

Coordination Homopolymerization of ω -undecenyl Poly(styrene-*block*-isoprene) Macromonomers in the Presence of CGC-Ti/MAO Complexes

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Summary: This paper deals with the coordination homopolymerization of ω -undecenyl poly(styrene-*block*-isoprene) macromonomers. The synthesis of the macromonomers made use of an anionic living poly(styrene-*block*-isoprene) copolymer which is deactivated at low temperature by 11-bromo-1-undecene. The ability of these macromonomers to get involved in coordination homopolymerization in the presence of selected titanium catalysts was discussed. Special emphasis was given to the influence of polymerization temperature, macromonomer molar mass and concentration on the yield of homopolymerization and average degree of polymerization (DP_n). In the presence of the CGC-Ti/MAO catalyst, macromonomer conversion, determined by SEC, was between 35 to 52 wt.-%, and DP_n was between 5 to 14 depending upon the experimental conditions. However, as revealed by SEC/LS, the resulting *comb*-shaped polymers (PE-*graft*-(PI-*block*-PS), are characterized by sharp molar distributions. Increasing macromonomer molar mass, led to only a slight decrease of DP_n whereas conversion increased moderately. Other titanium catalysts such as Cp^*TiCl_3 /MAO and Cp^*TiCl_3 /MAO only caused macromonomer dimerization.

Keywords: *comb*-shaped; Constrained Geometry Catalyst (CGC); homopolymerization; macromonomer; titanium; ω -undecenyl poly(styrene-*block*-isoprene)

Introduction

Macromonomers are macromolecules (usually of low molar mass) with polymerizable groups at one or both chain ends. They provide an easy access to a large number of *graft*- and *comb*-shaped polymers^[1–3] via various (co-) polymerization processes including coordination polymerization.^[4–6] However, most of the macromonomers involved in these (co-) polymerizations are based on polystyrene or poly(ethylene oxide). In recent years, the synthesis of materials constituted of poly(styrene-*block*-

isoprene) copolymers has gained more interest. They led to many applications such as bottom up templates in nanotechnological applications.^[7] The spontaneously formed vesicles of copolymer materials in water are potentially useful as vectors for drug delivery and as biomimetic models of biological cells.^[8] New *comb*-shaped topologies with poly(styrene-*block*-isoprene) branches, were synthesized by anionic polymerization^[6] or by coordination polymerization^[9] of ω -styrenyl poly(styrene-*block*-isoprene) macromonomers. We showed in the recent paper that, besides ω -styryl polystyrene macromonomers, ω -undecenyl polystyrene macromonomers can be also polymerized in the presence of CGC-Ti/MAO catalyst to yield a *comb*-shaped poly(ethylene-*graft*-styrene) polymer characterized by DP_n values going from 20 to 28.^[10] The first section of the present work

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is devoted to the synthesis by anionic polymerization of a series of ω -undecenyl poly(styrene-*block*-isoprene) macromonomers and their characterization. The second part discusses the ability of these macromonomers to undergo coordination homopolymerization in the presence of selected titanium catalysts. Special emphasis will be given to the influence of the nature of the catalyst, of polymerization temperature, macromonomer molar mass and concentration on homopolymerization yield and degree of polymerization (DP_n).

Experimental

Materials

All reactions, including solvent purifications, were performed in Schlenk flasks under argon. Toluene was made free of deactivating impurities by distillations on sodium wire first, and then from *sec*-butyllithium, in the presence of a few drops of 1,1-diphenylethylene, acting as indicator. Tetrahydrofuran was distilled on sodium/benzophenone. Both solvents were collected in previously dried burets fitted with Teflon stop-cocks, and kept under argon. *Sec*-butyllithium (*sec*-BuLi) was synthesized by reacting 2-chlorobutane with pieces of lithium metal, in cyclohexane solution. The molarity of BuLi solution was determined by acetanilide method. Styrene (Merck, 98%) was distilled twice on sodium wire under reduced pressure to remove inhibitors and protonic impurities. Isoprene (Aldrich) was predried over calcium chloride and distilled on sodium wire. 11-bromo-1-undecene was distilled under reduced pressure on CaH₂, and kept in inert atmosphere. The catalysts of CpTiCl₃ (Aldrich), Cp*₃ (Aldrich) and Cp*(SiMe₂N^tBu)TiCl₂ (Boulder Scientific Company) were stored under argon. Methylaluminoxane (MAO) 10wt.-% (Aldrich) was used as a white powder which was obtained after evaporation of solvent (60 °C, 3h). This treatment reduces the amount of residual trimethylaluminum to about 3 mol. %.

Synthesis of ω -Undecenyl Poly(Styrene-Block-Isoprene) Macromonomers

In a typical macromonomer synthesis, a reactor was equipped with six burets for styrene, isoprene, 11-bromo-1-undecene, *sec*-BuLi, dry THF and toluene, respectively. The system was purged with argon, and then evacuated and backfilled with argon five times. After that, the pressure was monitored to ensure the absence of leaks. Then a chosen volume (200–250 mL) of toluene was introduced at room temperature. Traces of protonic impurities were neutralized by a few drops of *sec*-BuLi (styrene acting as indicator). Next, the amount of initiator solution to get the chosen polystyrene block was added at once. The reaction medium was cooled to 7 °C and the monomer (styrene) was added under stirring, and it was kept at this temperature for 20 min to allow initiation to proceed quantitatively. The mixture was then heated to 40 °C for 2 hours, and the polymerization proceeded to completion. An aliquot (5 mL) of the solution was sampled out for characterization. To the rest of the living precursor polymer solution, cooled to 7 °C, the chosen volume of isoprene was added at once, under stirring. The solution was heated to 40 °C for 2 hours, cooled to –60 °C, and dry THF was added. At –70 °C, 11-bromo-1-undecene was introduced rapidly, in a slight excess. The polymer solution was stirred overnight at room temperature, and then was concentrated. The remaining solid product was dissolved in toluene, filtrated and precipitated in methanol. Methanol solution was decanted off, the polymer (solid or oily) was recovered, and dried in vacuum. The yields of polymerization were found to be quantitative. The macromonomers were characterized by SEC and ¹H NMR to attest molar mass and functionality.

Homopolymerization of Macromonomers

A Schlenk was charged with 1 g of macromonomer, dried and purged with several vacuum/argon cycles, and 1 mL of

toluene was introduced. The desired amount of MAO, dissolved in toluene (0.5 mL), was added with a syringe. The reaction mixture was heated to the desired temperature (50 °C or 70 °C) and CGC catalyst (1 mg dissolved in 1 mL of toluene) was added. The sample was stirred during 48 hours, quenched with a mixture of methanol and hydrochloric acid and washed with a solution of H₂O/EtOH/HCl (5/4/1) to remove the excess aluminium chloride. The raw product (containing the polymacromonomer as well as the residual macromonomer) was precipitated in methanol, dried and characterized.

Characterization

Weight or number average molar masses and molar mass distributions were determined by SEC/RI or online light scattering (LS) at room temperature on a Waters apparatus equipped with five PL gel columns (Polymer Laboratories Ltd), an autosampler Waters WISP 717, a differential refractometer Shimadzu RID 6A and a multi-angle laser light scattering (LS) detector Wyatt DAWN DSP (laser: $\lambda = 632.8$ nm). THF was used as eluent at a flow rate of 1.0 mL·min⁻¹. Standard linear polystyrenes (M_n : 1350 to 3.2·10⁶ g/mol) were used for calibration. For SEC/LS analysis ($\partial n/\partial c$) values determined from the copolymer composition and ($\partial n/\partial c$) values taken from literature^[11] were used. ¹H NMR spectra were recorded on a Bruker 400 apparatus using CDCl₃ as solvent at 25 °C. Degree of functionalization was

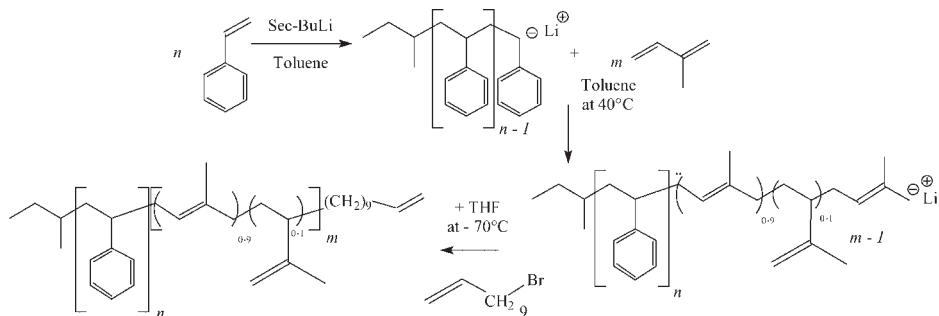
determined by ¹H NMR spectroscopy using an internal standard of C₂H₂Cl₄.

Results and Discussion

Synthesis of ω -Undecenyl Poly(styrene-*block*-isoprene) Macromonomers by Induced Ionic Deactivation

Once the synthesis of the poly(styrene-*block*-isoprene) copolymer by sequential anionic polymerization has been completed, the “living” anion was reacted with the unsaturated deactivator 11-bromo-1-undecene (Scheme 1). To decrease the probability of the unsaturation to get involved in side reactions, the deactivation had to be conducted in THF at -70 °C.^[12]

The resulting ω -undecenyl poly(styrene-*block*-isoprene) macromonomers require a careful characterization to establish whether every single molecule is fitted with a terminal double bond. The SEC curves of the diblock macromonomers displayed narrow molar mass distributions, which demonstrates the efficiency of the initiator used. SEC measurements confirmed also the absence of coupling product (no shoulder in SEC curves). However, the weight or number average molar mass of the macromonomers determined by SEC are overestimated as SEC was calibrated with standard PS samples. The quantitative analysis of the terminal unsaturation was performed by ¹H NMR, and provides strong evidence for quantitative end-capping (>98%).



Scheme 1.

Synthesis of ω -undecenyl poly(styrene-*block*-isoprene) macromonomers.

The copolymer composition is in good agreement with the respective amount of monomers used. From these values, the specific refractive index increment $(dn/dc)_{\text{cop}}$ of the copolymers could be calculated (Table 1). As expected for a polymerization reaction carried out in non polar solvents, and with lithium as counter-ion, the 1,4 content (*cis* and *trans*) is close to 90%. Maldi-Tof MS measurements are now under progress, the results will be published in a forthcoming paper.^[13]

The results of macromonomer homopolymerization by CGC-Ti/MAO catalysts as shown in scheme 2 are summarized along with experimental conditions in Table 2.

Homopolymerization of the same macromonomers with other titanium catalysts such as $\text{CpTiCl}_3/\text{MAO}$ and $\text{Cp}^*\text{TiCl}_3/\text{MAO}$ failed, only macromonomer dimerization took place. The latter result is not too surprising as these catalysts are not very efficient for the polymerization of higher α -olefins, and the propagation rate in the case of macromonomers, must be even lower. This is the reason why emphasis will be given to the homopolymerization of ω -undecenyl poly(styrene-*block*-isoprene) macromonomers in the presence of CGC-Ti/MAO catalysts, characterized by a more opened geometry.^[14] The influence of several parameters such as polymerization temperature, macromonomer molar mass and concentration on homopolymerization yield and degree of polymerization (DP_n) is discussed below. A typical SEC curve of the raw reaction product is presented in Figure 2. The SEC curves of two runs made at 50 °C and 70 °C are almost identical. Consequently, it can be estimated that a



Table 1.Molecular characteristics of ω -undecenyl poly(styrene-*block*-isoprene) macromonomers.

Run	ω -undecenyl macromonomer	$M_n, \text{SEC}^{\text{a)}$ ($\text{g} \cdot \text{mol}^{-1}$)		wt.-% of blocks ^{b)}		$(dn/dc)_{\text{COP}}^{\text{c)}$	$M_w/M_n, \text{SEC}$	D.F. (%) ^{d)}
		PS	Macro.	PS	PI			
1	PS ₁₀₀₀ - <i>b</i> -PI ₁₀₀₀	1000	2500	47	45	0.141	1.06	98
2	PS ₁₀₀₀ - <i>b</i> -PI ₂₀₀₀	1000	3700	32	61	0.132	1.09	99
3	PS ₅₀₀₀ - <i>b</i> -PI ₁₀₀₀	4600	6400	83	14	0.171	1.07	98
4	PS ₅₀₀₀ - <i>b</i> -PI ₅₀₀₀	5600	15300	49	50	0.150	1.09	98
5	PS ₁₀₀₀₀ - <i>b</i> -PI ₁₀₀₀	10400	13200	90	9	0.178	1.06	98

^{a)} Number average molar mass determined by SEC, calibration with linear PS standards.^{b)} Calculated from ¹H NMR signals of phenyls proton of PS chain, olefin proton of PI chain, methyl proton of *sec*-Butyl group and olefin proton of undecenyl end-group.^{c)} Specific refractive index increment: $(dn/dc)_{\text{COP}} = x (dn/dc)_{\text{PS}} + (1-x) (dn/dc)_{\text{PI}}$, where x is weight fraction of polystyrene, $(dn/dc)_{\text{PS}} = 0.186$, and $(dn/dc)_{\text{PI}} = 0.118$.^{d)} D.F. : Degree of functionalization determined by ¹H NMR spectroscopy with internal C₂H₂Cl₄ standard.

change in temperature does not really affect the yield of homopolymerization (36wt.-%) or DP_n at least over the temperature range considered in the present work.

From homopolymerization data presented in Table 2, it can also be concluded that conversion only slightly increases with increasing macromonomer molar mass. This observation is somewhat in contradiction with the evolution generally obser-

ved for the controlled polymerization of macromonomers. However, DP_n slightly decreases with increasing molar mass of the precursor. Similar effect was observed in anionic polymerization of macromonomers.^[15] Impurities may have a predominant effect in some cases and do not really allow to quantify molar mass or concentration effects. When M_n of precursor macromonomer increases, besides

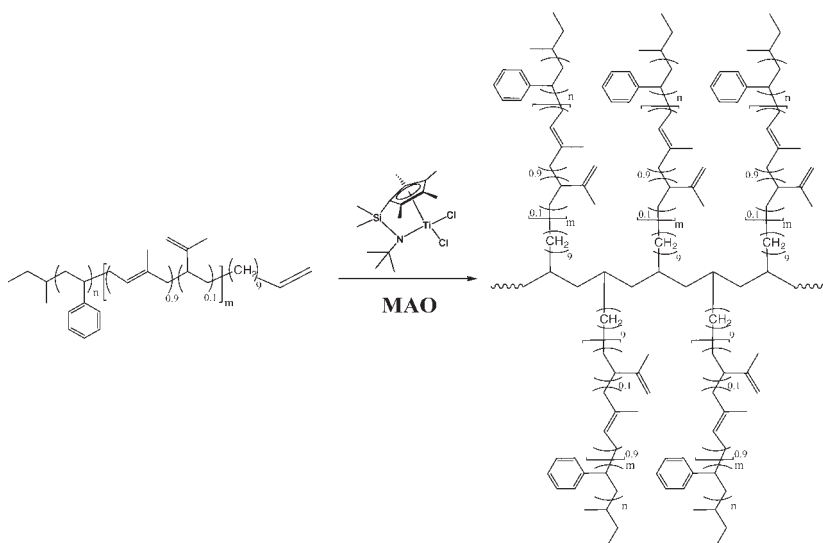
**Scheme 2.**Homopolymerization of ω -undecenyl poly(styrene-*block*-isoprene) macromonomers.

Table 2.Homopolymerization of ω -undecenyl PS-*block*-PI macromonomers.

ω -Undecenyl Macromonomer	Temp.	$M_{n, SEC}^a)$	$M_{w, SEC}^a)$	$M_w/M_n^a)$	$M_{w, LS}^b)$	$DP_n^d)$	Conv. ^{a)}
Precursor	(°C)	(g/mol)	(g/mol)		(g/mol)		(wt.-%)
PS ₁₀₀₀ - <i>b</i> -PI ₁₀₀₀	50	19600 (~100%)	23300	1.19	32000	13	36
	70	18100 (~100%)	21600	1.20	35800	14	35
	50	24 400 (~100%)	28 900	1.19	36 100	10	44
PS ₁₀₀₀ - <i>b</i> -PI ₂₀₀₀	50 ^{c)}	25 400 (~100%)	30 500	1.20	35 300	10	45
	70	23 000 (~100%)	28 200	1.23	32 900	9	41
	50	16400 (17%) ^{e)}	19300	1.17	13000	2	52
PS ₅₀₀₀ - <i>b</i> -PI ₁₀₀₀		46700 (83%)	50800	1.09	75800	12	
	70	16400 (20%) ^{e)}	18200	1.11	13900	2	48
		38700 (80%)	42600	1.10	59000	9	

General conditions: CGC-Ti (0.001 g, 2.72 μ mol)/1 mL of toluene; MAO (0.157 g, 2.72 mmol)/0.5 mL of toluene; macromonomer (1.0 g)/1 mL of toluene; [Al]/[Ti]=1000; polymerization time: 48 hours.

^{a)} Measured by SEC in THF (RI detector), calibration with linear PS standards.

^{b)} Measured by SEC with online light scattering.

^{c)} 4 g. Macro/3 mL toluene, 3 mg, CGC-Ti/3 mL toluene, MAO/1.5 mL toluene.

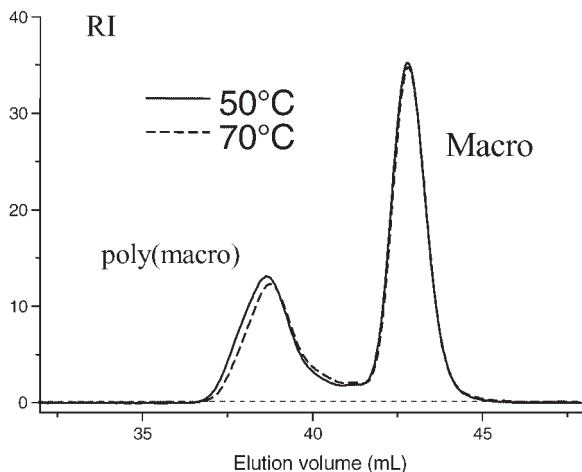
^{d)} $M_{w, LS}$ (polymacro.)/ $M_{w, SEC}$ (macro.).

^{e)} Molar mass of the dimer was estimated from following relation: $M_{SEC} = y M_{Poly(Macro)} + (1-y) M_{Dimer}$, where y is the weight percentage of precursor macromonomer obtained from SEC deconvolution.

homopolymerization, dimerization takes place, as revealed by the SEC traces (not presented here) (see also Table 2). Increasing macromonomer molar mass probably enhances transfer reactions. That point will be discussed later.

The different polymacromonomer samples were characterized in THF by SEC with PS standards and by SEC online light scattering (LS). The residual macromonomer content was calculated from RI detector

evolution. The molar masses determined by SEC online LS are significantly higher than those obtained by SEC/RI. This is expected from the much smaller hydrodynamic volume of the polymacromonomers compared to the linear homologous. However, the polydispersity values M_w/M_n , estimated by SEC, lie around 1.2 which is much smaller than for samples obtained by free radical homopolymerization^[16] or by coordination polymerization of ω -styryl

**Figure 2.**

Influence of the reaction temperature on the evolution of SEC curves for the homopolymerization of a ω -undecenyl PS₁₀₀₀-*block*-PI₁₀₀₀ macromonomer.

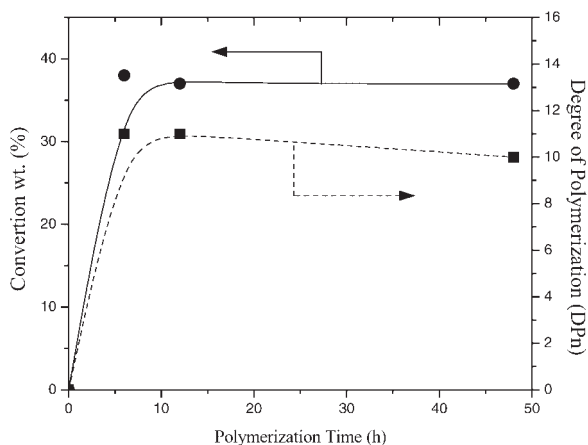


Figure 3.

Kinetics of homopolymerization of ω -undecenyl PS₁₀₀₀-block-PI₁₀₀₀ macromonomer at 50 °C.

polystyrene macromonomers^[5] or of ω -methacryloyloxypolystyrene macromonomers.^[17]

For homopolymerization reactions carried out at 50 °C or 70 °C over a period of 48 hours, DP_n only slightly changes with macromonomer molar mass. However, the stability of the catalyst over such a long period may be questionable. This prompted us to study, at 50 °C, the influence of reaction time on homopolymerization yield and DP_n . The results, based on SEC data, are presented in Figure 3 and Table 3 which indicate that homopolymerization reaction of an ω -undecenyl PS₁₀₀₀-block-PI₁₀₀₀ macromonomer reaches a maximum in conversion after 6 hours (37wt.-%) with a DP_n of 11.

Therefore it can be concluded from these results, that a polymerization time of 6 hours seems to be sufficient.

Average degrees of polymerization of polymacromonomers obtained by coordination homopolymerization of ω -undecenyl macromonomers do not exceed 20 whatever the experimental conditions. A possible explanation may be the occurrence of chain transfer processes. Besides transfer of propagating site to MAO, two additional chain transfer processes β -hydride elimination and chain transfer to macromonomer have to be considered.

Therefore, we calculated in the case of homopolymerization of a ω -undecenyl PS₁₀₀₀-block-PI₁₀₀₀ macromonomer the rate

Table 3.

Kinetics of polymerization of ω -undecenyl PS₁₀₀₀-block-PI₁₀₀₀ macromonomers.

Time	Macro	$M_{n, SEC}^{a)}$	$M_{w, SEC}^{a)}$	$M_w/M_n^{a)}$	$M_{w, LS}^{b)}$	DP_n	Conv. ^{a)}
(hours)	(g)	(g/mol)	(g/mol)		(g/mol)		(wt.-%)
6	0.5	18 700 (~100)	22 300	1.19	28 300	11	38
12	0.5	19 000 (~100)	22 700	1.19	29 300	11	37
48	0.5	17 300 (~100)	21 200	1.23	26 700	10	37
48	1.0	19 600 (~100)	23 300	1.19	32 000	13	36
48	2.0	22 300 (~100)	26 900	1.20	40 300	16	29

Generals conditions: CGC-Ti: 0.001 g (2.72 μ mol)/1 mL toluene, co-catalyst: MAO: 0.157 g (2.71 mmol)/0.5 mL toluene, macromonomer was dissolved in 1 mL toluene, $[Al]/[Ti] = 1000$, Temp. = 50 °C, volume of toluene: 2.5 mL.

^{a)} Measured by SEC in THF (RI detector), calibration with linear PS standards.

^{b)} Measured by SEC with online light scattering.

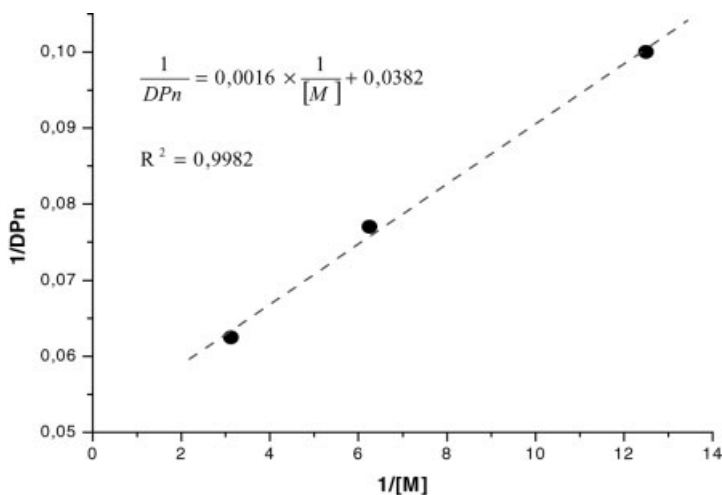


Figure 4.

Evolution of $1/DP_n$ as a function of $1/[M]$ for the homopolymerization of ω -undecenyl PS₁₀₀₀-block-PI₁₀₀₀ macromonomer (Table 3).

constant of transfer and propagation. The molecular characteristics of the resulting samples are given in Table 3. The kinetic constants were obtained from the following equation^[18]:

$$\frac{1}{DP_n} = \frac{k_{tr}^M}{k_p} \times \frac{1}{[M]} + \frac{(k_{tr}^\beta + k_{tr}^A)}{k_p}$$

where, DP_n is the degree of polymerization, $[M]$ the macromonomer concentration (mol/L), k_{tr}^M the rate constant of chain transfer to macromonomer (s^{-1}), k_{tr}^β the rate constant of β -hydride elimination (s^{-1}), k_{tr}^A is rate constant of transfer of propagating chain to MAO (s^{-1}), and k_p the rate constant of chain propagation (s^{-1}). From the plot $1/DP$ versus $1/[M]$ (Figure 4) for poly(macromonomer) obtained from homopolymerization of ω -undecenyl PS₁₀₀₀-block-PI₁₀₀₀ macromonomer, $k_{tr}^M/k_p = 1.6 \times 10^{-3}$ and $(k_{tr}^\beta + k_{tr}^A)/k_p = 38.2 \times 10^{-3}$ were calculated.

These results evidenced that β -hydride transfer reactions and transfers of propagating chain to MAO are 23 times faster than chain transfer to the macromonomer. Therefore, the limiting factors in coordination homopolymerization of macromonomers are essentially the termination processes by β -hydride transfers and the

transfer of propagating chain to MAO ($(k_{tr}^\beta + k_{tr}^A) > (k_{tr}^M)$). Similar studies were made for the coordination homopolymerization of ω -styrenyl polystyrene macromonomers in the presence of CpTiF₃/MAO.^[19] In that case, the values of the ratios of transfer constant to macromonomer to propagation constant ($k_{tr}^M/k_p = 3.9 \times 10^{-3}$) are of the same order than the value of β -elimination constant to aluminum or by β -elimination ($k_{tr}^\beta + k_{tr}^A = 4.4 \times 10^{-3}$).

Conclusion

Homopolymerization of ω -undecenyl poly(styrene-*block*-isoprene) macromonomers with CGC-Ti/MAO catalyst provided access to a new type of *comb*-shaped poly(*graft*-poly(styrene-*block*-isoprene)) copolymer characterized by sharp molar mass distributions and DP_n values from 9 to 14. However, homopolymerization yields were never quantitative. Conversion and DP_n do not change significantly over a temperature range between 50 °C and 70 °C. Further studies are now under progress in order to isolate the *comb*-shaped polymer by fractional precipitation. This will be discussed in an available paper together with some

data on electron microscopy characterization.

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