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Molecular Weight and End Group Control of Isotactic Polystyrene Using Olefins and Nonconjugated Diolefins as Chain Transfer Agents

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ABSTRACT: Styrene was isospecifically polymerized on dichloro[1,4-dithiabutandiyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)]titanium (**1**) activated with methylaluminoxane in the presence of monoolefins such as 1-hexene, cyclopentene, and norbornene and nonconjugated diolefins such as 1,9-decadiene, 1,7-octadiene, and dicyclopentadiene. The molecular weight of isotactic polystyrene was varied from 2000 to 600 000 g/mol as a function of the olefin/styrene molar ratio without sacrificing high catalyst activities. Chain transfer constants were determined, with the highest values found for linear mono- and nonconjugated diolefins. In contrast to norbornene, 1-olefin incorporation was very low. End groups were identified by means of ^{13}C NMR investigations of polymers containing ^{13}C-labeled 1-octene. Olefin- and diolefin-terminated isotactic polystyrenes including novel vinyl-terminated macromonomers were obtained in high yields.

Introduction

The molecular design of single site catalysts represents a very effective tool for tailor-making polyolefin materials based on insight into correlations between catalyst and polymer architectures.[1−3] Significant progress has been made in stereospecific styrene homo- and copolymerization. Syndiotactic polystyrene, developed by Ishihara in 1985, is formed on trivalent mono(cyclopentadienyl)titanium catalysts.[4] In a recent advance, isotactic polystyrene, previously only available with heterogeneous Ziegler−Natta catalysts, was prepared with homogeneous group 4 single site catalysts.[5] These isospecific postmetallocene catalysts contain a tetradentate ligand having two phenolato units linked by a 1,ω-dithiaalkanediyl bridge $S(CH_2)_2S$. They have a C_2-symmetric structure and are highly active in the isospecific polymerization of styrene and 4-methyl-1,3-pentadiene[6] and the copolymerization of styrene with ethylene[7] or propylene.[8] Homopolymerization of styrene leads to high molecular weight polymers with weight-average molecular weights (M_w) of about 1 million. These high molecular weight polymers are not suitable for melt compounding. Therefore, control of molecular weight is an important challenge in the development of isospecific styrene polymerization on single site catalysts. In syndiospecific styrene polymerization, several routes to chain transfer were explored, for example, hydrogen or main group metal compounds like organo-aluminum compounds and boranes.[9] Another approach toward molecular weight control was the living isospecific styrene polymerization.[10] Since in living polymerization one catalyst complex is attached to the polymer chain end, the catalyst demand and the cost for making low molecular weight oligomers are very high. In a recent research, the addition of 1-olefins has been recognized to have significant impact on molecular weight of isotactic polystyrenes.[11] In fact, bisphenolato catalysts (**1**) are very active in isospecific styrene polymerization, leading to polymers with high molecular weights. However, in the case of 1-olefins, only oligomers can be obtained. Styrene/propene copolymerization gave poor molecular weights, with the molecular weight decreasing with increasing propene/styrene molar ratio.[8]

Table 1. Polymerization of Styrene on Bisphenolato Titanium Catalyst (1) Activated by Methylaluminoxane[a] in the Presence of Monoolefins

run[a]	olefin[b]	[olefin]/[styrene]	activity (kg/mol·h)	M_n[c] (g/mol)	M_w/M_n[c]	olefin incorp[d] (mol %)	T_m[e] (°C)
0		0.00	840	608 900	1.3		224
1	hex	0.005	760	151 500	2.1	< 0.5	224
2	hex	0.02	780	34 400	2.6	< 0.5	223
3	hex	0.04	840	18 400	2.6	< 1.0	223
4	hex	0.12	920	10 600	1.9	2.0	219
5	hex	0.20	790	8300	1.7	3.9	215
6	hex	0.30	870	5600	1.6	6.1	211
7	hex	0.40	760	5000	1.6	6.2	203
8	hex	0.50	850	4100	1.4	7.9	199
9	hex	0.60	950	3300	1.4	10	189
10	hex	0.70	900	2700	1.4	11	175
11	cypent	0.02	790	249 700	1.7	0.5	219
12	cypent	0.06	1100	244 900	1.8	1.0	215
13	cypent	0.20	800	122 600	1.7	4.9	199
14	cypent	0.40	830	58 900	1.8	7.8	*f*
15	cypent	0.56	840	47 800	1.8	9.2	*f*
16	cypent	0.79	890	40 400	1.8	11	*f*
17	cypent	0.96	1100	29 900	1.8	12	*f*
18	cypent	1.13	1030	21 000	2.0	13	*f*
19	cypent	1.30	1110	17 700	2.0	12	*f*
20	norb	0.01	220	162 400	1.7	0.7	216
21	norb	0.08	70	89 100	1.3	7.8	*f*
22	norb	0.13	50	55 700	1.3	20	*f*
23	norb	0.19	35	34 400	1.4	34	*f*
24	norb	0.24	30	24 700	1.6	34	*f*
25	norb	0.30	25	24 500	1.4	50	*f*

[a] Polymerization conditions: 62.5 μmol/L complex (**1**), Al/Ti = 1500, 1.67 mol/L styrene in toluene, total reaction volume 120 mL, T_p = 40 °C, t_p = 1 h. [b] Key: hex = 1-hexene, cypent = cyclopentene, norb = norbornene. [c] Determined by gel permeation chromatography. [d] Determined by ^{1}H NMR. [e] Determined by differential scanning calorimetry. [f] No melting peak.

The objective of this research was to examine the role of different chain transfer agents such as 1-olefins, cycloolefins,

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Table 2. Polymerization of Styrene on Bisphenolato Titanium Catalyst (1) Activated by Methylaluminoxane[a] in the Presence of Nonconjugated Diolefins

run[a]	olefin[b]	[olefin]/[styrene]	activity (kg/mo•h)	M_n[c] (g/mol)	M_w/M_n[c]	olefin incorp[d] (mol %)	T_m[e] (°C)
0		0.00	840	608 900	1.3		224
26	decd	0.005	1020	199 100	1.7	< 0.1	223
27	decd	0.01	840	46 800	1.9	< 0.1	223
28	decd	0.03	850	24 600	1.9	0.9	222
29	decd	0.05	1020	19 700	1.9	1.2	215
30	decd	0.14	790	7400	1.7	2.5	206
31	decd	0.23	1050	4500	1.9	3.3	209
32	decd	0.27	820	3500	1.6	5.9	201
33	decd	0.35	780	2500	1.5	8.9	183
34	decd	0.52	760	2400	1.4	12	176
35	decd	0.62	1060	2100	1.3	15	144
36	octd	0.003	790	145 400	2.0	< 0.5	223
37	octd	0.01	800	60 000	2.7	1.1	223
38	octd	0.05	850	16 400	2.0	1.6	218
39	octd	0.10	800	9700	1.9	2.3	214
40	octd	0.20	790	5500	1.7	4.1	203
41	octd	0.30	930	4400	1.6	6.9	195
42	octd	0.40	870	3800	1.5	9.9	182
43	octd	0.50	800	3400	1.4	11	175
44	octd	0.60	940	2900	1.4	14	158
45	dicycp	0.02	240	220 000	1.5	< 0.5	218
46	dicycp	0.04	170	158 300	1.5	0.5	214
47	dicycp	0.11	86	93 400	1.3	1.4	201
48	dicycp	0.37	32	25 500	1.7	4.6	*f*
49	dicycp	0.56	23	17700	1.6	13	*f*

[a] Polymerization conditions: 62.5 μmol/L complex (**1**), Al/Ti = 1500, 1.67 mol/L styrene in toluene, total reaction volume 120 mL, T_p = 40 °C, t_p = 1 h. [b] Key: hex = 1-hexene, cypent = cyclopentene, norb = norbornene. [c] Determined by gel permeation chromatography. [d] Determined by ^{1}H NMR. [e] Determined by differential scanning calorimetry. [f] No melting peak.

Table 3. Chain Transfer Constants Calculated from the Plot of the Reciprocal Degree of Polymerization of Styrene ($1/P_{n,\ styrene}$) vs [Olefin]/[Styrene] for the Different Examined Olefins (see Figure 2)

olefin	transfer const
1-hexene	5×10^{-2}
cyclopentene	4×10^{-3}
1,9-decadiene	1×10^{-1}
1,7-octadiene	7×10^{-2}
dicyclopentadiene	1×10^{-2}

and nonconjugated diolefins in isospecific styrene polymerization. In addition, it was of interest to investigate the microstructures of the obtained polymers. Another objective was to exploit the highly effective isospecific styrene polymerization and chain transfer with olefins and diolefins to produce novel mono- and diolefin-terminated isotactic polystyrenes, which are attractive intermediates for the synthesis of block copolymers and functionalized isotactic polystyrenes. The chain transfer with nonconjugated dienes such as 1,9-decadiene represents an attractive route to novel vinyl-functional isotactic oligostyrene macromonomers.

Experimental Section

Materials. All manipulations and reactions were performed under dry argon atmosphere using standard Schlenk tube and glove box techniques. Dichloro[1,4-dithiabutandiyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)]titanium (**1**)[12] and 1-^{13}C-labeled 1-octene[13] were prepared as described in the literature. Methylaluminoxane (MAO, 10 wt % solution in toluene) was purchased from Crompton GmbH, Bergkamen and used without further purification. Toluene (Merck) was distilled over Na prior to use. Styrene (99%, Fluka), 1-hexene (97%, Aldrich), cyclopentene (97%, Fluka), norbornene (99%, Aldrich), 1,9-decadiene (97%, Aldrich), 1,7-octadiene (97%, Aldrich), and dicyclopentadiene (Aldrich) were dried over CaH_2 and distilled under argon.

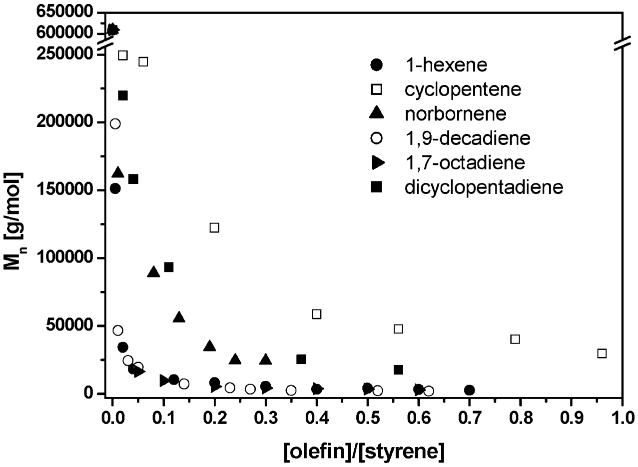


Figure 1. Dependence of number-average molecular weight (M_n) on the olefin/styrene molar ratio for different linear and cyclic mono- and diolefins.

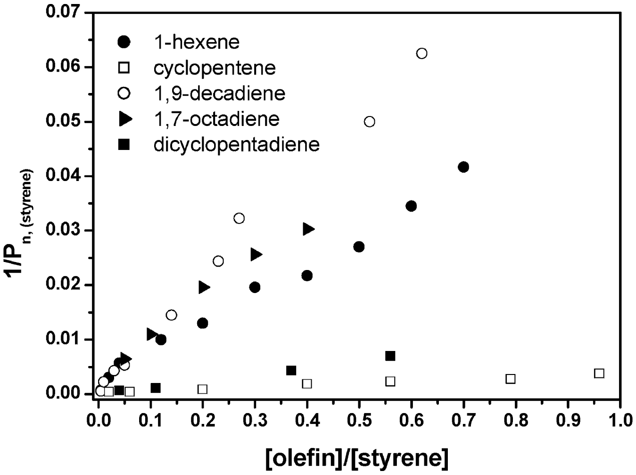


Figure 2. Plots of the reciprocal degree of polymerization of styrene ($1/P_{n,styrene}$) against olefin/styrene molar ratio in the reaction feed for different linear and cyclic mono- and diolefins used as chain transfer agents.

Characterization. *NMR Spectroscopy.* NMR spectra were recorded in $CDCl_3$ at 25 or 120 °C in $C_2D_2Cl_4$ on a Bruker ARX300 spectrometer at 300 MHz with 32 scans for ^{1}H and at 75 MHz with 3000 scans for ^{13}C. The solvent peak was calibrated at 7.25 ppm for ^{1}H and 70.0 ppm for ^{13}C ($CDCl_3$) and 5.93 ppm for ^{1}H and 74.42 ppm for ^{13}C ($C_2D_2Cl_4$), respectively.

Gel Permeation Chromatography (GPC). Number- (M_n) and weight-average (M_w) molecular weights and polydispersities (M_w/M_n) were determined by GPC versus polystyrene standards. The GPC measurements were carried out at 30 °C in chloroform with PSS-SDV columns (8.0 mm x 30 mm, 5 μm particles, 10^3, 10^4, 10^5, 10^6 Å pore size) or at 140 °C in 1,2,4-trichlorobenzene (stabilized with Irganox1010 (Ciba)) using a PL-GPC 220 with triple column set (PLgel mixed-bed, 900 mm, 10 μm). For detection a refractive index detector was used.

Thermal Analysis. Melting points were recorded on a DSC Seiko 6200 at heating rates of 10 K/min. After the first scan from 25 to 260 °C, the samples were annealed at 170 °C for 24 h. Then the melting points (T_m) were determined in a scan from 30 to 260 °C as the endothermic maximum. For calibration, indium and tin standards were used.

Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS). MALDI-TOF spectra were recorded on a Bruker REFLEX II spectrometer equipped with a 337 nm nitrogen laser (3 ns pulse width). Samples for the MALDI-TOF−MS were prepared by mixing the polymer (10 mg/mL, 5 μL), a matrix (dithranole, 20 mg/mL, 20 μL), and a cationizing

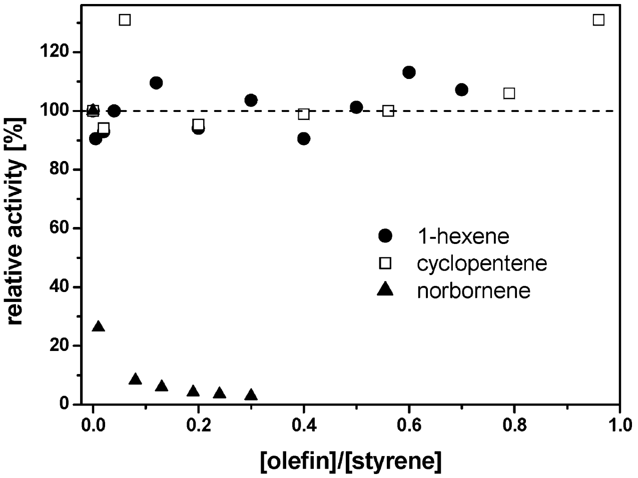


Figure 3. Influence of linear and cyclic monoolefin chain transfer agents on the catalyst activity of styrene polymerization with respect to styrene homopolymerization in the absence of chain transfer agents (activity set to 100%).

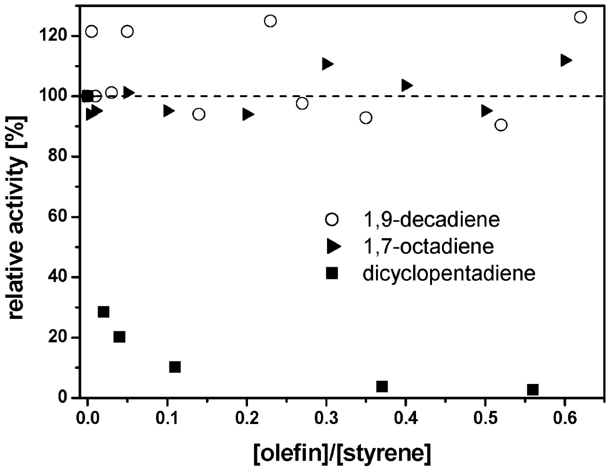


Figure 4. Influence of nonconjugated and bicyclic diolefin chain transfer agents on the catalyst activity of isospecific styrene polymerization with respect to the styrene homopolymerization in the absence of chain transfer agents (activity set to 100%).

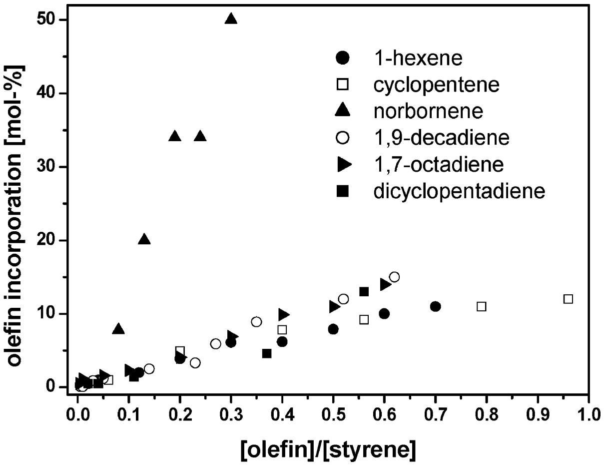


Figure 5. Molar contents of the mono- and diolefins in the isotactic polystyrene chain (including the olefin at the chain end) as a function of the olefin/styrene molar ratio in the reaction feed.

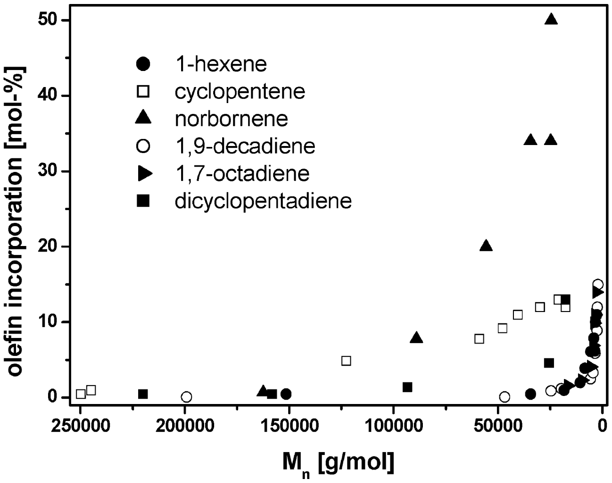


Figure 6. Incorporation of the chain transfer agent in the polymer chain (including the olefin at the chain end) as a function of the number-average molecular mass (M_n) of isotactic polystyrene.

agent (silver trifluoromethanesulfonate, 10 mg/mL, 5 μL) in chloroform. The ions were accelerated to 21.50 kV and measured in the reflection mode of the spectrometer.

Polymerizations. A typical polymerization (run 5) is as follows. A 250 mL Schlenk flask equipped with a magnetic stirrer was subsequently filled with toluene (75 mL), 1-hexene (5.0 mL, 0.040 mol, 0.34 mol/L), and MAO (7.0 mL, Al:Ti = 1500). Then the solution was stirred for 5 min at room temperature. Afterward styrene (23.0 mL, 0.20 mol, 1.67 mol/L) was added and the reaction mixture was heated to 40 °C. The catalyst complex (**1**) (4.02 mg, 7.5 μmol, 62.7 μmol/L) was dissolved in toluene (10 mL), and the reaction was initiated by the injection of the catalyst solution. After 1 h, the polymerization was stopped by pouring the reaction solution into acidified methanol (500 mL). The precipitated polymer was recovered by filtration, washed with methanol, and dried in vacuum at 60 °C to a constant weight. Yield: 5.9 g. $M_{n,GPC}$ ($CHCl_3$) (M_w/M_n): 8300 g/mol (1.7). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K, δ): 7.04 (m, *m*-, *p*-H), 6.59 (m, *o*-H), 5.15 (m, $-CHPh-CH_2-CH{=}C\mathit{H}-CH_2-CH_2-$), 5.02 (m, $-CHPh-CH_2-C\mathit{H}{=}CH-CH_2-CH_2-$), 2.33−1.98 (m, br, CH backbone), 1.82−1.28 (m, br, CH_2 backbone), 1.29−0.98 (m, br, $C\mathit{H}_2$ alkyl), 0.95 (d, $\mathit{H}_3C-CHPh-$), 0.74 (m, $C\mathit{H}_3$ alkyl). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K, δ): 146.3 (*ipso*-C), 131.8 ($-CHPh-CH_2-\mathit{C}H{=}\mathit{C}H-CH_2-$), 128.1 (*o*-C), 127.4 (*m*-C), 125.7 (*p*-C), 42.9 ($\mathit{C}H_2$ backbone), 40.5 (*C*H backbone), 39.0 ($-CHPh-\mathit{C}H_2-CH{=}CH-$), 36.6 ($H_3C-\mathit{C}HPh-$), 34.5 ($\mathit{C}H_2$ alkyl), 29.1 ($\mathit{C}H_2$ alkyl), 22.5 ($\mathit{C}H_2$ alkyl), 20.8 ($H_3\mathit{C}-CHPh-$), 14.1 ($\mathit{C}H_3$ alkyl), 13.6 ($\mathit{C}H_3$ alkyl).

Results and Discussion

Styrene was polymerized on dichloro[1,4-dithiabutandiyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)]titanium (**1**) activated with methylaluminoxane (MAO) in the presence of different monoolefins such as 1-hexene, cyclopentene, and norbornene and also nonconjugated diolefins as 1,9-decadiene, 1,7-octadiene, and dicyclopentadiene (see Scheme 1). The molar ratio of olefin to styrene was varied in order to examine its influence on molar mass, catalyst activity, and olefin incorporation. The polymerization results are shown in Table 1 and Table 2.

Control of Molecular Weight. The polymerization results demonstrate that mono- and diolefins are very effective chain transfer agents. The dependence of molar mass on the olefin/styrene molar ratio for different olefins is shown in Figure 1.

Small amounts of linear mono- and diolefins such as 1-hexene, 1,9-decadiene, and 1,7-octadiene result in a significant decrease of molecular weight. An olefin/styrene molar ratio of 0.01 leads to a molar mass of about 50 000 g/mol in comparison with more than 600 000 g/mol for the styrene homopolymerization in the absence of olefin chain transfer agents. At high olefin/styrene molar ratios, low number-average molecular

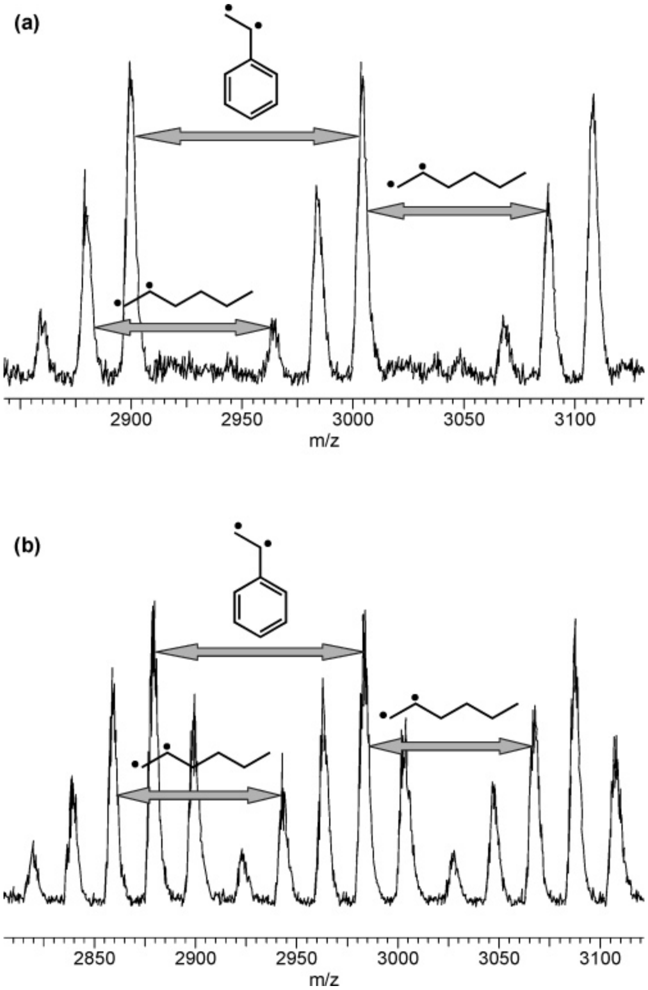


Figure 7. MALDI-TOF spectra (section) of 2-hexen-1-yl-terminated isotactic polystyrenes with (a) $M_n = 8300$ g/mol (run 5) and (b) $M_n = 3300$ g/mol (run 9).

weights of about 2000−3000 g/mol were obtained without sacrificing catalyst activity. In contrast to linear olefins, cycloolefins are less effective chain transfer agents with the lower limit at molecular weights of around 20 000 g/mol. In order to quantify chain transfer effectiveness, chain transfer constants were determined. The plot of the reciprocal degree of polymerization ($1/P_{n,\text{styrene}}$) against olefin/styrene molar ratio for different olefins is shown in Figure 2. The polymerization degree for each polymer sample was determined by combining results from gel permeation chromatography (GPC) and ^{1}H NMR analysis.

For the determination of the transfer constants, only samples with olefin incorporation via copolymerization below 10 mol % were considered (see Table 3). Since norbornenes are copolymerized very effectively, no chain transfer constants were determined for norbornenes.

The chain transfer constant values emphasize the efficiency of linear olefins as better chain transfer agents compared to cycloolefins.. For example 1,9-decadiene is about 1.5 orders of magnitude more effective than cyclopentene.

The very effective control of molecular weight can be explained by the different nature of styrene and linear or cyclic mono- or diolefins in isospecific styrene polymerization. So the phenyl ring of the last inserted styrene on the growing polymer chain can stabilize the metal center by coordination. After the insertion of an olefin, this additional stabilization is lost and β-H elimination after olefin insertion is much faster with respect to that observed after styrene insertion. This results in a decrease of molecular weight in the obtained iPS.

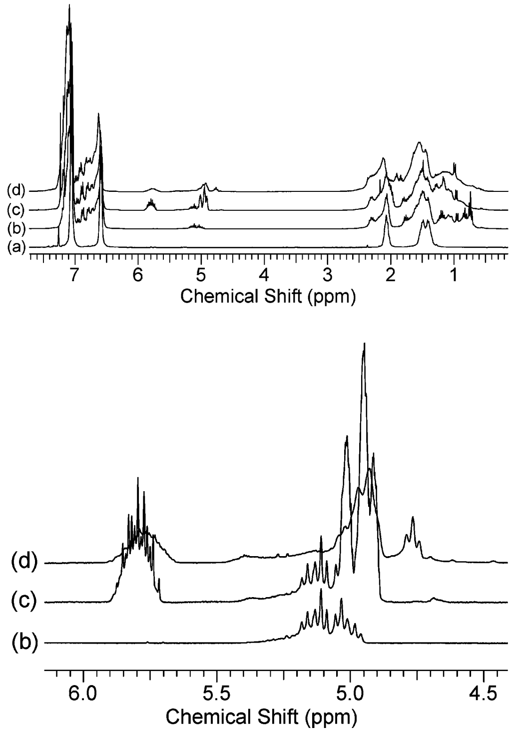
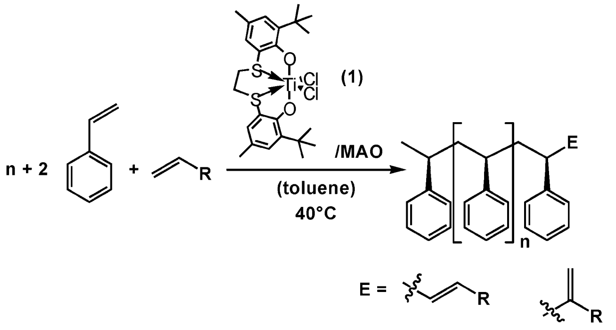


Figure 8. ^{1}H NMR spectra of (a) isotactic polystyrene homopolymer (run 0) and low molecular weight iPS obtained by polymerization in the presence of (b) 1-hexene (run 10), (c) 1,9-decadiene (run 35), and (d) 1,7-octadiene (run 44). For (b), (c), and (d) also an expansion of the olefinic region is shown.

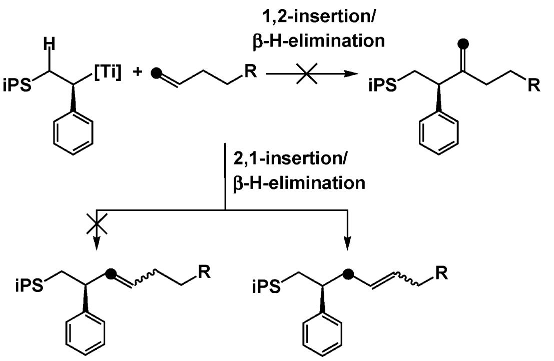
Scheme 1. Isospecific Polymerization of Styrene on Bisphenolato Titanium Catalyst (1) Activated by Methylaluminoxane in the Presence of Olefins to Control Molecular Weight and End Groups (E)[a]



[a] For clarity the possibility of copolymerization of the olefin is not considered.

The GPC analyses of all isotactic oligo- and polystyrenes confirm monomodal molecular weight distributions with polydispersity indices around two, as expected for single-site catalysts. In some cases, the polydispersity values decrease with decreasing molecular weights. This is attributed to fractionation of low molecular weight fractions during precipitation in methanol. Melting temperatures were measured by means of thermal analysis (DSC). After the first scan from 25 to 260 °C, the complete molten samples were annealed at 170 °C for 24 h to achieve crystallization, even for the low molecular weight polystyrene samples. Then the melting temperatures were determined in a scan from 30 to 260 °C with a heating rate of 10 K/min. In general, the melting temperatures decrease with decreasing molecular weight from 223 °C for the iPS homopolymer and polymers with molecular weights of 20 000

Scheme 2. Possible End Groups after 1,2 and 2,1 Insertion of the 1-^{13}C-Labeled 1-Olefin in the Polymer Transition Metal Bond and Hydrogen Elimination[a]



[a] After 2,1 insertion hydrogen elimination from C1 or C3 of the 1-olefin can take place. The ^{13}C-labeled carbon atoms are as marked.

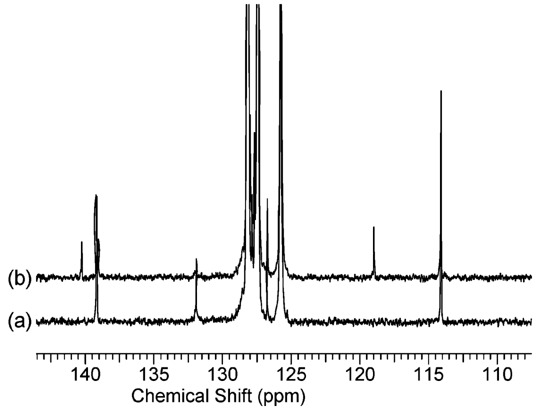


Figure 9. Expansion of the olefinic region in the ^{13}C NMR spectrum of isotactic polystyrene obtained in the presence of (a) 1,9-decadiene (run 35) and (b) 1,7-octadiene (run 44).

g/mol minimum to about 175 °C for polymers with number-average molecular weights in the range of 3000 g/mol. This decrease of melting temperatures can be assigned to shorter styrene sequences in the polymers due to slight incorporation of linear olefins and lower molecular weights. High incorporation rates of olefins prevent crystallization, as in the case of isotactic polystyrenes (M_n < 100 000 g/mol) produced in the presence of cycloolefin chain transfer agents. No melting was detected even after annealing at 170 °C for 24 h. The formation of amorphous isotactic polystyrene is due to the random incorporation of cycloolefins into the isotactic polystyrene backbone via copolymerization.

Polymerization Activities. The influence of olefin/styrene molar ratio on catalyst activity was investigated and compared to the catalyst activity of isoselective styrene polymerization in the absence of chain transfer agents (Figures 3 and 4). The addition of chain transfer agents such as linear mono- and diolefins did not affect high catalyst activities. As a consequence, low and very high molecular weight isotactic polystyrenes were obtained in very similar high yields. In contrast to linear mono- and diolefins and cyclopentene chain transfer agents, addition of bicyclic olefins such as norbornene and dicyclopentadiene accounted for significant losses of polymerization activities. In fact, at high bicyclic olefin/styrene molar ratios, severe poisoning of the catalyst was observed.

Polymer Microstructure and End Group Analysis. Structural analysis of the obtained polymers was carried out by ^{1}H, ^{13}C NMR, and MALDI-TOF spectroscopy to gain information about the incorporation of the chain transfer agent and the end group. In addition to chain transfer via β-H elimination immediately after olefin insertion, it is possible that olefins are copolymerized with styrene, resulting in incorporation of olefins into the isotactic polystyrene backbone. For 1-hexene, cyclopentene, 1,9-decadiene, 1,7-octadiene, and dicyclopentadiene, respectively, the incorporation reaches a maximum at 12−15 mol % for olefin/styrene molar ratios larger than 0.5 (see Figure 5). Only norbornenes are copolymerized very effectively. At the norbornene/styrene molar ratio of about 0.30, the content of the copolymerized norborne was 50 mol %. NMR analysis showed a random distribution of norbornene in the polystyrene backbone.

Related to the molecular masses of isotactic polystyrenes, the olefin incorporation increased with decreasing molar mass of the polymer (Figure 6). Interestingly, clear differences between linear and cyclic olefins were observed. In the case of linear olefins, significant incorporation is detected only for low molecular weight samples. For example, 10 mol % of olefin incorporation, equivalent to two to three 1-olefins per chain including end groups, was observed for oligostyrenes with number-average molar masses of about 3000 g/mol. In sharp contrast, much higher olefin incorporation was observed with cylcoolefins even for polystyrenes with molecular masses above 100 000 g/mol.

MALDI-TOF spectra were recorded for polymers with different molecular weights and are shown in Figure 7 exemplarily for different iPS samples polymerized in the presence of 1-hexene. For number-average molecular weights above 10 000 g/mol, only peaks with a mass difference of 104 amu, corresponding to one styrene unit, can be observed. Spectra of samples with lower molecular weights show for each polymerization degree of styrene a group of peaks representing polymers with the same number of polymerized styrene units but with different 1-hexene content. In this case, the characteristic *m*/*z* difference is 84 amu besides 104 amu for styrene. As mentioned above, the molar rate of incorporated olefin increases with decreasing molecular weight, which can also be substantiated from the MALDI-TOF spectra. So the iPS with $M_n = 8300$ g/mol (run 5) shows three main species for each polymerization degree of styrene, the main product with only a terminal 1-hexene unit and others with one and two 1-hexene units incorporated, respectively. On the other hand, the sample with $M_n = 3300$ g/mol (run 9) consists of five species for each polymerization degree of styrene, where the main product has a terminal and one incorporated 1-hexene unit. Also 1-alkyl chain ends could be formed via addition of transition metal hydrides to the olefin at high olefin concentrations. The alkanyl and alkenyl end groups, both resulting from 1-olefin insertion, could account for this behavior (typical only for lower molecular weights). Isotactic polystyrene samples obtained by the polymerization in the presence of other linear olefins, including diolefins, show similar behavior.

Information concerning the polymer end group is obtained from ^{1}H and ^{13}C NMR spectroscopic investigations of polymer samples with low molecular weights. Therefore, we focused our attention to isotactic polystyrenes obtained by polymerization in the presence of linear olefins. Figure 8 shows the ^{1}H NMR spectra of an isotactic polystyrene homopolymer (a) and low molecular weight iPS obtained by polymerization in the presence of 1-hexene (b), 1,9-decadiene (c), and 1,7-octadiene (d). The peaks at 5.15 and 5.02 ppm can be assigned to the vinylene group formed after β-hydride abstraction on the last α-olefin inserted in the 2,1 mode. The absence of vinylidene end groups indicates that chain transfer occurred exclusively after 2,1 insertion of the 1-olefin. Due to the vicinity of the phenyl rings

Table 4. ^{1}H and ^{13}C NMR Shifts of Vinylene and Vinyl End Groups in Isotactic Polystyrene Samples Obtained via Polymerization of Styrene in the Presence of Linear 1-Olefins and 1,9-Decadiene.

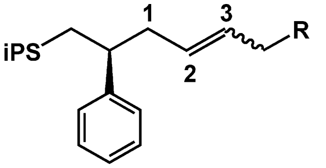
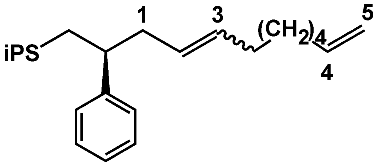
chain end groups in iPS samples	^{1}H and ^{13}C NMR chemical shifts (ppm relative to chloroform)			
	H^1	2.37	C^1	39.0
	H^2	5.02	C^2	131.8
	H^3	5.15	C^3	131.8
	H^4	5.80	C^4	139.2
	H^5	4.96	C^5	114.1

Table 5. Comparison of the Number-Average Molecular Weights Obtained from GPC in Chloroform and from ^{1}H NMR End Group Analysis via Integration of the Vinylene Group (5.15 and 5.02 ppm)

run	olefin	[olefin]/ [styrene]	$M_{n,GPC}$ (g/mol)	$M_{n,NMR}$ (g/mol)
4	1-hexene	0.12	10 600	13 200
5	1-hexene	0.20	8300	8600
6	1-hexene	0.30	5600	6700
7	1-hexene	0.40	5000	5700
8	1-hexene	0.50	4100	4900
9	1-hexene	0.60	3300	4000
10	1-hexene	0.70	2700	2600
29	1,9-decadiene	0.05	19 700	19 500
30	1,9-decadiene	0.14	7400	6900
31	1,9-decadiene	0.23	4500	5300
32	1,9-decadiene	0.27	3500	4000
33	1,9-decadiene	0.35	2500	2800
34	1,9-decadiene	0.52	2400	2400
35	1,9-decadiene	0.62	2100	2100

of the styrene units, the chemical shift difference of the two olefinic protons decreases in comparison to low molecular weight compounds. So the chemical shift difference is in the range of vicinal coupling constants leading to a second-order spectrum. As a consequence, the multiplicity of the signal does not follow simple rules anymore, and so the complex signal pattern can be explained.

In the spectrum of the 2,9-decadien-1-yl-functionalized iPS, the peaks of the vinylene group can also be found, where the peak at 5.02 ppm is overlapped by the methylene protons of the terminal double bond (4.96 ppm). The signal of the terminal methine protons corresponds to the multiplet at 5.80 ppm. Therefore, the evidence for the formation of vinyl group terminated isotactic polystyrene is present. However, the ^{1}H NMR spectrum of isotactic polystyrene obtained in the presence of 1,7-octadiene shows two additional peaks in the olefinic region at 5.36 and 4.73 ppm, resulting from isomerization of the terminal double bond and cyclization at the polymer chain end, respectively.

These structural observations can also be confirmed by ^{13}C NMR spectroscopy. Further structural details about the end group formed after 1-olefin insertion were obtained when 1-^{13}C-labeled 1-octene was used as chain transfer agent in isospecific styrene polymerization. An 2-octen-1-yl-terminated isotactic polystyrene with a number-average molecular weight of 3100 g/mol was obtained. 1-Octene shows the same chain transfer behavior as 1-hexene. Two feasible mechanistic pathways are illustrated in Scheme 2. First, β-hydride elimination after 1,2 insertion of the olefin forms vinylidene end groups. Second, β-hydride elimination after 2,1 insertion of the olefin produces either 1-octen-1-yl or 2-octen-1-yl end groups. Labeling of 1-octene at the C1 was used to examine the end groups.

A peak of the secondary carbon atom of a vinylidene end group can be expected around 110 ppm in ^{13}C NMR spectra. Since no signals can be observed in low molecular weight samples (run 10) in this region and in the ^{13}C-labeled polymer (M_n = 3100 g/mol) (only traces at 110.4 ppm can be found), the 1,2 insertion of the 1-olefin can be ruled out. Comparison of peak intensities in the spectra of the ^{13}C-labeled isotactic polystyrene with those of non-^{13}C-labeled isotactic polystyrenes with similar molecular weights (runs 9 and 10) gave information about the β-hydrogen elemination after 2,1 insertion of the 1-olefin. Since the peak at 131.8 ppm corresponding to the unsaturated carbons of the vinylene end group showed no increased intensity, the hydrogen elimination occurs exclusively at the C3 of the inserted 1-olefin. In addition, this is supported by the strong increase of intensity of the peak at 39.0 ppm corresponding to the methylene carbon between the last inserted styrene and the vinylene group. Furthermore, only very small signals for the incorporation of the 1-olefin in the polystyrene chain were found. In Table 4 the ^{1}H and ^{13}C NMR shifts of vinylene and vinyl end groups in isotactic polystyrenes formed after 2,1 insertion of an 1-olefin or 1,9-decadiene, respectively are compiled.

The signals from the 2,1 insertion of a styrene on a Ti−H bond can be located at 36.6 and 20.8 ppm.[8] Analysis of the ^{13}C NMR spectrum of 2,9-decadien-1-yl-terminated iPS also shows the signal of the vinylene group at 131.9 ppm. In addition, peaks of the terminal vinyl group can be seen at 139.2 and 114.1 ppm (see Figure 9).

The ^{13}C NMR spectrum of isotactic polystyrene obtained in the presence of 1,7-octadiene (run 44) on comparison with the spectrum of 2,9-decadien-1-yl-terminated iPS (run 35) shows two additional peaks at 140.3 and 119.0 ppm due to cyclization at the chain end (see Figure 9). According to these observations, 1,9-decadiene is the preferred chain transfer agent for producing vinyl-terminated isotactic polystyrenes with adjustable molecular weight that are a new class of vinyl-functional isotactic polystyrene macromonomers.

End group analysis to determine number-average molecular weights is possible for samples with both relative low molecular weights and end groups exclusively consisting of vinylene groups. So in the case of 2-hexen-1-yl- and 2,9-decadien-1-yl-terminated isotactic polystyrenes, the molecular weight can be calculated from the ^{1}H NMR spectra. Therefore, the peaks of the vinylene group at 5.15 and 5.02 ppm were set to 2H for 2-hexen-1-yl-terminated polymers and the peak at 5.15 ppm was set to 1H for 2,9-decadien-1-yl-terminated isotactic polystyrenes, respectively (see Table 4). The results in comparison to GPC values are shown in Table 5.

The NMR analysis shows the same trend as discussed above for the GPC measurements. In addition, the number-average molecular weights obtained from different methods are in correspondence, taking the deviations into account. Consequently, it can be assumed that the functionalization of the chain end is nearly quantitative and the formation of saturated end groups through chain transfer to aluminum alkyls can be neglected. In accordance with NMR measurements and thermal analyses, it is obvious that the linear 1-olefins are very effective chain transfer agents with chain transfer occurring immediately after insertion of the 1-olefin.

Conclusions

Styrene was isospecifically polymerized on dichloro[1,4-dithiabutandiyl-2,2′-bis(6-*tert*-butyl-4-methylphenoxy)]titanium (**1**) activated with MAO in the presence of different linear and cyclic mono- and diolefins as chain transfer agents. It was possible to control the molecular mass of isotactic polystyrene over a very wide range by changing the olefin/styrene molar ratio. The highest chain transfer constants were found for linear mono- and diolefins such as 1-hexene, 1,9-decadiene, and 1,7-octadiene. In the presence of linear mono- and diolefins as chain transfer agents, the molecular mass of isotactic polystyrene varied between 2000 and 600 000 g/mol without adversely affecting high catalyst activities. Only bicyclic olefins caused severe catalyst poisoning at high olefin contents. In contrast to cyclic olefins, especially norbornene, the incorporation of linear mono- and diolefins into the backbone was very low. For linear mono- and diolefins, the chain transfer occurred immediately after 2,1 olefin insertion. NMR analysis indicated that vinylene-type end groups were formed exclusively when 1-olefins were added as chain transfer agents. Much more reactive vinyl end groups were formed when nonconjugated dienes such as 1,9-decadiene were added as chain transfer agents. Chain transfer by 1,9-decadiene afforded the novel class of isotactic polystyrene, containing one end group with two double bonds consisting of one vinyl and one vinylene group. Since vinyl groups are much more reactive with respect to vinylene groups, the novel family of vinyl-terminated isotactic oligostyrenes are very attractive macromonomers and intermediates for block copolymer synthesis and for the preparation of novel functionalized isotactic polystyrenes.

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