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A Novel Route to Block Copolymers by Changing the Mechanism from Living Ring-Opening Metathesis Polymerization of Cyclic Olefins to Aldol Condensation Polymerization of Silyl Vinyl Ethers

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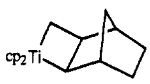
ABSTRACT: Polynorbornene and poly(*exo*-dicyclopentadiene) with one aldehyde end group were synthesized by the living ring-opening olefin metathesis polymerization (ROMP) and the successive reaction with terephthalaldehyde. The aldehyde end group served as an initiator for the silyl aldol condensation polymerization of *tert*-butyldimethylsilyl vinyl ether to give polynorbornene-*block*-poly(silyl vinyl ether) and poly(*exo*-dicyclopentadiene)-*block*-poly(silyl vinyl ether) diblock copolymers with narrow molecular weight distributions. The cleavage of the silyl groups resulted in hydrophobic–hydrophilic block copolymers with poly(vinyl alcohol) as the second polymer block. DSC analyses revealed phase separation for these block copolymers.

Introduction

The transition-metal-catalyzed ring-opening polymerization of cyclic olefins[1] is an important application of the olefin metathesis reaction.[2] Several unsaturated polymers made by this process are currently produced on an industrial scale, including polynorbornene,[3] polyoctenamer,[4] and polydicyclopentadiene.[5]

Over the past few years, titanium,[6,7] tantalum,[8] and tungsten[9] complexes have been developed, which initiate the living polymerization of norbornene.

A comprehensive study[6] has demonstrated the value of the bis(η^5-cyclopentadienyl)titanacyclobutane compounds **1**–**3** as initiators for the ring-opening metathesis polymerization of strained cyclic olefins (eq 1). The polymerization proceeds without termination and chain transfer to give polynorbornene with a narrow molecular weight distribution (polydispersity index = $M_w/M_n < 1.1$). The polymer chain **4** possesses a titanacyclobutane end group which can be reactivated for further polymer growth by heating in the presence of monomer to temperatures above 65 °C. The successive addition of different monomers, such as dicyclopentadiene, benzonorbornadiene, and 6-methylbenzonorbornadiene, results in AB- and ABA-type block copolymers[10] with controlled molecular weights and low polydispersity indexes.



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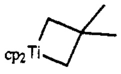

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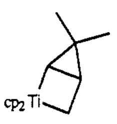

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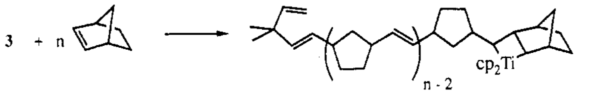

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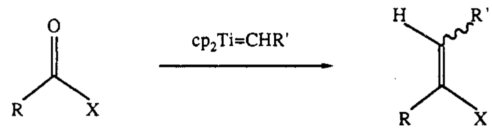
The recently developed aldol condensation polymerization[11] is a new technique for the preparation of poly(vinyl alcohol) precursors. Silyl vinyl ethers are polymerized by an aldehyde initiator in the presence of a Lewis acid. The molar ratio of monomer to initiator controls the molecular weight of the polymer.

The present work demonstrates a new route to well-defined AB diblock copolymers by combining olefin metathesis polymerization and aldol condensation polymerization through the transformation of the metathesis-active end group[12] into an initiator for the aldol-group-transfer polymerization (aldol-GTP). The living character of both polymerization methods enables the synthesis of uniform block copolymers of predictable composition, microstructure, and molecular weight.

Results and Discussion

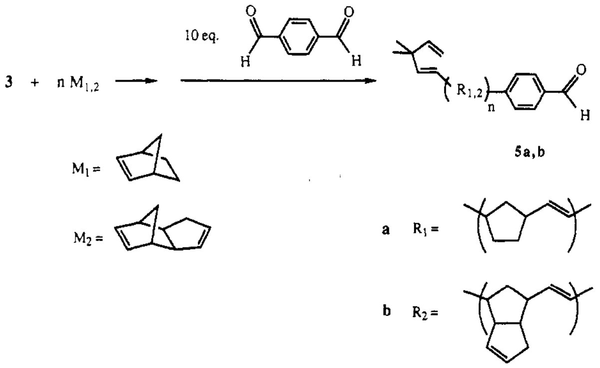
Polynorbornene and Poly(*exo*-dicyclopentadiene) with *p*-Formylstyrene End Groups. Titanium carbenes, generated from titanacyclobutanes and other sources, are known to react with aldehydes, ketones, esters, and amides in a Wittig-analogous reaction[13] (eq 2). The corresponding products are olefins, enol ethers, and enamines. Through these reactions, desired functional groups can be placed at chain ends of polymers.



(2)

X = H, R'', OR'', NR''R'''

By the use of **3** as an initiator, norbornene, and *exo*-dicyclopentadiene were polymerized, and the resulting living polymers were reacted with terephthalaldehyde to give polymers with one aldehyde end group, **5a,b** (eq 3).



5a,b

(3)

A 9-fold molar excess of the dialdehyde was used to favor the one-sided addition over the formation of the diadduct **6**. Heating the toluene solution at 50 °C for 30 min was necessary in order to completely dissolve the dialdehyde. Then the temperature was raised above 65 °C, enabling the metallacycle to open to the corresponding carbene.

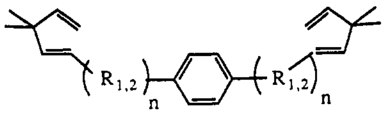


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Table I
Polynorbornene and Poly(*exo*-dicyclopentadiene) with One *p*-Formylstyrene End Group

no.	polymer[a]	theor. M_n[b]	M_n (GPC)[c]	M_w (GPC)[c]	PDI[d]	M_n (corr.)[e]	yield, %
1	**5a**	3380	6700	7400	1.10	3470	80
2	**5a**	7060	14300	15800	1.10	7400	84
3	**5a**	15200	36000	39600	1.10	18700	92
4	**5b**	6670	11900	14300	1.20	6230	89

[a] Polynorbornene **5a**, poly(*exo*-dicyclopentadiene) **5b** as in eq 2. [b] Number-average molecular weight calculated from the molar ratio of monomer to initiator. [c] M_n = number-average molecular weight and M_w = weight-average molecular weight as determined by GPC versus polystyrene standards. [d] Polydispersity index PDI = M_w/M_n. [e] Corrected molecular weight M_n, calculated by dividing M_n(GPC) by a correction factor of 1.93, which was determined by vapor-phase osmometry for the given molecular weight range.

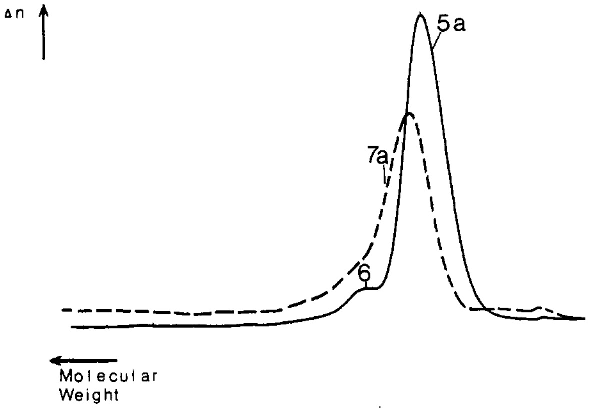


Figure 1. GPC analyses of polynorbornene with one *p*-formylstyrene end group **5a** (solid curve) containing 5 M % of the diadduct **6** and polynorbornene-*block*-poly(*tert*-butyldimethylsilyl vinyl ether) **7a** (broken curve). Block copolymer **7a** was obtained after the polymerization of *tert*-butyldimethylsilyl vinyl ether onto the polymer presented by the solid curve.

Table I lists aldehyde-terminated polymers with molecular weights from 3500 to 18700. The corresponding GPC curves show a second small peak at twice the molecular weight of the main peak, which corresponds to 5–10 M % of diadduct **6** (Figure 1). The presence of **6** increases the polydispersity in comparison to the equivalent polymer end capped with acetone. Samples from the second and fourth polymerizations (Table I) were removed from the reaction mixtures before the addition of terephthalaldehyde and capped with acetone. The PDI for the second polymer was 1.06 when capped with acetone and 1.1 when capped with dialdehyde; for the fourth polymer, the respective PDI values were 1.1 and 1.2. Unreacted terephthalaldehyde was completely removed from the polymer after 24 h of extraction with acetone.

The ^1H NMR spectrum (Figure 2A) shows two sets of signals for the aromatic aldehyde end group, corresponding to a ratio of 60/40 for trans to cis carbon–carbon double bond formation in the end-capping reaction. The cis end group shows one singlet for the aldehyde proton (d = 9.97 ppm), a doublet for the aromatic protons ortho (d = 7.83 ppm), and a second doublet for the aromatic protons meta to the aldehyde group (d = 7.53 ppm). Correspondingly, the trans end group shows a singlet for the aldehyde proton at 9.94 ppm and a doublet each for the aromatic protons ortho and meta at 7.79 and 7.60 ppm, respectively. These spectral data demonstrate a preference for the E isomer in the reaction (eq 3). This contrasts with the predominant formation of Z isomers in Wittig reactions of polymeric and low molecular weight phosphorylides with terephthalaldehyde under anhydrous conditions.[14]

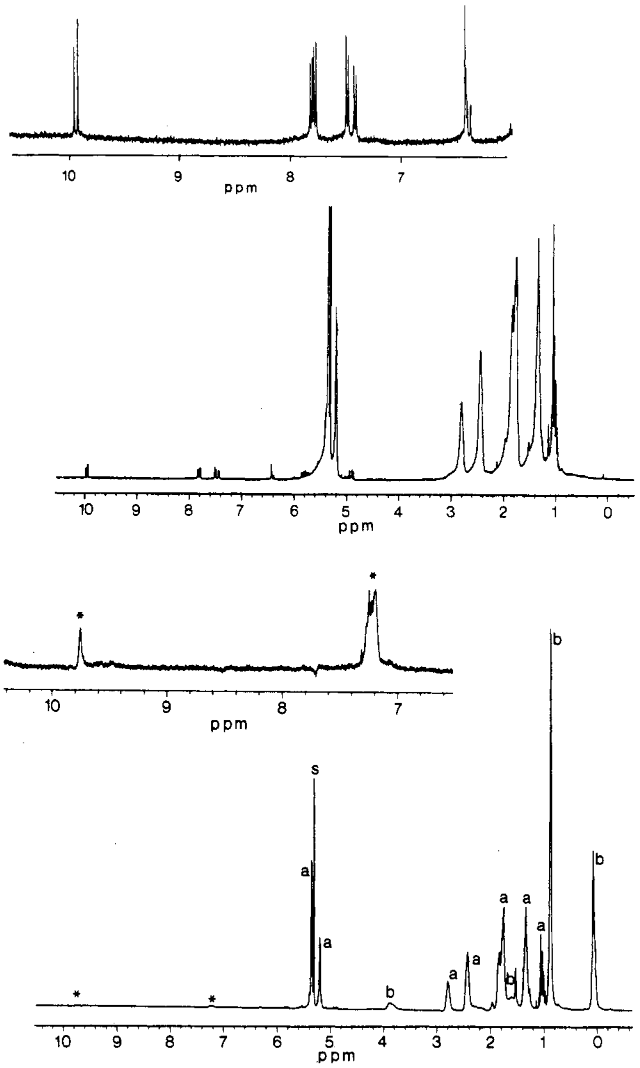
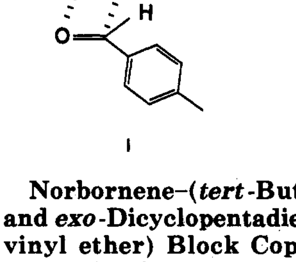


Figure 2. (a) 400-MHz ^1H NMR spectrum of polynorbornene with one *p*-formylstyrene end group **5a** containing 35 monomer units of norbornene in CD_2Cl_2. The signals with a chemical shift above 7 ppm show the aromatic aldehyde end group. (b) 400-MHz ^1H NMR spectrum of polynorbornene-*block*-poly(*tert*-butyldimethylsilyl vinyl ether) [77 monomer units of norbornene (marked by a) and 30 monomer units of the silyl vinyl ether (marked by b)] in CD_2Cl_2; * = aromatic protons and the aliphatic aldehyde proton.

The similar E/Z ratios for the end group of **5a,b** and the internal carbon–carbon double bonds of the polynorbornene chain (62/38)[6] indicate similar steric requirements for the addition of terephthalaldehyde and norbornene to the ring-opened titanacyclobutane group of **4**. The transition state outlined in I is slightly preferred over that of II.



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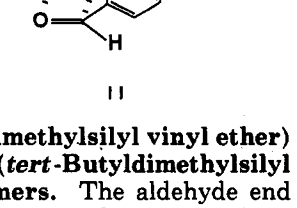
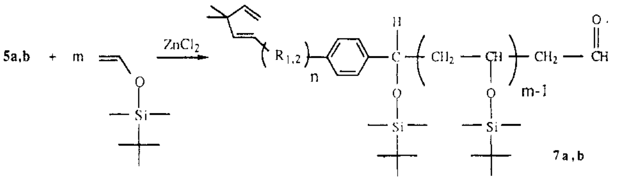


II

Norbornene–(*tert*-Butyldimethylsilyl vinyl ether) and *exo*-Dicyclopentadiene–(*tert*-Butyldimethylsilyl vinyl ether) Block Copolymers. The aldehyde end group of **5a,b** is the initiator for the subsequent polymerization of *tert*-butyldimethylsilyl vinyl ether (eq 4). In



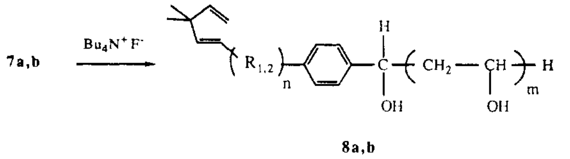
(4)

a crossed aldol condensation reaction, the silyl vinyl ether adds with carbon–carbon bond formation to the aldehyde group, which is activated by a Lewis acid ($ZnCl_2$). Simultaneously, the silyl group migrates to the oxygen of the aldehyde group, and a new aldehyde group is generated, which then initiates the addition of the next monomer unit. This process continues forming the second polymer block. Table II lists block copolymers containing from 20 to 66 monomer units (m) of the silyl vinyl ether.

The relative ratio of the two monomer units of $R_{1,2}$ and silyl vinyl ether was determined by ^{1}H NMR spectroscopy (Figure 2b). Assuming complete incorporation of the second monomer into the block copolymer, i.e., no formation of homopolymer, integration of the signal at d = 0.09 ppm (6 H, $Si(CH_3)_2$) versus the integration of the olefinic protons of the monomer units $R_{1,2}$ (2 H for norbornene, 4 H for dicyclopentadiene) in combination with n (calculated from M_n(corr.) in Table I) gives m. No remaining signals of the initiating aromatic aldehyde end group can be detected for the polymers of Table I. Instead, the spectrum shows a broad multiplet for the four aromatic protons of **7a,b** at d = 7.22 ppm and a singlet for the new aliphatic aldehyde proton at d = 9.76 ppm (Figure 2b). This indicates the complete transformation of the original polynorbornene and poly(*exo*-dicyclopentadiene) into block copolymer **7a,b** in accordance to a shift of the GPC (gel permeation chromatography) curve to a higher molecular weight (Figure 1).

Relatively high concentrations of $ZnCl_2$ (0.4–2.6 mmol/g of polymer) were employed to ensure the completion of the silyl vinyl ether polymerization within 24 h. The presence of some silyl vinyl ether homopolymer (22% by weight of low molecular weight homopolymer) was detected only for the polymer produced in run 8a (Table II). The high concentration of Lewis acid was probably responsible for its formation. After extracting the homopolymer by treatment with acetone and ethyl acetate, pure block copolymer was obtained, thereby reducing the PDI from 1.58 to 1.22 (polymer 8a, Table II).

Norbornene–(Vinyl alcohol) and *exo*-Dicyclopentadiene–(Vinyl alcohol) Block Copolymers. Treatment of **7a,b** with tetrabutylammonium fluoride,[15] followed by the addition of methanol as a proton source, resulted in the cleavage of the silyl groups to produce hydrophobic–hydrophilic AB diblock copolymer **8a,b** with poly(vinyl alcohol) as the hydrophilic segment (eq 5).



(5)

8a,b

β-Hydroxy aldehydes are known to undergo cleavage in a retrograde aldol reaction in the presence of nucleophiles and bases.[16] To prevent any polymer degradation by this mechanism, the aldehyde end group of **7a,b** was reduced with $NaBH_4$ to the corresponding alcohol group prior to the desilylation reaction. After reduction, the ^{1}H signal at d = 9.76 ppm had completely disappeared, indicating complete conversion. It was difficult to find a solvent for the direct characterization of **8a,b** by NMR spectroscopy due the different solubility behavior of the two polymer blocks. Block length as low as 30 for the poly(vinyl alcohol) segment made **8a,b** insoluble in many typical NMR solvents, including THF, toluene, chlorform, dichloromethane, DMF, and DMSO. Derivatization of the poly (vinyl alcohol) segment by acetylation afforded a soluble block copolymer, thus providing an indirect method to characterize **8a,b** by ^{1}H NMR spectroscopy. By integration of the ^{1}H NMR signals of the acetyl protons at d = 2.02 ppm (Figure 3) versus the olefinic protons of the polynorbornene, 25 monomer units for the poly(vinyl acetate) segment were calculated for converted polymer **6** (Table II). This value lies well within the experimental error of the expected value of 30. The sizes of the signals at d = 0.09 ppm (residual $Si(CH_3)_2$) and at d = 4.05 ppm (residual C(H)OH) demonstrate a higher than 98% conversion for the desilylation reaction and more than 95% acetylation.

Table II
AB Diblock Copolymers with *tert*-Butyldimethylsilyl Vinyl Ether Segments

no.[a]	n[b]	m[b]	m(theor.)[c]	M_n[d]	M_w[d]	PDI[e]
5	35	20	25	8 500	10 250	1.2
6	77	30	40	18 000	20 100	1.1
7	77	66	73	13 700	18 600	1.4
8	45	49	51	10 800	17 100	1.6
8a	45	29	51	14 900	18 200	1.2

[a] Block copolymers 5–7 were prepared from polynorbornene **5a**; 8 was prepared from poly(*exo*-dicyclopentadiene) **5b**. [b] n = monomer units of ring-opened cyclic olefin; m = monomer units of silyl vinyl ether in **6**. [c] Theoretical m, calculated from the ration of monomer to initiator and monomer conversion. [d] M_n,M_w = number- and weight-average molecular weight determined by GPC. [e] Polydispersity index.

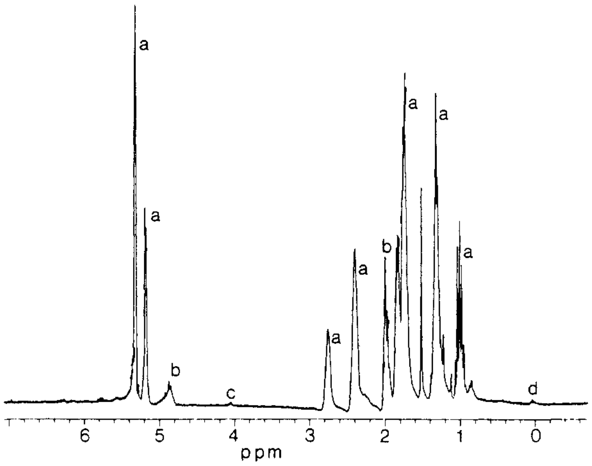


Figure 3. 400-MHz ^{1}H NMR spectrum of polynorbornene-*block*-poly(vinyl acetate) in $CDCl_3$; a = norbornene units, b = vinyl acetate units, c = residual vinyl alcohol units, and d = residual silyl vinyl ether units.

The acetylated block copolymer was isolated by precipitation with methanol. Methanol is known to be a good solvent for poly(vinyl acetate) homopolymers. The presence of the poly(vinyl acetate) segment after this work-up procedure presents further proof for its attachment to the polynorbornene block as a block copolymer.

Desilylation and acetylation are only two examples of a variety of polymer functionalization reactions, such as esterification and etherification. The resulting structural changes will enable properties such as hydrophilicity and polarity of the polymer to be fine tuned.

Thermal Properties. Previous DSC (differential scanning calorimetry) studies on norbornene–*exo*-dicyclopentadiene diblock and triblock copolymers[10] showed that these polymers were amorphous. A single homoge-

Table III
DSC Analyses of Homopolymers and Block Copolymers

polymer[a]	M_n(A)[b]	M_n(B)[b]	T_g(A)[c], °C	T_g(B),[c] °C	T_m(B),[c] °C
NBE	7400		32		
NBE–SiVE	7400	4 740	36		
NBE–SiVE	7400	19 500	37	63	
NBE–VAI	7400	1 320	35	67	
x-DCP	6230		107		
x-DCP–SiVE	6230	7740	112	71	
x-DCP–VAI	6230	2 160	109		202

[a] Homopolymers NBE = norbornene, *x*-DCP = *exo*-dicyclopentadiene. Block copolymers: NBE–SiVE = polynorbornen-*block*-poly(*tert*-butyldimethylsilyl vinyl ether), VAI = vinyl alcohol segment. [b] M_n(A) and M_n(B) = number-average molecular weights of block A (NBE or *x*-DCP) and blocks B (SiVE or VAI). [c] T_g(A) and T_g(B) = glass transition temperature of blocks A and B, T_m = melt transition temperature of B.

neous phase was formed due to their similar structure. Those studies involved block copolymers with molecular weights up to 15 000.

Data for the DSC analysis of the norbornene–(*tert*-butyldimethylsilyl vinyl ether), norbornene–(vinyl alcohol), *exo*-dicyclopentadiene–(*tert*-butyldimethylsilyl vinyl ether), and *exo*-dicyclopentadiene–vinyl alcohol block copolymers are presented in Table III. No phase separation can be detected by DSC for the norbornene/(silyl vinyl ether) system with low molecular weight segments (7400/4740). Phase separation occurs when the silyl vinyl ether block is larger (M_n = 19 500), and two glass transitions are observed: T_{g1} = 37 °C for the polynorbornene segment and T_{g2} = 63 °C for the silyl vinyl ether block. A possible explanation for the small increase of T_{g1} (32 °C for the corresponding homopolymer) is the existence of some phase mixing at the interphase of both segments. A molecular weight of 7740 for the silyl vinyl ether block is large enough for phase separation to occur in the *exo*-dicyclopentadiene/silyl vinyl ether system.

Polynorbornene-*block*-poly(vinyl alcohol) forms two separated phases when the molecular weight of vinyl alcohol block is as low as 1320: T_{g2} = 67 °C. This block copolymer is amorphous. At higher molecular weights, crystallization of the phase-separated vinyl alcohol segment occurs. An *exo*-dicyclopentadiene–vinyl alcohol block copolymer with a vinyl alcohol block of M_n = 2160 shows a melt transition: T_m = 202 °C.

Conclusion

New block copolymers with narrow molecular weight distributions were prepared by combining two different polymerization methods: ring-opening olefin metathesis polymerization and aldol-group-transfer polymerization. The first polymer segment [polynorbornene and poly(*exo*-dicyclopentadiene)] was obtained by olefin metathesis. A Wittig-analogous reaction converted the metathesis active end group of the polymer chain into an initiator for the synthesis of the second segment. Processes, by which the polymerization mechanism can be changed to suit the monomers being polymerized, extend the range of possible monomer combinations in block copolymer.

Further modifications of the block copolymers resulted from chemical reactions on the monomer unit of the second polymer block. These reactions were the cleavage of Si–O bonds and the acetylation of the resulting hydroxyl groups. The resulting block copolymers combine hydrophobic and hydrophilic blocks. These polymers could be applied[17] as dispersants, emulsifiers, flocculants, demulsifiers, wetting agents, foam stabilizers, and agents to make polymer blends compatible. Furthermore, poly(vinyl alcohol) has a low permeability for oxygen,[18] and additional applications may arise from this property.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed by using standard high-vacuum, Schlenk, or drybox (Vacuum Atmospheres) techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. ^{1}H NMR spectra were recorded on a JEOL GX-400 (399.65 MHz). A Perkin-Elmer 1310 infrared spectrophotometer was used for IR spectroscopy. Gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary use (column: 0.25 mm × 50 m DBI, SE 30) and equipped with a Hewlett-Packard Model 339A integrator. Flash chromatography was performed by the procedure of Still et al.[17] using silica gel 60 (230–400-mesh ATM, EM Reagents).

Gel permeation chromatographic (GPC) analyses utilized Shodex KF-803, KF-804, and KF-805 columns and a Knauer differential refractometer. All GPC analyses were performed on 0.50% w/v solutions of polymer in CH_2Cl_2. An injection volume of 0.100 mL and a flow rate of 1.5 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polysciences) ranging from M_n = 3550 to 600 000. The molecular weight averages and distribution were calculated by standard procedures[18] from the refractive index and were not corrected for peak broadening.

Vapor-phase osmometry (VPO) was performed on polymer solutions in benzene (concentration range: 10^{-3}–10^{-2} mol/L) at 47 °C using a Wescan molecular weight apparatus Model 233.

Materials. Metallacycle 3 was prepared as previously described.[6] Norbornene was purchased from Aldrich, refluxed over sodium, and distilled prior to use.

exo-Dicyclopentadiene (Wiley Organics, 95% exo, 5% endo) was stirred over sodium for 12 h and then vacuum distilled. Terephthalaldehyde (Aldrich) was sublimed. *tert*-Butyldimethylsilyl vinyl ether was synthesized according to the literature procedure[19] and spinning band distilled under argon.

Zinc chloride (Aldrich) was dried under vacuum at 250 °C. Toluene and THF were vacuum transferred from sodium benzophenone ketyl into a dry vessel equipped with a Teflon valve closure and stored under argon. Pyridine (Baker, grade photorex) was dried over 4-Å molecular sieves. A 1 M solution of tetrabutylammonium fluoride in THF (Aldrich) and benzene (Aldrich, glass distilled) were used as obtained from the manufacturer. Reagent grade methanol, acetic anhydride, and glacial acetic acid were used without further purification. Dichloromethane was distilled from CaH_2 under argon.

Preparation of the Aldehyde-Terminated Polymers. A standard solution of norbornene was prepared from 10.6 g of norbornene and 11.77 g of toluene. A heavy-walled glass tube equipped with a female 14/20 joint and a Teflon valve[10] was charged with 57 mg (0.219 mmol) of metallacycle 3 and 3.17 g of the standard norbornene solution (16 mmol, 73 equiv of norbornene). Toluene was added to give a total volume of 10 mL. The solution was stirred (magnetic stirrer) in an oil bath at 74 °C, and the polymerization was followed by capillary VPC. The monomer was consumed at a rate of 24 equiv/h. at 98% completion, the reaction mixture was allowed to cool at 25 °C. By syringe, 0.5 mL of the solution was transferred into a similar glass tube. The first tube (reaction 1) was charged with 279 mg (2.08 mmol, 10 equiv/Ti) of terephthalaldehyde and the second (reaction 2) with 40 μL of acetone (0.55 mmol, 50 equiv/Ti). Reaction 1 was heated at 50 °C for 0.5 h to dissolve the dialdehyde. The temperature was raised to 75 °C, and both glass tubes were heated for 0.5 h. The initial dark-red solution became dark brown for reaction 1 (terephthalaldehyde) and pale orange for reaction 2 (acetone). After cooling to 25 °C, both solutions were flash chromatographed (toluene) and the polymers isolated by precipitation with methanol. The pale-yellow, aldehyde-capped polymer was Soxhlet extracted with acetone for 24 h. Both polymers were dried under vacuum (10^{-3} Torr) for 24 h. Yield of the isolated aldehyde-terminated polymer: 1.17 g (84%, polymer 2, Table I). The other polymers of Table I were prepared under identical conditions (86–98% conversion of monomer; the reactions were terminated before complete consumption of monomer) with different ratios of monomer to initiator.

exo-Dicyclopentadiene was polymerized at 78 °C. The polymerization rate was 8 equiv/h.

Synthesis of Polynorbornene-*block*-poly(*tert*-butyldimethylsilyl vinyl ether). A heavy-walled glass tube equipped with a female 14/20 joint and a Teflon valve was charged with 380 mg (51.3 μmol) of polymer 2 ($M_n = 7400$), 85 mg (0.625 mmol) of $ZnCl_2$, 20 mg of toluene (internal standard for VPC), and 8 mL of dichloromethane. Following the addition of 351 mg (2.45 mmol) of *tert*-butyldimethylsilyl vinyl ether, the reaction vessel was heated to 30 °C with an oil bath and then stirred (magnetic stirrer) for 18 h. A small amount of $ZnCl_2$ remained undissolved. Capillary VPC showed 92.6% conversion of the monomer. The polymer was isolated by precipitation with methanol and dried under vacuum (10^{-3} Torr) for 24 h. Yield: 590 mg (81%) (polymer **6**, Table II). The other polymers of Table 2 were prepared similarly.

Reduction of the Aldehyde End Group. In a Schlenk flask, 570 mg (47 μmol) of block copolymer (polymer **6**, Table II) was dissolved in 8 mL of $THF \cdot NaBH_4$ (50 mg, 1.32 mmol), 40 μL of H_2O was added, and the mixture was stirred at room temperature for 5 h. The polymer was precipitated with methanol, and the stirring was continued for 1 h to ensure decomposition of unreacted $NaBH_4$. The polymer was dried under vaccum for 24 h. Yield: 520 mg (88%). The other polymers of Table II were reduced in a similar fashion.

Polymer from run 8 (Table II) was further treated by dissolving it in chloroform and reprecipitating it in acetone 3 times. The polymer was stirred with ethyl acetate, isolated by centrifugation, washed with acetone, and dried under vacuum to give **8a** (Table II). The combined centrifugates contained 22% by weight of silyl vinyl ether homopolymer.

Cleavage of the Silyl Groups. In a Schlenk flask, 460 mg (38 μmol) of polymer 6 (Table II) was dissolved in 25 mL of THF, and 4 mL (2.5 M excess) of tetrabutylammonium fluoride solution (1.0 M solution in THF) was added. The solution turned yellow while stirring for 4 h at room temperature. Subsequently, 2 mL of methanol (distilled from Mg) was added, and the stirring was continued for an additional 2 h at room temperature. The solution remained homogeneous. The polymer was isolated by precipitation with methanol and was dried under vacuum for 24 h. Yield: 300 mg (91%). The same procedure was applied to the reduced polymer of 8 (Table II).

Acetylation of the Vinyl Alcohol Segment. A Schlenk flask equipped with a condenser was charged with 75 mg (9 μmol) of polynorbornene-*block*-poly(vinyl alcohol) derived from polymer **6** (Table II), 0.7 mL of acetic anhydride, and 0.7 mL of acetic acid. The mixture was heated to reflux for 2 h. After 1 h, the polymer completely dissolved. The acetylated block copolymer was isolated by precipitation with methanol and dried under vacuum (10^{-3} Torr) for 24 h. Yield: 79 mg (92%).

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References and Notes

(1) Ring-opening polymerization reviews: (a) Calderon, N. *J. Macromol. Sci., Rev. Macromol. Chem.* **1972**, *C7*(1), 105. (b) Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219. (c) Reference 2.

(2) Olefin metathesis reviews: (a) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*; Wiley-Interscience: Chichester, 1985. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 8, pp 499–551. (d) Banks, R. L. *Catalysis (London)* **1981**, *4*, 100. (e) Basset, J. M.; Leconte, M. *CHEMTECH* **1980**, *10*, 762.

(3) (a) Ohm, R.; Stein, C. In *Encyclopedia of Chemical Technology*, 3rd ed.; Grayson, M., Ed.; Wiley-Interscience: New York, 1982; Vol. 18, pp 436–442. (b) Ohm, R. F. *CHEMTECH* **1980**, *10*, 198. (c) Le Delliou, P.; Manager, H. D. *Gummi, Asbest, Kunstst.* **1977**, *30*, 518.

(4) (a) Streck, R. *CHEMTECH* **1983**, *13*, 758. (b) Dräxler, A.; Konietzny, A. *Lichtobogen* **1986**, *35* (No. 205), 24. (c) Dräxler, A. *Katusch. Gummi, Kunsts.* **1983**, *36*, 1037. (d) Reference 2a, p 331.

(5) (a) Newburg, N. R. (Hercules Inc.) Eur. Pat. Appl. EP 139170, 1985. (b) Newburg, N. R. (Hercules Inc.) U.S. Patent 4,535,097, 1985. (c) Nguyen, T. T. (Hercules Inc.) Eur. Pat. Appl. EP 142861, 1985.

(6) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

(7) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1488.

(8) Wallace, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 448.

(9) (a) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macomolecules* **1987**, *20*, 1169. (b) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 874.

(10) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1988**, *21*, 1961.

(11) (a) Sogah, D. Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*(1), 163. (b) Sogah, D. Y.; Webster, O. W. *Macromolecules* **1986**, *19*, 1775.

(12) Risse, W.; Grubbs, R. H., submitted for publication in *Makromol. Chem., Rapid Commun.*

(13) (a) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2316. (b) Clawson, L. E.; Buchwald, S. L.; Grubbs, R. H. *Tetrahedron Lett.* **1984**, *5733*. (c) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (d) Pine, S. H.; Zahler, R.; Evans, D. A. *Grubbs*, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

(14) (a) Castells, J.; Font, J.; Virgili, A. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1. (b) Delmas, M.; Le Bigot, Y.; Gaset, A.; Gonichon, J. P. *Synth. Commun.* **1981**, *11*, 125.

(15) Corey, E. J.; Snider, B. B. *J. Am. Chem. Soc.* **1972**, *94*, 2549.

(16) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985.

(17) (a) Schmolka, I. R. *J. Am. Oil Chem. Soc.* **1977**, *54*, 110. (b) Lundsted, L. G.; Schmolka, I. R. In *Block and Graft Copolymerization*; Ceressa, R. J., Ed.; Wiley: New York, 1976; Vol. 2, pp 1–111. (c) Dominguez, R. J. G. (Texaco, Inc.) U.S. Patent 4,273,884, 1981.

(18) Martins, J. G.; Mowry, N. I. (Monsanto) U.S. Patent 3,516,960, 1970.

(19) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(20) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Chromatography*; Wiley: New York, 1979.

(21) Jung, M. E.; Blum, R. B. *Tetrahedron Lett.* **1977**, 3791.