiro(bicylo[2.2.1]-hept-2-ene-7,1′-cyclopropane) (1) was synthesized[18] by the following reaction sequence: cycloaddition of spiro[2.4]hepta-4,6-diene[19] and 1,2-dibromoethylene (mixture of cis and trans isomers), isolation of the *endo-cis*-1,2-dibromospiro(bicyclo[2.2.1]-heptane-7,1′-cyclopropane) isomer by distillation and crystallization, hydrogenation with Raney nickel and treatment with zinc dust in methanol. Spiro-monomer 1 was subsequently dried over sodium and distilled under vacuum.

Preparation of Poly[2,1′-spirocyclopropane-1,3-cyclopentylenevinylene] (2). A heavy-walled glass tube equipped with a female NS 14.5 joint and a Teflon valve[20] was charged with 8.36 mg (32 μmol) of ruthenium trichloride hydrate, 4 mL of toluene, and 0.5 mL of ethanol. A monomer solution of 0.96 g (8.0 mmol) of spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) (1) in 3 mL of toluene was added to the red catalyst solution. The mixture was heated to 75 °C for 4 h. The viscous solution was diluted with 15 mL of toluene and poured into 100 mL of methanol to precipitate the polymer. Yield: 0.92 g (96%), M_n = 73 000 (GPC, calibrated with polystyrene).

^{1}H NMR (CDCl$_3$): δ 4.95 (m, $H^{2,3}$, trans, meso), 4.91 (m, $H^{2,3}$, trans, racemic), 2.71 (m, $H^{1,4}$, cis), 2.37 (m, $H^{1,4}$, trans), 1.86 (m, $H^{5,6}$), 1.49 (m, $H^{5,6}$), 0.22 (m, $H^{8,9}$, meso), 0.19 (m, $H^{8,9}$, racemic). ^{13}C NMR (CDCl$_3$): δ 132.35, 132.24, 132.21, 132.11, 132.02 and 131.93 ($C^{2,3}$, trans); 131.76, 131.60, 131.48 (partially unresolved, $C^{2,3}$, cis); 48.62 ($C^{1,4}$, trans–cis, racemic); 48.37 ($C^{1,4}$, trans–cis, meso); 48.10 ($C^{1,4}$, trans–trans, racemic–meso); 47.93 ($C^{1,4}$, trans–trans, racemic–racemic); 47.83 ($C^{1,4}$, trans–trans, meso–meso); 47.67 ($C^{1,4}$, trans–trans, meso–racemic); 41.92 ($C^{1,4}$, cis–trans, racemic); 41.78 ($C^{1,4}$, cis–trans, meso); 32.63 ($C^{5,6}$, cis–trans, meso); 32.22 ($C^{5,6}$, cis–trans, racemic); 31.57 ($C^{5,6}$, trans–trans, meso); 31.43 ($C^{5,6}$, trans–trans, racemic); 29.42 (C^7, trans, meso–meso); 29.32 (C^7, trans, racemic–meso (=meso–racemic)); 29.33 (C^7, trans, racemic–racemic); 6.16 (C^9, trans, meso–meso); 5.76 (C^9, trans, racemic–meso (=meso–racemic)); 5.31 (C^9, trans, racemic–racemic); 3.89 (C^8, trans, meso–meso); 3.80 (C^8, trans, racemic–meso(=meso–racemic)); 3.68 (C^8, trans, racemic–racemic). Anal. Calc for $(C_9H_{12})_n$ [(120.19)$_n$]: C, 89.94; H, 10.06. Found: C, 89.89; H, 10.10.

Preparation of Poly[2,1′-spirocyclopropane-1,3-cyclopentyleneethylene] (3). A 100-mL flask equipped with a condenser was charged with 0.4 g (3.33 mmol) of poly[2,1′-spirocyclopropane-1,3-cyclopentylenevinylene] (2), 50 mL of toluene, and 3.1 g (16.6 mmol) of *p*-tosylhydrazine. This mixture was heated to reflux for 25 h. After cooling, the precipitated product was filtered, washed with methanol and dried in vacuum. Yield: 0.38 g (95%).

^{1}H NMR (bromobenzene-d_5, 70 °C): δ 2.11 (m, 2H, $H^{2,3}$), 1.93 (m, 2H, $H^{2,3}$), 1.57 (m, 2H, $H^{5,6}$), 1.44 (m, 1H, $H^{1,4}$), 1.25 (m, 2H, $H^{5,6}$), 1.08 (m, 1H, $H^{1,4}$), 0.63 (m, 4H, $H^{8,9}$). ^{13}C NMR (bromobenzene-d^5, 70 °C): δ 45.82 ($C^{1,4}$, meso), 45.11 ($C^{1,4}$, racemic), 31.60 ($C^{2,3}$, meso), 31.27 ($C^{2,3}$, racemic), 31.17 ($C^{5,6}$, meso–meso), 31.14 ($C^{5,6}$, meso–racemic), 30.98 ($C^{5,6}$, racemic–meso), 30.96 ($C^{5,6}$, racemic–racemic), 30.41 (C^7, meso–meso), 30.31 (C^7, meso–racemic (=racemic-meso)), 30.23 (C^7, racemic–racemic), 10.20 (C^9, meso–meso), 10.13 (C^9, meso–racemic (=racemic–meso)), 10.00 (C^9, racemic–racemic), 4.70 (C^8). Anal. Calcd for $(C_9H_{14})_n$ [(122.21)$_n$]: C, 88.45; H, 11.55. Found: C, 88.68; H, 11.32.

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(11) A very recent report mentions the metathesis polymerization of spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane): Makovetsky, K. L.; Finkel'shtein, E. S.; Ostrovskaya, I. Y.; Portnykh, E. B.; Gorbacheva, L. I.; Golberg, A. I.; Ushakov, N. V.; Yampolsky, Y. P. *J. Mol. Catal.* **1992**, *76*, 107. These results were presented after we had finished our experimental investigations. NMR spectroscopic analyses of the polymer microstructure have not been reported, yet.

(12) The high trans olefin content, 95% (Table I), of spiropolynorbornene **2** prepared with $RuCl_3$–hydrate is less characteristic, as this catalyst typically leads to methathesis polymers with a high amount of trans olefin units.[8]

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(14) Alternatively, the signals at δ 0.22 and δ 0.19 (Figure 1b,c) could be assigned to $H^{8,9}$, which originate from the syn and anti protons of **1**, respectively. However, the intensity of these signals is not the same but correlates with the ratio of m to r units determined by ^{13}C NMR spectroscopy. The intensity of the signal at δ 0.22 (relative to the intensity of δ 0.19) is lower for polymer **2** prepared with $RuCl_3$ (Figure 1c) than for **2** prepared with the W-based catalyst (Figure 1b). These results indicate that an assignment as m and r is preferable.

(15) The assignment of the ^{13}C NMR signals of polymer **2** is based on the microstructure analysis provided for poly(*anti*-7-methylnorbornene).[8a] The line order of the signals corresponding to the trans and cis olefin carbons $C^{2,3}$ (δ 132.5–131.5) is inverted. This difference is affected by a small upfield shift for the repeating units containing cis carbon–carbon double bonds due to the presence of two substituents linked to C^7. However, the line order for trans/cis of $C^{5,6}$, and in particular $C^{1,4}$, is identical with that of the polymer based on *anti*-7-methylnorbornene.

(16) The different substitution pattern of C^7 of **2** might affect the relative chemical shifts for the individual mm, mr, rm and rr triads. The mm/mr (=rm)/rr sequence for C^7 of poly(*syn*-7-methylnorbornene) is in the reversed order to that of poly(*anti*-7-methylnorbornene);[10] however the sequence for the more distant carbons $C^{5,6}$ remains unaffected (K. J. Ivin, private communication). These results correlate with the assignments of the triad sequences of **2**.

(17) An endothermic transition at 209 °C indicates an ordered melt below this temperature. This has not been characterized yet.

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