New Materials Designed by Coordination Polymerization of ω-undecenyl Macromonomers

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Summary: The major part of the present paper discusses the ability of well-defined ω-undecenyl polystyrene, polyisoprene or poly(styrene-*block*-isoprene) macromonomers to undergo coordination homopolymerization in the presence of selected titanium catalysts. Special emphasis is given to the influence of the nature of the catalyst, the polymerization temperature and the macromonomer molar mass and concentration on homopolymerization yield and average degree of homopolymerization (DP_n). Titanium-based catalytic systems such as $CpTiCl_3$/MAO and Cp^*TiCl_3/MAO only yielded dimers. The use of the homogeneous metallocene catalyst with constrained ligand geometry (CGC-Ti/MAO) having an open active site, significantly improved the degree of polymerization. Increasing macromonomer molar mass, causes only a slight decrease of DP_n whereas conversion increased moderately. The final section briefly discusses the copolymerization of ω-undecenyl polystyrene macromonomers with ethylene in the presence of Versipol[TM] catalysts.

Keywords: *comb*-shaped; Constrained Geometry Catalyst (CGC); homopolymerization; macromonomer; titanium

Introduction

Recent advances in the search for new polymer topologies have caused the controlled synthesis by anionic or free (or controlled) radical polymerization of macromonomers (polymer chains fitted at the chain end with a polymerizable group) of complex macromolecular architectures named polymacromonomers (PM). These comb-shaped (co)polymers represent a special class of well-defined branched polymers characterized by a high segment density of branches (homopolymeric or copolymeric) and shape ranging from spherical to non-spherical depending on the number of branches.[1–5] However, neither control of the tacticity of the backbone, nor polymerization of macromonomers with allyl- or undecenyl end-groups could be achieved by anionic or free radical polymerization. A few years ago, coordination polymerization was also tested for the polymerization of polystyrene (PS) macromonomers whereupon syndiotactic PS-*graft*-atactic PS stereo combs could be synthesized.[6] Nevertheless, homopolymerization yields were always low. The system could be improved recently by Lutz and coll.[7] who made a systematic investigation of the influence of the nature of the coordination catalyst on the homopolymerization yield and the average degree of polymerization. In the same paper, these authors reported the first successful coordination polymerization of ω-undecenyl PS macromonomers in presence of the CGC-Ti/MAO

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catalyst yielding a *comb*-shaped poly(ethy-lene-*graft*-styrene) polymer with DP_n values around 20.

In the present work, the coordination homopolymerization of ω-undecenyl PS macromonomers can be further examined. The influence of several parameters such as macromonomer molar mass, concentration or polymerization temperature on the homopolymerization yield and the average degree of polymerization are studied. These polymacromonomers are character-ized by a chemically inert core and an outer polystyrene shell, well-suited for further chemical reactions. Due to the limited number of branches, the properties of these PMs should be comparable to those of star-shaped polymers. Increasing interest has been devoted to star-shaped polymers with poly(styrene-*block*-isoprene) branch-es. These structures revealed interesting morphologies. Therefore the synthesis and the homopolymerization of ω-undecenyl poly(styrene-*block*-isoprene) macromono-mers was attempted. The results are dis-cussed in the second section together with some data on the synthesis and the homo-polymerization of ω-undecenyl polyiso-prene macromonomers. The final section summarizes, based on data taken from literature, the results obtained for the copolymerization of the ω-undecenyl PS macromonomers with ethylene in the presence of the Versipol™ catalyst.

Experimental

Materials

For the procedures concerning purification of solvents, monomers, initiators or cata-lysts used in the present work, the reader is invited to consult reference 9.

Synthesis of ω-Undecenyl Polystyrene (PS), Polyisoprene (PI) or Poly(styrene-block-isoprene) Macromonomers

Macromonomer synthesis was discussed in the previous papers.[7–9] Briefly, a reactor (purged via vacuum –argon exchanges and kept under a slight argon over pressure)

fitted with six burets [styrene (and / or isoprene), 11-bromo-1-undecene (or allyl bromide), *sec*-butyllithium (BuLi), THF and toluene)] was used. Once toluene was introduced, the remaining traces of proto-nic impurities were neutralized by addition of few drops of BuLi (styrene acting as indicator). Next, the amount of initiator solution needed to get the chosen molar mass was added at once. Then the poly-merization of styrene (or isoprene) was conducted according to well established procedures. An aliquot of the polymer solution (20 to 40 mL) was separated from the main solution, deactivated with a few drops of methanol, and characterized. The reaction mixture was cooled to $-70\,°C$, dry THF was added, followed by addition, of a slight molar excess of 11-bromo-1-unde-cene. The solution was stirred overnight at room temperature and concentrated. The residue was dissolved in toluene, filtered and precipitated in methanol. Methanol solution was decanted off, and macromo-nomer was dried under vacuum at $35\,°C$. Poly(styrene-*block*-isoprene) macromono-mers were synthesized as described in reference 9. The different macromonomers were characterized by SEC, ^{1}H NMR, and MALDI-TOF MS.

Homopolymerization Procedure

One g of macromonomer was dissolved in 1 mL of toluene, 0.5 mL of MAO solution was added via a cannula. Reaction solution was stirred for 10 minutes at desired reaction temperature ($50\,°C$ or $70\,°C$), 0.001 g of catalytic complex dissolved in 1 mL of toluene was added via cannula. Solution was stirred for 48 hours and quenched with 5 mL of methanol, thereafter 10 mL of a H_2O/EtOH/HCl (5/4/1) solution were added. This solution was stirred one day in order to dissolve all aluminum chloride. Reaction product was precipitated in methanol and recovered. Each homopolymerization test was carried out at least two times.

Analysis and Characterization

Molar masses and molar mass distributions were obtained by SEC with RI detection or

SEC online LS as described earlier.[7] Yields of functionalization were determined by ^{1}H NMR spectroscopy on a Bruker 400 apparatus using $CDCl_3$ as solvent at 25 °C, by chemical titration or by matrix-assisted laser desorption ionization time of flight (MALDI-TOF MS) mass spectrometry on a Bruker Reflex II apparatus.

Results and Discussion

ω-Undecenyl Polystyrene Macromonomers

Synthesis and Characterization
ω-Undecenyl PS macromonomers covering a molar mass domain from 1000 to 25000 g/mol were prepared as indicated in the experimental part. They were submitted to characterization to assess molar mass, molar mass distribution and functionality. Some characteristics of these macromonomers are given in Table 1. Well-defined species with narrow molar mass distributions and free of coupling products (no shoulder detected on the SEC diagram peak) were obtained. Experimental and theoretical molar masses are in good agreement. Yield of functionalization determined by chemical titration or ^{1}H NMR is almost quantitative. The samples were analyzed by MALDI-TOF MS (Figure 1).

ω-Undecenyl Polystyrene Macromonomers

Homopolymerization
The ω-undecenyl PS macromonomers were polymerized in the presence of $CpTiCl_3$/MAO, Cp^*TiCl_3/MAO or CGC-Ti/MAO. Homopolymerization data obtained in the presence of CGC-Ti/MAO are depicted in Table 2.

SEC characterization (not presented) of samples homopolymerized in the presence of $CpTiCl_3$, Cp^*TiCl_3/MAO showed the presence of a main peak (whose elution volume corresponds to the precursor macromonomer) and an other one corresponding to a dimer. This observation was already made in a preliminary work. These results are not a surprise as it is well established that hemi-metallocene catalysts are not very efficient for the polymerization of allyl type double bonds. However, SEC characterization of the samples obtained in the presence of the CGC-Ti/MAO catalyst revealed the presence at lower elution volumes of the expected *comb*-shaped polymer. This can be explained by the open structure of the CGC-Ti/MAO catalyst favoring the access of the polymerizable entity located at the chain end to the active site. Homopolymerization of macromonomers of molar masses up to 12000 g/mol could be achieved. The molar mass distributions are much lower than generally observed in coordination polymerization.

Table 1.
Molecular characteristics of ω-undecenyl polystyrene macromonomers.

Run	$M_{n, th}$ a) (g/mol)	$M_{n, NMR}$ b) (g/mol)	$M_{n,SEC}$ c) (g/mol)	$M_{w,SEC}$ c) (g/mol)	$M_{w,SEC}/M_{n,SEC}$ c)	DF d) (%)	DF e) (%)
M-PS1$_{1400}$	1400	1640	1400	1500	1.07	99	77
M-PS2$_{5000}$	5000	6500	5100	5400	1.06	98	86
M-PS3$_{11000}$	11000	11000	11400	12000	1.05	98	95
M-PS4$_{25000}$	25000	25400	25300	27300	1.08	98	99

a) M-PSX refers to ω-PS macromonomers with undecenyl end-groups, Theoretical average molar mass calculated from the ratio [Monomer converted]/[Initiator].
b) Experimental number average average molar mass measured by ^{1}H NMR spectroscopy.
c) Experimental number, weight average molar mass and molar mass distribution, respectively measured by SEC (with standard linear PS calibration).
d) Degree of functionalization measured by ^{1}H NMR using an internal standard ($C_2H_2Cl_4$).
e) Degree of functionalization measured by ^{1}H NMR using NMR signal of terminal methyls as reference.
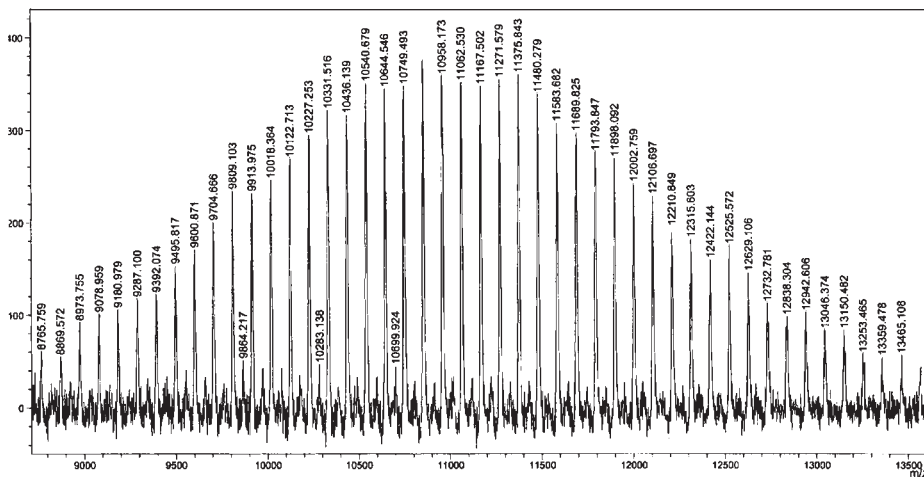
Figure 1.
MALDI-TOF MS Spectrum of M-PS3$_{11000}$.

Table 2.
Experimental conditions for the synthesis and molecular characteristics of polymacromonomers obtained by homopolymerization of ω-undecenyl polystyrene macromonomers in the presence of a CGC-Ti/MAO catalyst

Run	Temp. (°C)	$M_{n,SEC}$[a] (g/mol)*	$M_{w,SEC}$[a] (g/mol)	$M_{w,SEC}$[a]/$M_{n,SEC}$	$M_{w,LS}$[b] (g/mol)	DP_n	Conv.[c] (wt.-%)
PM-PS1$_{1400}$	50	12 200	14 900	1.22	21 900	16	33
	50	12 400	15 200	1.23	24 800	18	36
	70	11 200	14 000	1.25	20 900	15	40
	50	11 700(9%)	12 200	1.04	12 000	2	64
		27 900(91%)	31 500	1.13	42 600	8	
PM-PS2$_{5000}$	50	13 000(20%)	15 600	1.20	11 800	2	54
		32 600(80%)	36 100	1.11	55 500	11	
	70	11 900(9%)	12 400	1.04	11 600	2	55
		26 900(91%)	30 400	1.13	39 800	8	
PM-PS3$_{11000}$	50	24 100(28%)	25 600	1.06	25 500	2	64
		46 100(72%)	49 700	1.08	77 100	7	
	50	28 600(17%)	29 900	1.04	25 400	2	56
		58 800(83%)	63 800	1.09	89 100	8	
	70	23 900(28%)	25 300	1.06	25 300	2	61
		45 700(72%)	49 300	1.08	75 200	7	
PM-PS4$_{25000}$	50	47 200(26%)	49 100	1.04	55 200	2	59
		80 400(74%)	87 200	1.08	126 400	5	
	50	52 100(17%)	53 200	1.02	53 900	2	51
		80 200(83%)	88 800	1.11	104 200	4	
	70	48 200(4%)	48 500	1.01	58 900	2	56
		61 600(96%)	71 900	1.17	101 900	4	

Conditions: CGC-Ti: 0.001 g (2.72 μmol) /1 mL toluene, co-catalyst: MAO: 0.157 g (2.71 mmol) / 0.5 mL toluene, macromonomer: 1.0 g/1 mL toluene, [Al]/[Ti] = 1000, reaction time: 48 hours.
[a] Experimental number, weight average molar mass and molar mass distribution, respectively measured by SEC (with standard linear PS calibration).
[b] Weight average molar mass measured in THF by SEC with online light scattering.
[c] Conversion determined by SEC (RI trace).
* Data between brackets (when the case) correspond to dimer and polymacromonomer content, respectively (determined by SEC, 100% of the precursor polymer was recovered).

Table 3.
Molecular characteristics of ω-undecenyl PI macromonomers

Run	[Toluene] /[THF]	$M_{n,\ th}$[a] (g/mol)	$M_{n,exp}$[b] (g/mol)	$M_{w,exp}$[b] (g/mol)	$M_{w,SEC}$[b] /$M_{n,SEC}$	DF[c] (%)
M-PI1	1	2000	2900	3100	1.06	83
M-PI2	2.5	2000	2600	2800	1.07	88
M-PI3	2.5	2000	2700	2900	1.06	96
M-PI4	3.3	3000	3600	3850	1.07	85
M-PI5	2.5	10000	11300	12200	1.08	91

[a] Theoretical molar mass calculated from ratio [Monomer converted]/[Initiator].
[b] Experimental number, weight average molar mass and molar mass distribution, respectively measured by SEC (with standard linear PS calibration).
[c] Degree of functionalization determined by ^{1}H NMR (chemical titration is not possible in the case of polyisoprene chains).

The molar mass of the macromonomer only slightly influences the average degree of polymerization. However, yields of homopolymerization and average degrees of homopolymerization are much lower than those determined in the case of the homopolymerization of ω-styrenyl PS macromonomers with the same catalyst.

ω-Undecenyl Polyisoprene Macromonomers

Branched materials based on polydienes have attracted increasing interest because of the high density of elastomeric branches they exhibit, yielding original solution properties and solid-state behavior. However, most of these branched topologies concern star-shaped structures. Coordination polymerization of polyisoprene macromonomers could provide access to a new class of branched topologies with elastomeric branches. The efficiency of the macromonomer approach to design branched polymers of controlled structural parameters has been explained above in the case of ω-undecenyl PS macromonomers.

Synthesis and Characterization

Polyisoprene macromonomers were synthesized, as described in the experimental part, by quenching a living anionic polyisoprene directly with ally bromide or 11-bromo-1-undecene at −70 °C. They were characterized by SEC, ^{1}H NMR and by MALDI-TOF MS to assess their structural parameters (Table 3).

Results presented in Table 3 above and in Figure 2 are in many extends comparable to those obtained for ω-undecenyl polystyrene macromonomers: sharp molar molar distributions, good agreement between theoretical and experimental molar mass, quantitative functionalization. Results obtained for ω-allyl polyisoprene macromonomers are less satisfactory. Similar conclusions were made in the case of ω-allyl polystyrene macromonomers.

A typical MALDI-TOF MS spectrum of M-PI2 is given in Figure 3.

ω-Undecenyl Polyisoprene Macromonomers

Homopolymerization

The data on the homopolymerization of ω-undecenyl polyisoprene macromonomer (MP-I2) by CGC-Ti/MAO catalysts are summarized in Table 4 together with the experimental conditions.

Conversion of the macromonomer proceeded up to 40 wt.-% in the best case, at which point the increasing viscosity of the reaction mixture, and/or side reactions probably, prevented further homopolymerization. Homopolymerization degree values are identical to those of ω-undecenyl PS macromonomers. Homopolymerization yield increases with increasing macromonomer concentration (Figure 4) as generally observed. The PI macromonomers are characterized by the presence of the undecenyl double bond at the chain end
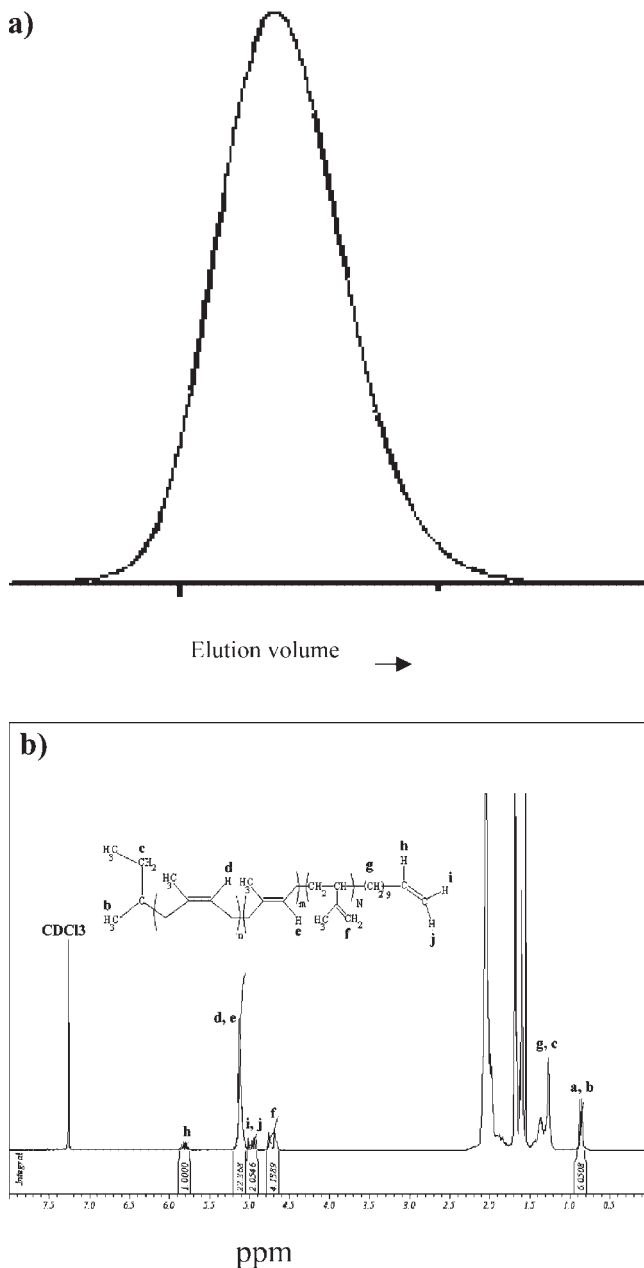
Figure 2.
SEC diagram (a) and ¹H NMR spectrum (b) of M-PI2.

(which should be involved in the coordination polymerization process) and the double bonds of the polyisoprene. The content of the later double bonds was determined by ¹H NMR. The values are in good agreement with those generally accepted for polyisoprenes obtained with BuLi in apolar solvents. However, these double bonds may also react during the coordination polymerization process. In fact no reaction took place when unfunctionalized PI chains were kept for 24h in the presence
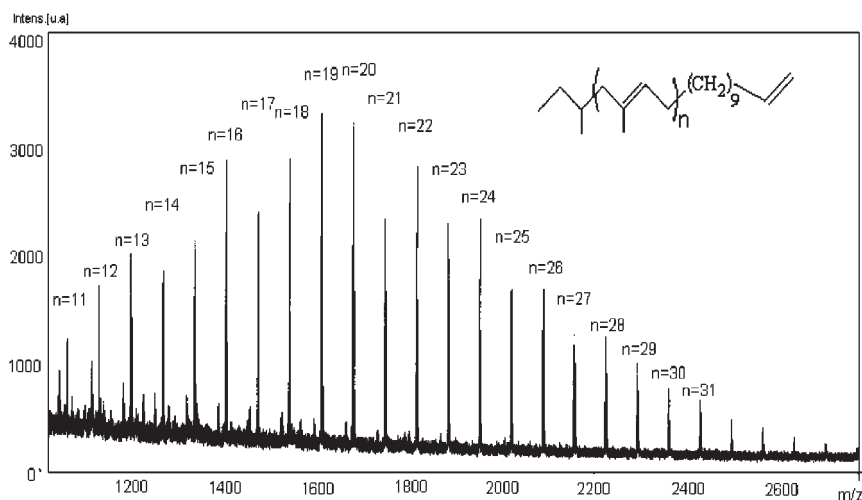
Figure 3.
MALDI-TOF MS spectrum of M-PI2.

of the CGC-Ti/MAO. This was confirmed unambiguously by SEC characterization made on the final product. This prompted to further work on the coordination homopolymerization of ω-undecenyl polyisoprene macromonomers and to extend it to the homopolymerization of ω-undecenyl poly(styrene-*block*-isoprene) macromonomers.

ω-Undecenyl Poly(styrene-block-isoprene) Macromonomers

Synthesis and Characterization

ω-Undecenyl poly(styrene-*block*-isoprene) macromonomers with well-defined molar

mass and functionality were synthesized as described in 9.

Homopolymerization

As already discussed in reference 9, homopolymerization of poly(styrene-*block*-isoprene) macromonomers, when carried out at 50 °C or 70 °C, yielded a *comb*-shaped polymer, constituted of a polyethylene backbone and poly(styrene-*block*-isoprene) branches. Homopolymerization yields revealed comparable to those obtained for the homopolymerization of *ω-undecenyl* polystyrene or polyisoprene macromonomers. The present work further discusses the influence of temperature or macromo-

Table 4.
Experimental conditions for the synthesis and molecular characteristics of polymacromonomers obtained by homopolymerization of ω-undecenyl polyisoprene macromonomer (M-PI2) in the presence of a CGC-Ti/MAO catalyst

Run	Temp (°C)	Time (in h)	$M_{n,\,SEC}$[a] (g/mol)	$M_{w,SEC}$[a] (g/mol)	$M_{w,SEC}$[a] /$M_{n,SEC}$	$M_{w,LS}$[b] (g/mol)	DP_n	Conv (wt.-%)
PM-PI2A	50	24	17100	20700	1.2	25800	10	47
PM-PI2B	50	24	15900	19200	1.2	21600	8	47
PM-PI2C	70	24	17000	20000	1.2	23800	9	33
PM-PI2D	70	48	15200	18400	1.2	19200	7	45
PM-PI2E	90	24	13900	18400	1.3	19200	7	39

General conditions: CGC-Ti (0.001 g, 2,72 μmol) 1/mL of toluene; MAO (0.157 g, 2,71 mmol)/1 mLof toluene; macromonomer (1 g/1 ml of toluene; [Al]/[Ti] = 1000.
[a] Experimental number, weight average molar mass and molar mass distribution, respectively measured by SEC (with standard linear PS calibration).
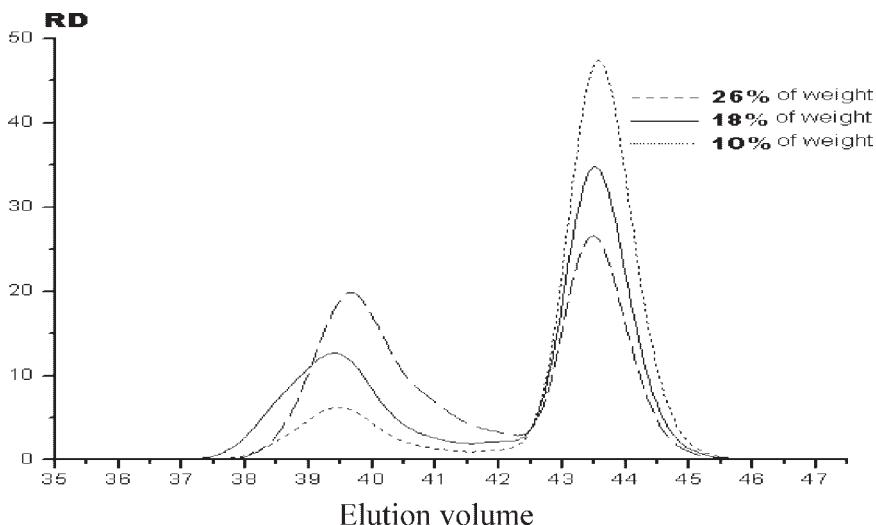[b] Measured by SEC with online light scattering.

Figure 4.
Evolution of the SEC diagrams of the homopolymerization of ω-undecenyl polyisoprene macromonomer with macromonomer concentration (CGC-Ti/MAO catalyst).

nomer concentration on the homopolymerization yield and the degree of polymerization. The characteristics of the diblock macromonomer used in this study are following: number average molar mass (estimated by SEC) is equal to 2600 g/mol, PS content wt.-% 53%, PI content wt.-% 47%. The microstructure of the PI block is identical to that of the PI chains.

The results presented in the Table 5 call for following comments:

Homopolymerization is possible over a temperature range going from 20 to 90 °C. Conversion seems to increase with increasing temperature up to 50 °C whereas homopolymerization degree does not really change with temperature. However homopolymerization degree increases with increasing macromonomer concentration. Whatever the experimental conditions, conversion is not quantitative, and the remaining macromonomer had to be iso-

Table 5.
Experimental conditions for the synthesis and molecular characteristics of polymacromonomers obtained by homopolymerization of ω-undecenyl poly(styrene-*block*-isoprene) macromonomers in the presence of a CGC-Ti/MAO catalyst

Run	Macro (g)	Temp (°C)	Time (in h)	$M_{n\ SEC}$[a] (g/mol)	$M_{w\ SEC}$[a] (g/mol)	$M_{w,SEC}$[a]/$M_{n,SEC}$	$M_{w\ LS}$[b] (g/mol)	DP_n	Conv. (wt.-%)
PM-PSPIA	0.50	20	24	17300	19500	1.1	19500	8	33
PM-PSPIB	0.50	50	24	16300	19300	1.2	21300	8	53
PM-PSPIC	0.50	70	24	17700	21400	1.2	23100	9	47
PM-PSPID	0.56	90	24	16200	19500	1.2	21300	8	39
PM-PSPIE	1	50	24	17100	20500	1.2	30400	12	47
PM-PSPIF	1	70	48	18000	21600	1.2	29200	11	37
PM-PSPIG	1	50	48	19600	23300	1.2	32000	12	36
PM-PSPIH	1.68	50	24	22000	25300	1.1	34600	13	37

General conditions: CGC-Ti (0.001 g, 2,72 μmol) 1/mL of toluene; MAO (0.157 g, 2,71 mmol)/1mL of toluene; macromonomer (1 g/1 mL of toluene; [Al]/[Ti] = 1000.
[a] Experimental number, weight average molar mass and molar mass distribution, respectively measured by SEC (with standard linear PS calibration).
[b] Measured by SEC with online light scattering.

lated. This could be achieved successfully by fractional precipitation as discussed in a forth coming paper.

Copolymerization of ω-Undecenyl Polystyrene Macromonomers with Ethylene

The coordination copolymerization of ω-allyl, ω-undecenyl and α,ω-undecenyl polystyrene macromonomers with ethylene with a cationic α-diimine palladium catalyst ([(ArN=C(Me)-C(Me)=NAr)Pd(CH$_2$)$_3$-(COOMe)]$^+$BAr$'_4^-$, Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$ and Ar$'$ = 3,5-(CF$_3$)$_2$-C$_6$H$_3$) was also studied by us[10]. It affords access to a new type of graft copolymers constituted of a polyethylene backbone and polystyrene grafts. It was shown that the environment of the terminal double bond of the PS macromonomers has a huge influence on the copolymerization behavior. Indeed, an undecenyl end-group is more reactive than an allyl end-group. The copolymerization of ethylene with α,ω-undecenyl polystyrene macromonomers lead to cross-linking for long polymerization time. Macromonomers having the lowest molar masses were the most reactive. The molar mass of the copolymer increased with ethylene pressure. As expected with such a chain walking catalyst, the copolymers presented moderately branched to highly branched structures depending on the ethylene pressure, like for the homopolymerization of ethylene. Finally, rheological investigations of the copolymers showed that a even a low percentage of polystyrene incorporation drastically changes the mechanical properties of the materials.

Conclusions

Coordination polymerization of ω-undeceneyl polystyrene, polyisoprene or poly-(styrene-*block*-isoprene) macromonomers could be achieved successfully in the presence of constrained geometry catalysts. The influence of several parameters (type of catalytic system, accessibility of the chain end, concentration and molar mass of the macromonomer) on the homopolymerization yield and the average polymerization degree was investigated. Comb-shaped samples characterized by a short polyethylene backbone and polystyrene grafts of DP values up to twenty were obtained with decent yields. The results were less satisfactory for ω-allyl macromonomers whatever the catalytic system.

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