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Homologous Poly(isobutylene)s: Poly(isobutylene)/High-Density Poly(ethylene) Hybrid Polymers

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ABSTRACT: We report on the synthesis of poly(*homo*-isobutylene) and poly(*homo*-α-methylstyrene) and the thermal properties of these new polymers. Based on the ring-opening metathesis polymerization (ROMP) of 3,3-dimethylcyclopropene and 3-methyl-3-phenyl-cyclopropene, the respective ring-opened polymers were generated. Several catalytic systems (first-generation (**I**), second-generation (**II**), third-generation Grubbs-type (**IV**) and the Schrock-type initiator Mo(N-2,6-*i*$Pr_2C_6H_3$)($CHCMe_2Ph$)($OCMe_3$)$_2$ (**III**) were used. Particularly **II**, **III** and **IV** offered access to living polymerization reactions in the case of 3-methyl-3-phenyl-cyclopropene, however, not with 3,3-dimethylcyclopropene. The obtained ROMP-polymers were hydrogenated using tosylhydrazide, furnishing poly(*homo*-isobutylene) and poly(*homo*-α-methylstyrene) in high yields. Thermal-measurements (DSC-measurements) revealed T_g- and T_m-values located between those of poly(isobutylene), poly(styrene), and high-density poly(ethylene).

Introduction

Homologous poly(olefin)s constitute a class of polymers that are derived from their well-known counterparts (i.e., vinyl-type polymers) by insertion of one or more $-(CH_2)-$ units into the repeat unit of the polymer. These polymers therefore often represent structural hybrids between 1,2-linked polymers and high-density poly(ethylene) (HDPE), thus reflecting a quite unusual mixture of material properties. As shown in Scheme 1, the homologue of poly(isobutylene) **1** would be poly(*homo*-isobutylene) **2a**; the homologue of poly(α-methylstyrene) **2c** would be poly(*homo*-α-methylstyrene) **2b**.

With some exceptions, syntheses and investigations of homologous polymers are rarely reported in literature since 1,3-based polymerization reactions are mechanistically relatively scarce reactions. The approach toward this class of polymers is therefore often achieved via hydrogenation strategies of unsaturated polymers, preceded by the synthesis of the appropriate olefinic-polymers.[1−4] Thus, poly(butadiene)s and poly(isoprene)s, easily accessible via radical or anionic polymerization, can serve as starting points for HDPE- and PE-*alt*-PP type polymers, respectively, after hydrogenation of the olefinic moieties within the chain.[5−8] With the advent of ring-opening metathesis polymerization (ROMP)[9−11] as a controlled polymerization process, the access to regular olefinic polymers has become broader.[12,13] Thus, various three-,[14] four-,[8,10,15−18] five-[19,20] and higher membered cycles[19] can be ring-opened and polymerized, yielding the respective substituted unsaturated polymers with controllable chain length and unsaturation. Surprisingly, the strategy to use these unsaturated polymers for the subsequent generation of homologous polymers has not been exploited intensely. Several authors have reported on the ROMP of pure and substituted cyclobutenes[8,10,15−18] as well as cyclopropenes,[14,21] but only two further hydrogenation reactions after the ROMP of cyclobutenes, however, without any further characterization of the respective homologous polymers, have been described.[8,16]

Alternatively, poly(*homo*-isobutylene) **2a** has been prepared previously via cationic polymerization using 3-methyl-1-butene, which is isomerized during the polymerization reaction.[22] However, since the process was not living, the structural control over the polymerization reaction was poor.

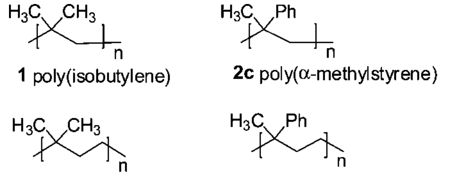
In the present work, we report on the synthesis of poly(*homo*-isobutylene) **2a** and poly(α-methylstyrene) **2b** by use of a combination of ROMP of substituted cyclopropenes and subsequent hydrogenation strategies (Scheme 2).

Since polymers **2a** and **2b** formally possess hybrid structures between the known PIB/poly(α-methylstyrene) and high-density poly/ethylene) (HDPE), the glass transition temperatures of **2a** and **2b** may well be expected to be located between the one found for HDPE and poly(α-methylstyrene). Since the differences in both T_g and T_m between PIB ($T_g \sim -80$ °C, only strain induced crystallization[23]) and HDPE ($T_g \sim -128$ °C to -30 °C; $T_m \sim 137-142$ °C)[24] are quite distinct, poly(*homo*-isobutylene), in particular, may be expected to represent an exciting material.

Experimental Section

General Data. Nuclear magnetic resonance (NMR) data were obtained on a Varian Gemini 2000 FT-NMR spectrometer (200

Scheme 1. Chemical Structures of Polymers 1 and 2



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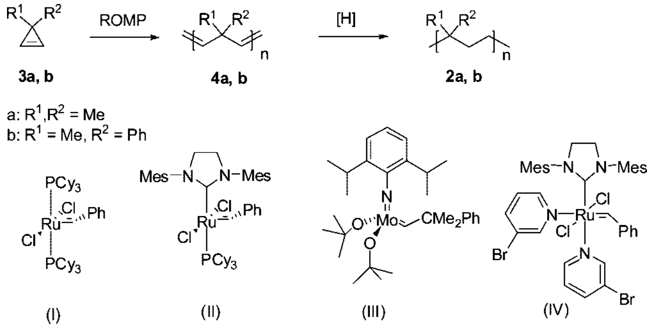
Scheme 2. Synthetic Strategy for the Preparation of 2a and 2b via Ring Opening Metathesis Polymerization (ROMP) Using the Initiators I−IV



and 400 MHz). Chloroform-d_1 (Isotec Inc. 99.8 atom % D) and benzene-d_6 were used as solvents. For the analysis of the FIDs, the Mestrec 4.7.0.0 program was used. Chemical shifts are reported in parts per million (*δ*) and referenced to the residual protonated solvent ($CDCl_3$, 7.26 ppm (^1H), 77.0 ppm (^{13}C); C_6D_6, 7.16 ppm (^1H)). Polymeric samples were measured at 50 °C in $CDCl_3$ and kinetics of **3b** were measured at 50 °C in $CDCl_3$ or at 22 °C in benzene-d_6. The polymerization kinetics of **3a** and **3b** by the action of **I−IV** were measured on a 200 and 400 MHz MMR spectrometer, respectively, using $CDCl_3$ or benzene-d_6. High-temperature size-exclusion chromatography and high-temperature size-exclusion-chromatography (GPC, HT-GPC) measurements for polymers **4a** and **2a** were carried out on a PL-GPC 220 High Temperature Chromatograph (Polymer Laboratories, Germany) at 145 °C in trichlorobenzene with a sample concentration of approximately 4 mg/mL, using three consecutive PLgel 10 *μ*m Mixed LS-columns (300 × 7.5 mm; Polymer Laboratories, Germany, 2 Polymer Laboratories Mixed B columns (10 *μ*m particle diameter, 300 × 7.5 mm), one Polymer Laboratories Mixed B LS column (10 *μ*m particle diameter, 300 × 7.5 mm)). Pore size distributions were not available (see: http://www.polymerlabs.com/products/000049.html); size-exclusion range: ~500−1 000 000 g mol^{-1}, a Precision Detectors PD2040 light scattering detector, an integrated RI-detector and a PL-BV 400 viscosimeter. In addition, poly(styrene) standards were used for external calibration. GPC measurements for **4b**, **2b** were carried out on a GPCmax VE 2001 (Viscothek) using a Styragel GMH_{HR} linear column (separation: linear range 500 to ~100 000 g mol^{-1}); tetrahydrofuran (THF) was used as carrier-solvent at 1 mL/min at room temperature. The sample concentration was approximately 3 mg/ml. Poly(styrene) standards (M_p = 1050−1 870 000 g/mol) were used for conventional external calibration using a Waters RI 3580 refractive index detector.

Thermal Measurements. Melting points for **4a** and **4b** and glass transition temperatures of **4b** were measured on a Mettler Toledo DSC 822e-differential scanning calorimeter (DSC-instrument). The baseline was subtracted from all graphs measured via (DSC) curves. The heating rate for DSC was adjusted at 10 K/min, sample weights were typically ~5 mg, and values for T_m and T_g were taken from the second heating run. For the determination of T_g, the DIN method was used. The melting point for **2a** and the T_g of **2a**, **2b** and **4a** were measured on a Perkin-Elmer Pyris Diamond DSC. For analysis, the Pyris Thermal Analysis version 5.00.02 was used. The sample weight was approximately 10 mg. The following temperature program was used for the determination of the melting point of **2a** and the glass transition temperature of **2a** and **2b**, respectively: the sample was held for 15.0 min at 25.00 °C, heated from 25.00 to 150.00 °C with 20.00K/min, held for 5.0 min at 150.00 °C, cooled from +150.00 °C to −100.00 °C with 20.00 K/min, held for 10.0 min at −100.00 °C, heated from −100.00 to +150.00 °C with 20.00 °C/min, and held for 5.0 min at 150.00 °C. Melting points and glass transition temperatures were taken from the second heating run. For the determination of the glass transition temperature for polymer **4a,** a stepwise heating procedure was applied, using the following temperature program: a stepwise scan from −80.0 to +60.0 °C with a heating rate of 4.0 K/min. Calibration in all cases was done using Al as internal standard.

TGA. This was measured on a Mettler Toledo thermogravimetric instrument-TGA/SDTA 851e with a heating rate of 10 K/min; the sample weight was approximately 5 mg. For determination of the decomposition temperature, the first derivative of the curve was formed and fitted with the Gaussian method.

IR Measurements. These measurements for the polymers were done on a Nicolet 205 FT-IR spectrometer using a scan-rate of 4 cm^{-1}. KBr pellets were used throughout.

Solvents/Reagents/Materials. Catalysts **I** and **II** were obtained from Sigma-Aldrich, catalysts **III** and **IV** were prepared according to published procedures.[25,26] Dichloromethane and chloroform were distilled from CaH_2 prior to use. Diethyl ether, toluene and xylene (all as p.a. reagent from Sigma-Aldrich) were distilled from sodium benzophenone prior to use. Ethylbromide (Sigma Aldrich) was purified by distillation. All other reagents were purchased from

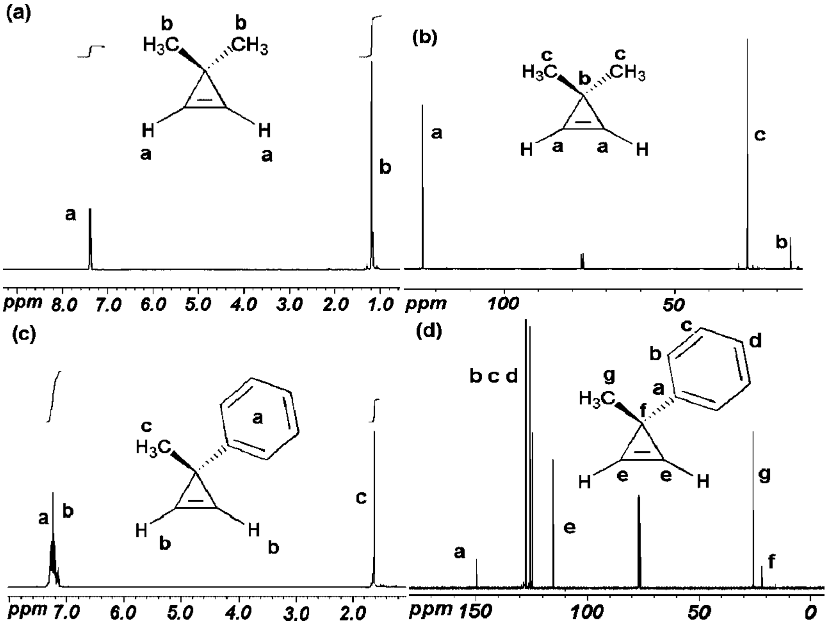


Figure 1. (a) ^1H NMR spectrum of **3a**; (b) ^{13}C NMR spectrum of **3a**; (c) ^1H NMR spectrum of **3b**; (d) ^{13}C NMR spectrum of **3b.** Compound **3a** is stable at room temperature, enabling NMR spectroscopy at 27 °C (bp (**3a**) 14 °C).

Table 1. Gel Permeation Results (GPC) for Polymers 4a, 4b Prepared from Monomers 3a and 3b by the Action of Catalysts I−III[a]

entry	monomer	initiator	solvent	*M*/*I*	$M_{n,\ calcd.}$	$M_{n,exp.}$[b]	M_w/M_n[b]	$M_{n,exp.}$[c]	PDI[c]
1	**3a**	II	CH_2Cl_2	149	9945	1800	3.9		
2	**3a**	II	CH_2Cl_2	311	23800	7600	2.4	23800	1.3
3	**3a**	II	CH_2Cl_2	635	43256	1000	3.8		
4	**3a**	II	toluene	14	923	6200	1.9	4200	5.6
5	**3a**	II	toluene	68	4614	5900	2.8	18000	1.5
6	**3a**	II	$CHCl_3$	199	13555	8100	2.8		
7	**3a**	I	CH_2Cl_2	114	7782	2000	2.5	5600	1.04
8	**3a**	III	toluene	162	10993	6200	2.2	7300	1.3
9	**3a**	III	CH_2Cl_2	147	9994	2500	2.5	5800	1.00
10	**3b**	II	CH_2Cl_2	64	8368	11600	1.3		
11	**3b**	II	CH_2Cl_2	68	8866	9000	1.4		
12	**3b**	II	CH_2Cl_2	137	17821	13300	1.4		
13	**3b**	II	CH_2Cl_2	946	123000	40600	1.1		
14	**3b**	II	CH_2Cl_2	296	38600	102700 8300	1.7 (20%)[d] 1.2 (80%)		
15	**3b**	II	CH_2Cl_2	197	25700	9400	1.3		
16	**3b**	II	CH_2Cl_2	141	18366	10900	1.3		
17	**3b**	II	CH_2Cl_2	35	4591	4500	1.4		
18	**3b**	I	CH_2Cl_2	63	8200	3300	1.4		
19	**3b**	I	CH_2Cl_2	98	12760	3300	1.4		

[a] Data for polymer **4a** were determined via high-temperature (HT-GPC). [b] Measured by GPC (THF, room temperature) by external calibration with poly(styrene). [c] Determined by high-temperature (HT)-GPC, analysis by light scattering, refractive index increment. [d] Bimodal distribution.

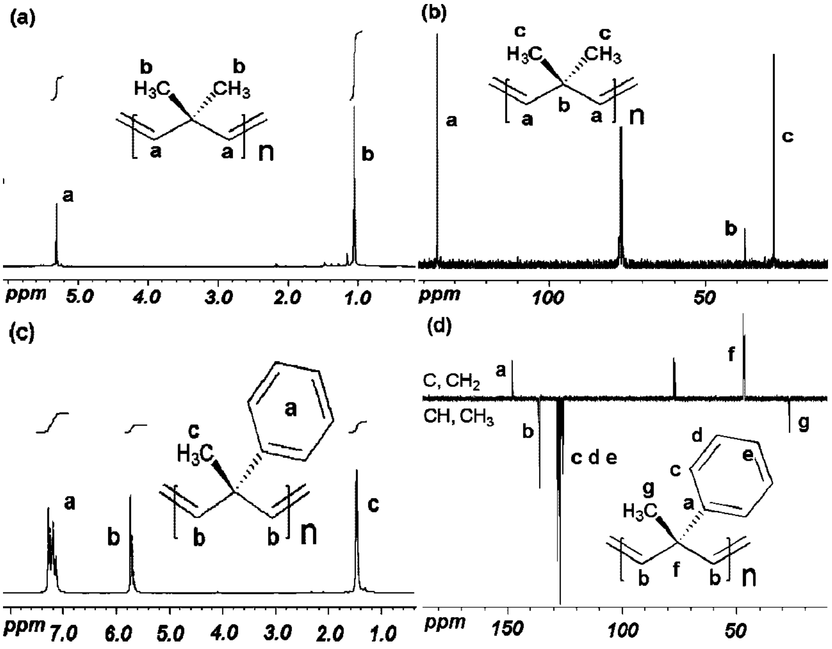


Figure 2. (a) ^{1}H NMR of **4a**; (b) ^{13}C NMR of **4a**; (c) ^{1}H NMR of **4b**; (d) ^{13}C NMR APT of **4b.** Polymers are prepared by catalyst **I** and **II**.

Sigma Aldrich (Germany) and used without further purification. 3,3-Dimethylcyclopropene (**3a**)[27] and 3-methyl-3-phenylcyclopropene (**3b**)[28] were prepared according to literature procedures (see Supporting Information for details).

ROMP of 3,3-dimethylcyclopropene (3a). A dry and argon-flushed glass tube equipped with a magnetic stir bar was charged with 3,3-dimethylcyclopropene **3a** (500 mg, 7.35 mmol), dissolved in dry dichloromethane (5 mL). **3a** was either diluted with precooled solvent or was added with the aid of a precooled glass syringe (concentration approximately 0.8 g/mL). 42 mg, 0.0494 mmol of **II**, dissolved in dry dichloromethane (1 mL) were then added to this solution. The resulting solution was stirred for 24 h. The reaction was quenched with ethyl vinylether (15 μL, 0.15 mmol). The polymer was precipitated in methanol (500 mL), collected by filtration and dried *in vacuo*. Yield of polymer **4a**: 250 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): 5.31 (2H, s, CH), 1.06 (6H, s, CH_3). ^{13}C- NMR (200 MHz, $CDCl_3$, 50 °C): 135.66 (C=C), 37.51 (quat. C), 28.25 (-CH_3). IR [cm^{-1}]: 937, 977, 1224, 1304, 1360, 1380, 1445, 1460, 2866, 2936, 2960, 3004. (M_n = 1800 g mol^{-1}; M_w/M_n = 3.5).

Polymerization of 3-methyl-3-phenylcyclopropene (3b). A heated and argon-flushed glass tube equipped with a magnetic stir bar was charged with 3-methyl-3-phenylcyclopropene **3b** (240 mg, 1.84 mmol), dissolved in dry dichloromethane (3 mL). To this solution was added **II** (11.4 mg, 0.013 mmol), dissolved in dry dichloromethane (0.35 mL). The resulting solution was stirred for 24 h. The reaction was then quenched with ethyl vinyl ether (4 μL, 0.04 mmol) and the resulting polymer was precipitated into methanol (300 mL), collected by filtration and dried *in vacuo*. Yield of polymer **4b**: 208 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.08−7.31 (5H, m, Ph), 5.74 (2H, m, CH), 1.47 (3H, s, CH_3). ^{13}C NMR (200 MHz, $CDCl_3$,): 147.96 (Phe), 135.9 (Phe), 128.09 (C=C), 126.99 (C=C), 125.89 (C=C), 46.66 (quat. C), 27.02 (−CH_3). IR [cm^{-1}]: 570, 699, 764, 799, 989, 1028, 1446, 1491, 1523, 1534, 1600, 1617, 1677, 2858, 2928, 2966, 3021. M_n = 10900 g mol^{-1}; M_w/M_n = 1.3.

Hydrogenation of 4a. Polymer **4a** (175 mg, 2.57 mmol) was dissolved in dry xylene (15 mL) and tosylhydrazide (2.8 g, 15.51 mmol) was added. The mixture was heated to 160 °C under argon for 6 h. The solution was cooled to room temperature and half of

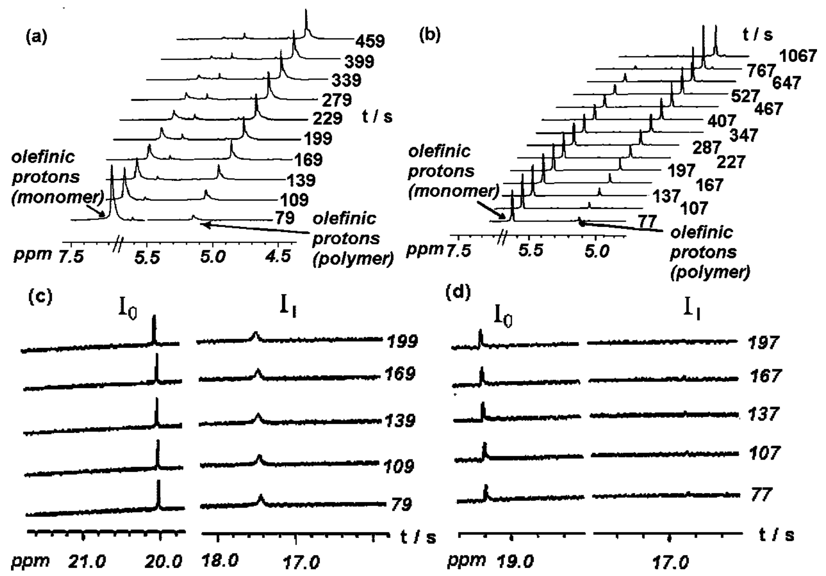


Figure 3. ^{1}H NMR (400 MHz, CDCl$_3$, 27 °C): (a, b) monomer consumption of **3a** and development of the olefinic signal of the polymer (a) **I**, CHCl$_3$, 27 °C, [M]/[I] = 40; (b) **II**, CHCl$_3$, 27 °C, [M]/[I] = 50, 5.31 ppm, olefinic protons of the polymer, 7.41 ppm, olefinic protons of the monomer, 8.20 ppm, doublet; (c, d) initiating (I_o) and propagating alkylidene (I_1) signal for the polymerization of **3a** with initiator **I** and **II**; (c) **I** with **3a**, [M]/[I] = 10; (d) **II** with **3a**, [M]/[I] = 100.

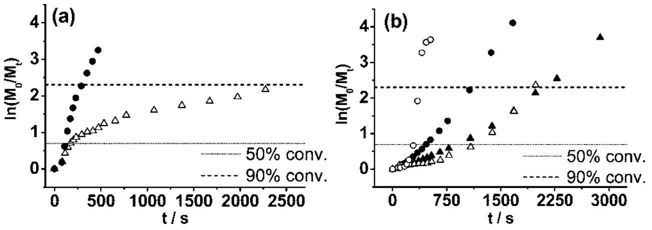


Figure 4. Monomer consumption as a function of time for **3a** (a) with **I**, (●) [M]/[I] = 40, (△) [M]/[I] = 120, (b) with **II**, (○) [M]/[I] = 7, (●) [M]/[I] = 50, (△) [M]/[I] = 100, (▲) [M]/[I] = 150. M_0: monomer concentration of **3a** at $t = 0$. M_t: monomer concentration during measurement [M]/[I]: monomer/initiator ratio.

the xylene was removed under reduced pressure. The concentrated solution was then precipitated into ice-cold methanol. The white solid was collected and dried *in vacuo.* Yield of **2a**: 164 mg (91%). ^{1}H NMR (400 MHz, CDCl$_3$, 50 °C): 1.11 (4H, s, CH$_2$), 0.84 (6H, s, CH$_3$). ^{13}C- NMR (100 MHz, CDCl$_3$,): 35.46 (−CH$_2$−), 32.24 (quat. C), 27.55 (−CH$_3$)). IR [cm^{-1}]: 1091, 1265, 1288, 1301, 1311, 1366, 1382, 1449, 1468, 2862, 2932, 2959. (M_n = 2000 g mol^{-1}; M_w/M_n = 3.5).

Hydrogenation of 4b. This was carried out as described above using **4b** (157 mg, 1.2 mmol), xylene (9 mL) and tosylhydrazide (1.35 g, 7.3 mmol). Yield of **2b**: 113 mg (71%). ^{1}H NMR (400 MHz, CDCl$_3$): 6.70−7.25 (5H, m, Ph), 0.9−1.19 (7H, m, CH$_2$, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, for detailed assignment see Figure 9c,d): 147.49, 127.84, 126.38, 125.03, 43.22, 40.23, 36.79, 29.73, 23.54. IR [cm^{-1}]: 463, 560, 698, 763, 800, 1030, 1073, 1379, 1444, 1496, 1601, 2871, 2939, 2964, 3023, 3057, 3087. M_n = 12 000 g mol^{-1}; M_w/M_n = 1.3.

Kinetic Experiments. A pyrene stock solution was prepared from 70 mg of pyrene dissolved in 2 mL of CDCl$_3$. **3a** was dissolved in CDCl$_3$ (~1.46 mol L^{-1}). An NMR tube was charged with the prepared solution of **3a** (25 mg, 0.25 mL) and 0.2 mL of the pyrene solution. Monomer **3b** (50 mg, 0.38 mmol) was dosed via a syringe and diluted with CDCl$_3$ (0.2 mL) inside the NMR tube. To this solution, the pyrene stock solution (0.2 mL) was added. Before adding the initiator solution, the ratio of the monomer to the internal standard was determined by NMR. On that basis, the monomer concentration at $t = 0$ was determined. A solution of the initiator in CDCl$_3$, [c] ~ 10 mg in 0.1 mL, was prepared and a defined volume was added via a syringe to yield the desired monomer to initiator ratio. After shaking, the tube was inserted into the NMR-spectrometer and the decrease of the monomer vs time was monitored. For determination of the monomer concentration at t= 0 and the monomer consumption, the following signals were integrated: for **3a,** the signal at 7.41 ppm (2H, s, CH) was compared to the one at 8.20 ppm (4H, d, =CH) from the internal standard pyrene; for monomer **3b,** the signal at 1.64 ppm (3H, s, CH$_3$) was compared to the one at 8.20 ppm (4H, d, CH) from the internal standard pyrene. The time between the addition of the initiator solution and the first measurement was added to the first measuring point. For the more sensitive Schrock initiator (**III**), all manipulations were done inside a glovebox. The adjustment of the monomer to initiator ratio was done by weighing both components exactly. A NMR tube was filled with a solution of the monomer (5 mg) in C$_6$D$_6$ and an internal standard (pyrene) in C$_6$D$_6$ (amount of internal standard approximately 7 mg), and the solution was frozen inside a fridge. This step was repeated with pure solvent and initiator solution (5 mg in 0.2 mL of C$_6$D$_6$). The total volume was approximately 0.6 mL. The tube with the frozen solution was quickly warmed to room temperature, initiator and monomer solution were mixed by shaking and the tube was inserted in the NMR-spectrometer. For monomer **3b**, the signal at 6.81 ppm (2H, s, CH) was compared to the one at 8.03 ppm from the internal standard pyrene.

Results and Discussion

Monomer Synthesis. The ROMP of cyclopropenes is strongly dependent on the purity of the often unstable compounds, which are highly reactive due to their high ring-strain of about 55 kcal/mol relative to cyclobutene (~30 kcal/mol) and cyclopentene (~5−6 kcal/mol) as calculated by Schleyer,[29] Goddard[30] and Wiberg.[31] For synthesis, we used a published strategy based on the addition of dibromocarbene to either isobutylene or 1,1-methylphenyl-ethylene,[32,33] yielding the corresponding dibromocyclopropanes, which were subsequently reduced in two steps to yield 3,3-dimethylcyclopropene **3a**[34] and 3-phenyl-3-methylcyclopropene **3b,** respectively (see supplementary). The monomers were obtained in gram quantities in one synthetic step by using an improved method for securing the monomer in a cooling trap and removing residual solvent via a precooling trap (see supplementary). The NMR-spectra of monomers **3a** and **3b** are shown in Figure 1, indicating high purity and the structural integrity of the compounds. However, despite several purification steps after the generation of monomer **3a**, traces of

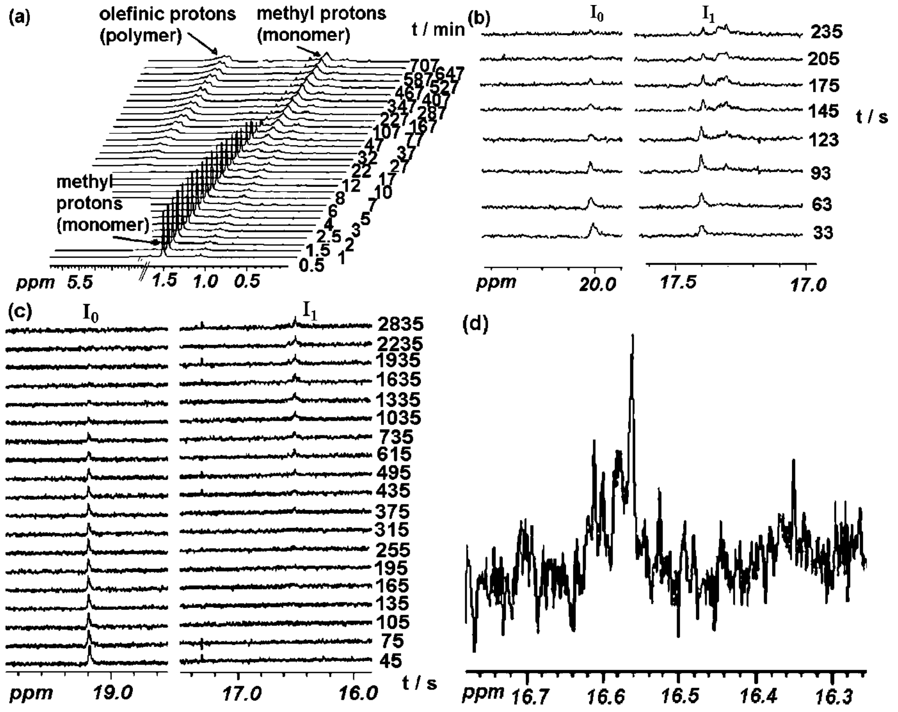


Figure 5. (a) Development of monomer and polymer signals for the polymerization of **3b** with **I** [M]/[I] =60 (50 °C, $CHCl_3$); (b) ^1H NMR (400 MHz, $CDCl_3$, 50 °C) initiating and propagating alkylidene signal for the polymerization of **3b** with **I**, [M]/[I] = 60; (c) initiating and propagating alkylidene signal for the polymerization of **3b** with **II**, [M]/[I] = 20; (d) propagating alkylidene species from the reaction of **II** with **3b.**

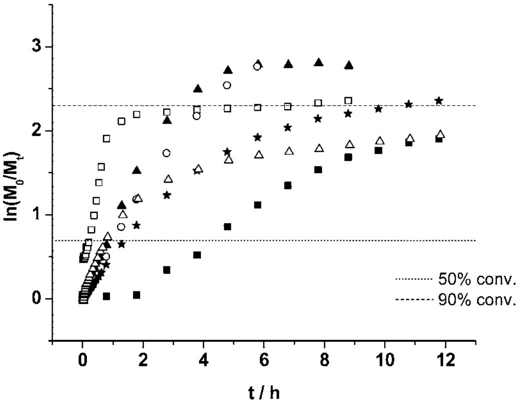


Figure 6. Monomer consumption as a function of time for **3b**. M_0: monomer concentration of **3b** at $t = 0$. M_t: monomer concentration at time t. [M]/[I]: monomer/initiator ratio, (■) [M]/[I] = 55 (27 °C, **II**); (□) [M]/[I] = 20 (50 °C, **II**); (▲) [M]/[I] = 62 (50 °C, **II**); (○) [M]/[I] = 100 (50 °C, **II**); (★) [M]/[I] = 200 (50 °C, **II**); (△) [M]/[I] = 60 (50 °C, **I**).

residual *tert.*-butanol (below 2%) are visible in the NMR-spectrum of **3a** (see Figures 1a and 1b). As the subsequently used Grubbs-initiators are compatible with tert.-butanol[35] and the monomer is instable, no further attempts to purify this monomer were undertaken.

Polymerization. The strategy for the preparation of the poly(*homo*-isobutylene)s **2a** and poly(*homo*-α-methylstyrene) **2b** is shown in Scheme 2. The protocol entails the ROMP of cyclopropenes **3a,b** followed by hydrogenation to yield the homologous polymers **2a,b**. Thus, besides the Schrock-type initiator **III** which was recently described to polymerize monomer **3b** in a living manner,[14,21] both **I** and **II** were investigated. The data for the polymerization reactions are summarized in Table 1.

Using **I** and **II** for the polymerization of 3,3-dimethylcyclopropene **3a**, the polymerization reaction proceeded very fast under generation of considerable amounts of heat, and the polymer precipitated from solution after several minutes. In order to check for solvent-dependent polymerization, several solvents (DCM, toluene, chloroform) were investigated, yielding polymers with molecular weights below 10 000 g mol^{-1} and polydispersities (PDI = M_w/M_n) around ~2−2.5 and higher, indicative of a nonliving polymerization process (entries 1−9). The use of **III** did not give raise to improved results with respect to control over molecular weight or PDI. In contrast, the polymerization of **3b** by the action of **I** yielded polymers with low PDI (~1.3−1.4) (entries 10−17) and a controlled molecular weight in the range between 4500 to 40 000 g mol^{-1}. The chemical structures of both polymers **4a** and **4b** were proven by ^1H and ^{13}C NMR spectroscopy (see Figure 2).

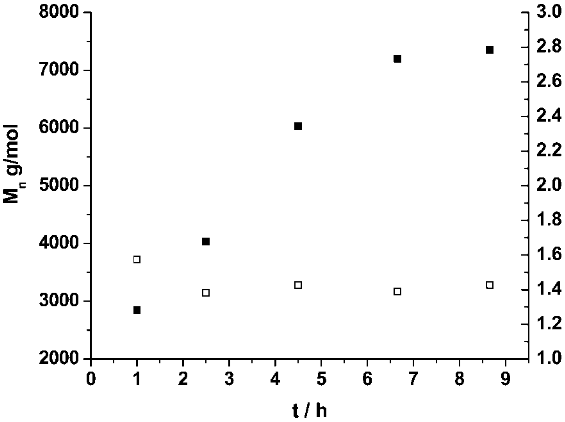


Figure 7. SEC analysis of polymer **4b**, development of the number average molecular mass over time, [M]/[I] = 60; in DCM, **II**, $T = 20$ °C (■, M_n);(□, M_w/M_n).

As expected, polymer **4a** shows only two main resonances at 5.31 and 1.06 ppm, respectively, indicative for the *vinyl-* and *methyl*-groups, polymer **4b** showed the expected main resonances at 7.2 (*aryl*)-, 5.76 (*vinyl*-) and 1.47 ppm (*methyl*-groups). Similar results were visible in the ^{13}C NMR-spectra (see Figures 2b, 2d). Polymer **4a** was characterized by one main signal in

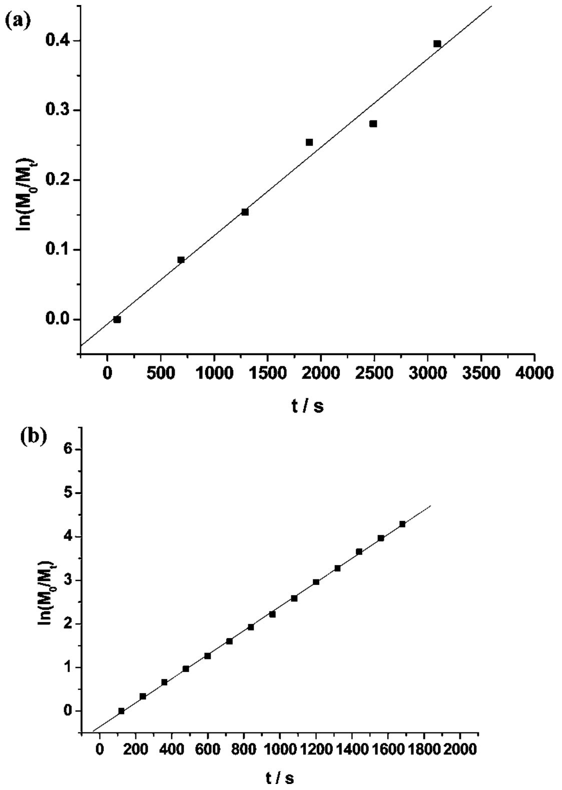


Figure 8. (a) Consumption of **3b** with **IV**, [M]/[I] = 9, benzene-d_6, 22 °C. (b) Consumption of **3b** with **III**, [M]/[I] = 5, benzene-d_6, 22 °C.

the olefinic region in the carbon NMR at 135.7 ppm. The IR spectrum (see Supporting Information) displayed a strong band at 976 cm^{-1}, suggesting that polymer **4a** was exclusively based on an all-*trans* configuration. Similarly, in accordance with the observation of Schrock et al.[14] for polymer **4b**, only one type of stereoisomer was generated, which is assigned to the *trans*-product.

Kinetic Analysis. In order to understand the differences between monomers **3a** and **3b**, extensive kinetic investigations were conducted using *in situ* ^{1}H NMR. In all experiments, pyrene was used as an internal standard for the quantification of both the monomer and polymer resonances. It can be seen (see Figure 3) that the polymerization of **3a** by either **I** or **II** results in the rapid consumption of the monomer, together with the occurrence of the polymer resonances at 5.31 and 1.06 ppm, respectively (see Figures 3a and 3b).

In addition to the occurrence of the propagating alkylidene-species (visible at 17.4 ppm and 16.8 ppm for **I** and **II**, respectively), the initial resonances of the alkylidene-species of the native initiators were still visible after 90 min at 20.0 and 19.2 ppm, respectively (see Figures 3c, 3d). Due to precipitation of the generated polymer the propagating alkylidene-species decreased in intensity. The kinetic results (ln(M_0/M_t)) for monomer **3a** with **I** and **II** are shown in Figure 4, parts a and b, respectively.

With **I**, a conversion >90% was reached within the first 500 s. In the initial stages of polymerization, there was a linear growth of the molecular weight vs time, followed by a decline in polymerization kinetics (k_p/k_i of ~ 50, estimated by integration of the respective initiating and growing alkylidene-resonances). Unfortunately, all attempts to decelerate the rate of polymerization by lowering the temperature failed due to rapid, concomitant precipitation of polymer. With **II**, the polymerization of **3a** proceeded slower, which is attributed to incomplete initiation.[36,37] In particular, for [M_0]/[I_0] = 7, the slow initial polymerization kinetics experienced a dramatic increase after 200 s, a finding that we tentatively attribute to a continuous initiation process and the concomitant increase in concentration of propagating species. In due consequence, no controlled polymerization could be obtained with **II**, too.

Compared to **3a**, the polymerization of monomer **3b** with both **I** and **II** was much slower, which is obviously a result of both the lower ring-strain of monomer **3b** and its increased steric bulk compared to monomer **3a** (Figure 5).

Thus, the initiating alkylidene was completely consumed in course of the polymerization of **3b** with **II** after ~2000 s. Conducting an experiment at 50 °C using [M]/[I] = 20, the resonance at 19.19 ppm disappeared within 46 min, whereas the growing species detected at 16.60−16.80 ppm remained (Figure 5c,d), estimating a k_p/k_i of ~17, as determined by ^{1}H NMR-spectroscopy according to Schrock et al.[9] With **I**, the initiating alkylidene disappeared within ~4 min (50 °C, [M]/[I] = 50), while the growing species at 17.41 ppm remained (Figure 5a,b). In comparison to the polymerization of **3a**, polymer **4b** prepared from **3b** did *not* precipitate from solution, thus allowing for a controlled polymerization. Figure 6 shows the kinetic analysis, which indicates a living polymerization of monomer **3b** with **II** at T=50 °C. Thus, a linear increase of M_n vs time was observed, with PDIs <1.6 (see Figure 7).

In order to check other initiators, **IV** and **III** were tested (see Figure 8a and Figure 8b), indicating a living polymerization process. Due to the excellent initiation efficiencies of **IV**,[25] no initiation period was observed. For purposes of comparison, the apparent rate constants of polymerization (k_p) were analyzed and are provided in Table 2 for all initiators used in the polymerization of monomer **3b**. Not surprising, the use of **III** resulted in the fastest polymerization, although still slower than the reported values for the polymerization of norbornene. However, also the Grubbs-type initiators **I**, **II** yielded useful values, furnishing polymer **4b** with narrow PDIs, though it has to be emphasized that particularly for **II**, the values for k_p obtained from kinetic measurements only represent the apparent rate constants (k_p(app.)).

Hydrogenation. The synthesis of the homologous polymers **2a**,**b** from the respective vinyl-polymers **4a**,**b** was accomplished by hydrogenation. As **4a**,**b** already showed limited solubility in most organic solvents, a complete hydrogenation seemed difficult. Thus, most of the conventionally used homogeneous- and heterogeneous methods[5,38−40] (H_2/Wilkinson catalyst,[39,40] H_2/Ni,[41,42] H_2/Pd,[41] or H_2/Rh[5,43]) failed to generate the respective fully hydrogentated polymers. However, the use of diazene, generated *in situ* via the decomposition of tosylhydrazone proved to be an excellent method for a simple hydrogenation reaction.[1,7,8] Several stoichiometric amounts of tosylhydrazone as well as reaction temperatures were tested, reaching 100% hydrogenated product **2a** at 160 °C (3−6 h) and a 6-fold excess of tosylhydrazone/olefinic moiety. In the case of **2b**, the degree of hydrogenation reached a maximum at 92%, despite several attempts at increased temperatures (see Table 3).

The NMR spectra of the hydrogenated polymers **2a**,**b** are shown in Figure 9. Both polymers were obtained in high purity after repeated precipitation to remove unreacted tosylhydrazone. As already mentioned, there was no residual olefinic bond in polymer **2a**, whereas the residual amount of olefin in **2b** was visible at ~5.30 ppm (*vinylic*) and ~2.4 ppm (*allylic*) (<8% as judged by integration). In the ^{13}C NMR of **2b,** three resonances at δ=147.2 − 148.8 ppm for the quaternary carbon in the phenyl moiety as well as three resonances for the methyl group at δ=27.2 −27.4 ppm could be observed, suggesting that all possible triads are present. On the basis of the ^{13}C NMR analysis for the homologous poly(α-methylstyrene),[44] the three peaks

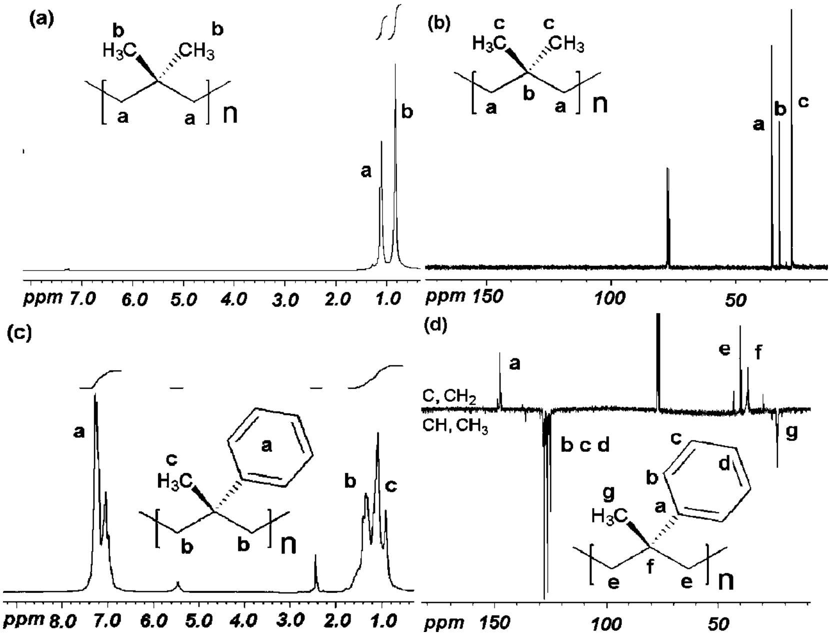


Figure 9. (a) ^1H NMR of **2a**; (b) ^{13}C NMR of **2a**; (c) ^1H NMR of **2b**; (d) ^{13}C NMR of **2b** (see Tables 1 and 3).

Table 2. (Apparent) Rate Constants of Propagation (k_p) of Different Initiators with Monomer 3b As Obtained From in Situ NMR Experiments

Initiator	[M]/[I]	solvent	temperature °C	I_0 (mol/L)	k_p (L/(mol·s))
II	65	$CDCl_3$	50	0.009	0.024
II	20	$CDCl_3$	50	0.037	0.014
II	100	$CDCl_3$	50	0.006	0.028
II	200	$CDCl_3$	50	0.0017	0.065
II	55	$CDCl_3$	27	0.011	0.00057
IV	9	C_6D_6	22	0.002	0.005
III	5	C_6D_6	22	0.020	0.133

Table 3. Results of Hydrogenation of Polymers 4a and 4b by the Use of Tosylhydrazide

compound	temperature (°C)	time (h)	molar ratio tosylhydrazide/ repeat units	hydrogenation efficiency (%)[a]	yield of **2a**, **2b** (%)
4a	120	3	6.4[b]	96	74
4a	160	5	6	~100	80
4a	160	6	6	100	91
4b	160	6	6	97	70

[a] The efficiency of hydrogenation was judged by ^1H NMR spectroscopy. [b] The ^1H NMR spectroscopy of the resulting polymer showed an incorrect ratio between aromatic and aliphatic protons, ~5:10 instead of the expected 5:7.

Table 4. Summary of Differential Scanning Calorimetry (DSC) and Thermogravimetric (TGA) Results

polymer	T_g (°C) (prediction)	T_m (°C) (prediction)	TGA (decomposition) (°C)
4a	−9 to −11[b] (−39.6)	121−128[c] (66)	403−407
2a	−19[a] (−74.9)	108[a] (−15)	452−453
4b	51−52[c] (175.7)	192−194[c] (226.5)	395−396
2b	93[a] (153.75)	 (181)	433

[a] Measured with a heating rate of 20 K/min. [b] Measured with a heating rate of 4 K/min. [c] Heating rate: 10 K/min.

can be assigned to the triads *mm*, *mr*, and *rr*. By comparing the relative intensities of the peaks, the fractions for the different triads can be estimated as 9% *rr*, 53% *mr*, and 38% *mm* triads, thus proving the basically atactic structure of **2b**.

Thermal Properties. In order to compare the properties of the homologous polymers **2a**,**b** with their polyisobutylene **1** and poly(α-methylstyrene) **2c** counterparts, thermal measurements were conducted. The measured T_g- and T_m-values as well as the thermogravimetric data (TGA) are provided in Table 4, together with predictions gained by functional-group increment calculation systems.[45]

Polymer **4a** showed a broad melting peak with a melting point between 121 and 128 °C and a glass transition T_g between −8 and −11 °C. In the same temperature range, polymer **2a** showed a melting point at 108 °C and a T_g at −19 °C. The hydrogenated polymer **2a** had a melting point 12 to 20 °C lower than the corresponding unsaturated polymer **4a** (T_m = 121−128 °C). The glass transition temperature decreased with hydrogenation, indicative for an increased flexibility of the main chain in **2a** compared to **4a**. Thus, the insertion of one methylene unit into the repeat unit of polyisobutylene (T_g = −80 °C, amorphous polymer) leads to a semicrystalline polymer (**2a**, T_g = −19 °C, T_m = 108 °C), displaying hybrid properties of both PIB and HDPE. In the literature, a T_g of −7 °C was reported for **2a**,[22,46] with the polymer prepared via cationic polymerization of 3-methyl-1-butene with subsequent rearrangement of the carbocation.[22] Since this mode of synthesis also leads to a very irregular backbone due to head-to-tail and head-to-head sequences, a comparison with the present, highly regular polymer appears inexpedient, the more as no melting point was reported for **2a**, presumably due to its irregular structure.

Polymer **4b** showed a T_g at 51−52 °C, followed by a cold crystallization at 109°, the latter being an indication of the amorphous precipitation of the polymer, and a T_m at 192−194 °C. Polymer **2b** showed a T_g at 93 °C, but no melting point, presumably due to its atactic nature (see NMR analysis). For polymer **4b**, Schrock et al.[14] have reported a T_g around 50 °C but no melting point. Thus the insertion of one methylene-unit into the repeat unit of poly(α-methylstyrene) (T_g = 98−102 °C, amorphous) leads to a decrease in T_g in **2b** (T_g = 93 °C, amorphous).

All four polymers showed high decomposition temperatures, with increasing thermostability upon hydrogenation. For polymer **2b**, a decomposition temperature around 400 °C, determined via TGA, was reported,[47] which would be supported by the present data. The predictions made by using incremental calculations[45] yielded a poor correlation with our experimental values, except for the melting point of **4b**.

Conclusion

We have reported the synthesis of homologous poly(isobutylene) and poly(α-methylstyrene) polymers **2a** and **2b** via a ROMP/hydrogenation strategy starting from 3,3-dimethylcyclopropene **3a** and 3-methyl-3-phenyl-cyclopropene **3b**. In contrast to **3a**, which leads to an uncontrolled polymerization reaction with all investigated initiators (Grubbs' first-, second-, and third-generation and Schrock-type-initiators), a living polymerization can be obtained in case of **3b** with all investigated initiators. As the ring string of monomer **3a** is much higher than the one in **3b**, polymerization proceeds too fast, additionally hampered by the precipitation of the resulting polymer **4a**. Hydrogenation was achieved in both cases preferentially using tosylhydrazide as agent, furnishing the respective homologous polymers **2a** and **2b** in high yields with a high degree of hydrogenation-efficiency (>97%). The resulting polymer **2a** showed thermal hybrid properties of both PIB and HDPE. Both polymers are currently under investigation as compatibilizers for PIB, PS, and HDPE-type polymers.

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Supporting Information Available: Text giving synthetic procedures, figures showing ^{1}H and ^{13}C NMR spectra, DSC curvers, and IR spectra, schemes showing and overview of the syntheses and the reaction apperatus, and tables of cis/trans ratios and solubility properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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