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Design of new styrene enriched polyethylenes via coordination copolymerization of ethylene with mono- or α,ω-difunctional polystyrene macromonomers

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Abstract

ω-Allyl, ω-undecenyl and α,ω-undecenyl polystyrene macromonomers, well defined in molar mass and functionality, were synthesized via anionic polymerization. Their coordination copolymerization with ethylene with a cationic α-diimine palladium catalyst $[(ArN=C(Me)–C(Me)=NAr)Pd(CH_2)_3(COOMe)]^+BAr'^-_4$, ($Ar=2,6\text{-}iPr_2–C_6H_3$ and $Ar'=3,5\text{-}(CF_3)_2–C_6H_3$) 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 polymerization 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 (18 h at 25 °C). The influence of several parameters (polymerization temperature, ethylene pressure, concentration) on molar masses and macromonomer incorporation yield was also investigated. 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 few percentage of polystyrene incorporation can change drastically the mechanical properties of the materials.

Keywords: Polystyrene macromonomers; Ethylene; Palladium catalyst

1. Introduction

Since their first utilization in 1958 for the synthesis of graft copolymers [1], macromonomers (polymers with polymerizable entities at one or both chain ends and generally of low molar masses) have raised increasing interest because of their ability to provide an easy access to a large number of (co)polymers of different chemical natures and various controlled topologies (comb-like, bottlebrush, star-like, graft copolymers,…) [2–7]. These products exhibit tunable solution or solid state properties. Over the years, macromonomers have been (co)polymerized using different polymerization processes. Free-radical and anionic processes were first employed. A lot of work was done on free radical polymerization procedures [8–14]. Several teams were also involved in the study of the anionic (co)polymerization of macromonomers [4,15–19]. Ring opening metathesis polymerization (ROMP) [20–28] or more recently, new free-radical processes such as atom transfer radical polymerization (ATRP) [6,7,29–32] were also employed to control the (co)polymerization of macromonomers. Finally, it is only in the past 10 years that the (co)polymerization of macromonomers (formed sometimes in situ) has been investigated via transition-metal based processes (Ziegler–Natta type). Metallocenes or late transition metal catalysts have been shown recently to be efficient for the homo- or copolymerization of ω-functionalized macromonomers with α-olefins [33–49]. Macromonomers terminal double bonds were either styrene-like or olefinic end groups, these latter being not polymerizable by classical free radical or

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anionic polymerizations. Besides, some palladium complexes containing symmetrical 1,4-diazadiene units with bulky substituents were very efficient for the polymerization of ethylene [50–52]. The unique feature of these catalysts is to provide access in the absence of any comonomer, to dendritic to hyperbranched to almost linear PEs just by changing the ethylene pressure [53–56]. The purpose of the present paper was to evaluate first the influence of macromonomer chain length and chain-end environment (allyl or undecenyl) on the reactivity of the terminal insaturation with such a complex. Special attention was given to the influence of ethylene pressure. Some solution properties will be discussed in the second part.

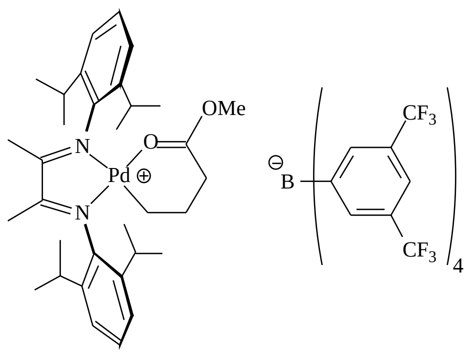
2. Experimental section

2.1. Materials

CH_2Cl_2 was first dried over $MgCl_2$ and then distilled under dry Argon over P_2O_5. Ethylene was used as received. Toluene and THF were distilled over sodium/benzophenone and kept under dry atmosphere.

2.2. Synthesis of the palladium catalyst

The diimine palladium catalyst $[(ArN{=}C(Me){-}C(Me){=}NAr)Pd(CH_2)_3(COOMe)]^+BAr'^-_4$ (VERSIPOL™, Ar=2,6-iPr$_2$–C_6H_3 and Ar′=3,5-$(CF_3)_2$–C_6H_3) (Scheme 1) has been synthesized according to procedures described in the literature [51].



Scheme 1. Versipol™ catalyst.

2.3. Synthesis of ω-allyl and ω-undecenyl polystyrene macromonomers

The polystyrene macromonomers with allylic or undecenyl end groups were prepared by induced anionic deactivation reactions (Scheme 2). 100 mL of dried toluene are poured into a round-bottomed flask. One drop of styrene is added as well as *sec*-Butyllithium until persistent yellow coloration (purification of the reaction medium). The solvent is cooled to 10 °C. The desired amount of *sec*-Buli is added and styrene is added drop by drop. After total addition of the styrene, the orange yellow solution is maintained at 10 °C during 20 min. The temperature is allowed to increase up to 40 °C. At the end of the polymerization, the reaction medium is cooled to −78 °C and 100 mL of THF are added drop by drop. Then, depending on the desired chain end, allyl bromide or undecenyl bromide is added until total loss of coloration of the solution. The solvents are evaporated. The obtained product is dissolved in THF and precipitated in cold methanol. The recovered macromonomer is dried under vacuum. An example of a MALDI-TOF spectrum obtained for these macromonomers is given on Fig. 1.

2.4. Synthesis of α,ω-undecenyl polystyrene macromonomers

The polystyrene macromonomers with two undecenyl end groups is prepared by induced anionic deactivation reactions (Scheme 2). 100 mL of dried THF are poured into a round-bottomed flask. Naphthalene-K is added until persistent slightly green coloration (purification of the reaction medium). Then the required amount of Naphthalene-K is introduced. The solvent is cooled to −78 °C. During the monomer addition, the reaction medium is maintained at −78 °C. At the end of the polymerization, undecenyl bromide is added until total loss of coloration of the solution. The polymer is precipitated in cold methanol. The recovered macromonomer is dried under vacuum.

2.5. Procedures for ethylene polymerizations

The polymerization runs were carried out at 25 or 35 °C in a 250 mL or 1 L Buchi reactor equipped with magnetic or mechanical stirring, purged via argon and vacuum exchange. After addition of the solvent (dichloromethane or toluene) and the catalyst, the reactor was pressurized with ethylene. The resulting polymers were precipitated two times from their solution into acidified methanol and dried in vacuum.

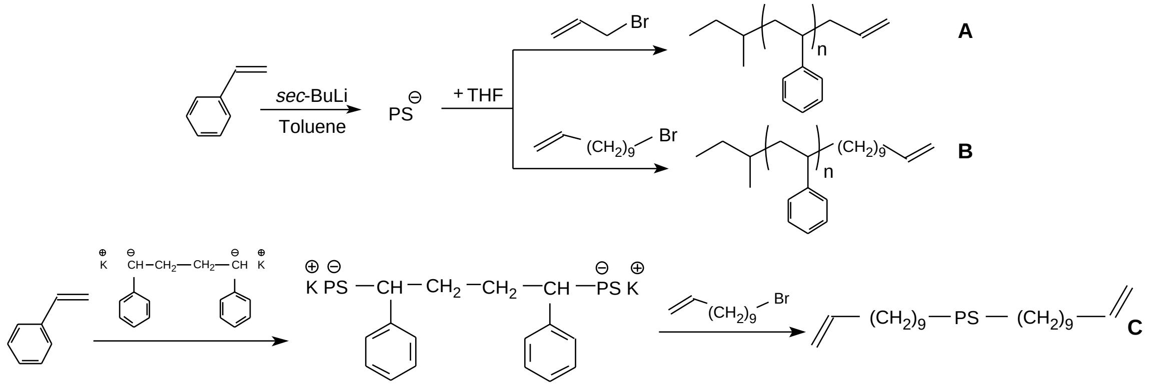
2.6. Copolymerization of ethylene with ω-allyl, ω-undecenyl or α,ω-undecenyl polystyrene macromonomers

Polymerizations were carried out in a 250 mL miniclave Büchi reactor. The reactor was charged with the PS macromonomer and purged with several vacuum/argon cycles. Then, under a low pressure of ethylene, the solvent and the catalytic system were added. Finally, the reactor was pressurized with ethylene. The resulting copolymers were precipitated in slightly acidified methanol, dried under vacuum and characterized by SEC, ^{1}H NMR and IR to certify the presence of the PS sequence in the copolymer.

2.7. Purification of the copolymers

Concerning the separation of the copolymers and the residual macromonomers, several methods were employed.

For macromonomers with molar mass lower than 1600 g/mol, the raw product is dissolved in THF (20 wt%) and precipitated in ethanol (10/1 with respect to THF).



Scheme 2. ω- or α,ω-polystyrene macromonomer synthesis by induced deactivation.

The macromonomer remains in ethanol. The precipitation is repeated three times to get rid of all the macromonomer.

For macromonomers with higher molar masses, the raw product is dissolved in THF (20 wt%) and methanol is added dropwise. At the beginning, the copolymer precipitates as a sticky material. When the medium becomes milky, it is the sign of the precipitation of the macromonomer as well, the addition of methanol is then stopped. This fractioned precipitation is repeated three times to get rid of all the residual macromonomer.

2.8. Characterization of the macromonomers and graft copolymers

^{1}H NMR spectra were recorded on a Bruker AC200 apparatus, in $CDCl_3$ at 25 °C. The MALDI-TOF spectra were recorded an a Bruker Reflex II. Molar mass determinations were made by SEC in THF at 25 °C on a Waters apparatus fitted with five PL gel columns, an autosampler Waters WISP 717, a differential refractometer Shimadzu RID 6A, a UV spectrometer Beckman 147 ($\lambda = 254$ nm) and a multi-angle laser light scattering detector Wyatt DAWN DSP (laser $\lambda = 632.8$ nm). Calibration was performed using linear PS standards. The concentration of the injected solutions was 5 mg/mL. The viscosity measurements were made with a Sematech equipment using a 0.5 mm capillary tube in THF at 25 °C. Static LS measurements were performed at 25 °C in THF with a Fica 50 equipment. The rheological behavior was studied using a Rheometrics Scientific ARES rheometer with parallel plate geometry. The angular frequency ω varied from 10^{-3} to 10^2 rad/s, and the temperature ranged from 298 to 473 K.

In many tables, the legend is the following.

$M_{w,LS}$, weight average molar mass determined by SEC with light scattering online; MMD, molar mass distribution; S incorp., styrene weight percentage in the purified copolymer determined by ^{1}H NMR

Macro.conv. = macromonomer conversation

$$= \text{wt\% S incorp.} \frac{\text{yield}}{m_{\text{macro}}}$$

$$\text{Grafts per chain} = \text{wt\% S incorp.} \frac{\bar{M}_{\text{w LS}}}{\bar{M}_{\text{n macro}}}$$

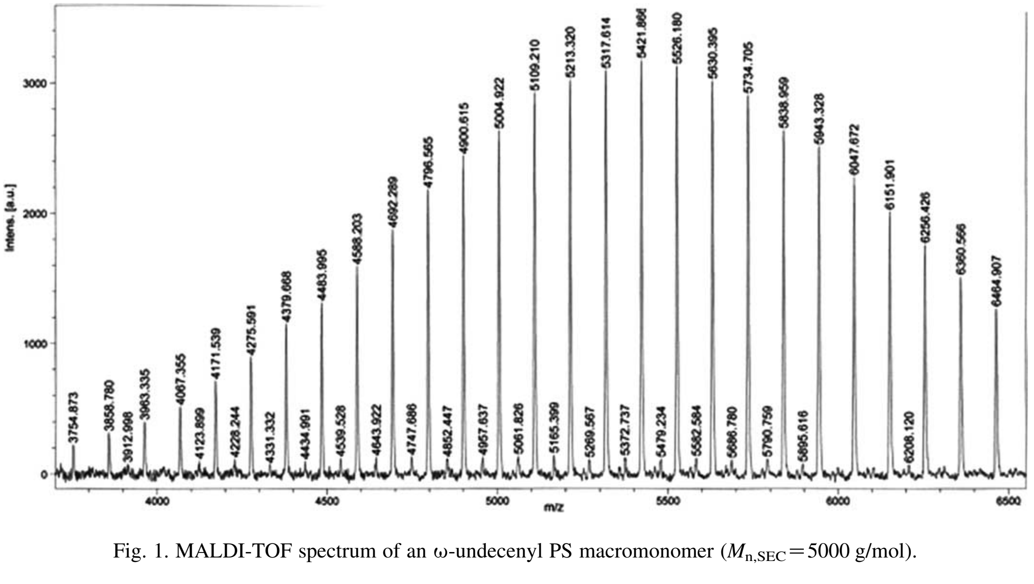


Fig. 1. MALDI-TOF spectrum of an ω-undecenyl PS macromonomer ($M_{n,SEC} = 5000$ g/mol).

Table 1
Characteristics of the PS macromonomers synthesized for this study

N°	Macromonomer type	$M_{n,th}$[a] (g/mol)	$M_{n,exp}$[b] (g/mol)	MMD	*f*[c] (%)
I	A	1000	1170	1.06	98
II	A	2000	2140	1.07	98
III	A	6000	6260	1.09	99
IV	B	1400	1410	1.05	97
V	B	1400	1650	1.03	98
VI	B	10,000	12,100	1.03	–
VII	C	2500	2650	1.30	96
VIII	C	5000	5000	1.24	98
IX	C	10,000	10,000	1.22	–

[a] Theoretical number average molar mass calculated from [styrene]/[initiator] ratio.
[b] Experimental number average molar mass measured by SEC (calibration with linear PS standards).
[c] Functionality determined by the Johnson and Fletcher reaction [57].

3. Results and discussion

3.1. Polystyrene macromonomers synthesis

Polystyrene macromonomers were synthesized by anionic polymerization. The main characteristics of the resulting macromonomers are presented in Table 1. The experimental molar masses are in good agreement with the expected ones. Moreover, the molar mass distribution is always sharp, and the functionalization yield over 95% (determined by chemical titration, ^{1}H NMR and MALDI-TOF see Fig. 1). In the case of α,ω-terminated macromonomers, the molar mass distribution is larger due to slow initiation.

3.2. Copolymerization of ethylene with ω-terminated PS macromonomers with Versipol™

The copolymerization of ethylene with ω-allyl PS macromonomers was first examined. Results are presented in Tables 2 and 3, together with the preparation conditions. First of all, actual copolymers are obtained as the traces obtained by SEC with UV–visible and refractive index detectors are the same (Fig. 2) for purified product (several precipitations were performed in order to get rid of the unreacted macromonomer, see Fig. 3 and Section 2). PS macromonomers could then be incorporated. As indicated in Tables 2 and 3, the PS macromonomer content is rather poor (less than 2 wt%). The best results were obtained at low ethylene pressure. Besides, the molar mass of the copolymers increases with the ethylene pressure, but remains below that obtained for PE under the same conditions.

It was then assumed that if the incorporation is low, it may be due to steric hindrance around the terminal double bond. In spite of limited incorporation yield, the use of macromonomers constitutes an interesting alternative to design materials combining the properties of PE with those of PS. This prompted us to examine the copolymerization of ethylene with ω-undecenyl PS macromonomers. Indeed, in this case, the terminal double bond will be ‘pushed away’ from the polystyrene chain through a flexible spacer and should thus

Table 2
Copolymerization of ethylene and ω-allyl PS macromonomers with Versipol™ in dichloromethane

Run	Loading (mmol)	$M_{n,Macro}$ (g/mol)	$P_{Eth.}$ (bar)	Yield (g)	$M_{w,LS}$ (g/mol)	MMD	S incorp. (wt%)	Macro. conv. (%)	Grafts per chain
1	0.05	1170	0.2	2	40,000	1.4	0.8	1.6	0.3
2	0.10	2140	0.2	4	23,500	1.5	0.5	2.0	0.1
3	0.10	2140	0.5	10	134,000	1.7	Pure PE	–	–
4	0.05	2140	1	11	64,000	1.8	Pure PE	–	–
5	0.10	2140	6	43	288,000	2.0	Pure PE	–	–

$m_{Macro} = 1$ g; $T = 35$ °C; $t = 18$ h; CH_2Cl_2 (150 mL).

Table 3
Copolymerization of ethylene and ω-allyl PS macromonomers with Versipol™ in toluene

Run	$M_{n,macro}$ (g/mol)	m_{macro} (g)	$P_{Eth.}$ (bar)	Yield (g)	$M_{w,LS}$ (g/mol)	MMD	S incorp. (wt%)	Macro. conv. (%)	Grafts per chain
6	1170	1	0.2	0.3	24,000	1.4	2.1	0.6	0.4
7	1170	1	0.5	0.6	60,000	1.7	2.0	1.2	1.0
8	1170	1	1	0.9	350,000	2.0	1.1	1.0	3.2
9	2140	1	0.2	0.3	15,000	1.5	1.9	0.6	0.1
10	2140	0.5	0.5	0.8	76,000	1.7	0.9	1.4	0.3
11	2140	0.5	1	1.3	41,000	1.8	Pure PE	–	–
12	2140	0.5	6	6.1	244,000	2.0	Pure PE	–	–

Loading, 10 μmol; $T = 25$ °C; $t = 5$ h; toluene (30 mL).

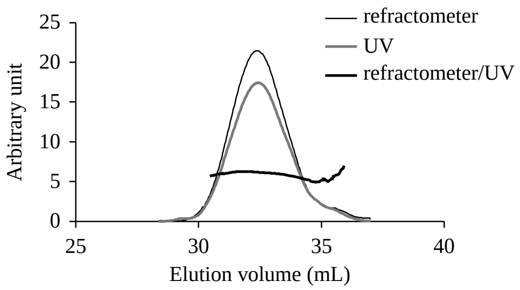


Fig. 2. SEC traces of a copolymer of ethylene and PS macromonomer.

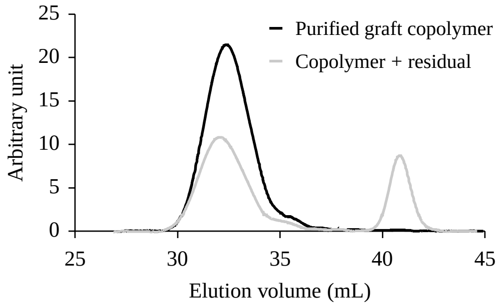


Fig. 3. SEC traces of a raw and a purified graft copolymer.

be more accessible. Results are presented in Table 4, as well as the preparation conditions.

It appears clearly that the styrene content, determined by UV (SEC) or ^{1}H NMR, increases compared to ω-allyl polystyrene macromonomers even if it remains inferior to 10 wt%. Again, the molar mass of the copolymer increases with ethylene pressure. Moreover, the number of grafts increases also with the molar mass of the copolymer. During the polymerization, the main transfer reaction is due to β-H transfer. Thus, the graft copolymers contain a terminal double bond. The increase of the molar mass may then be due to the reincorporation of these vinyl terminated graft copolymers, and as a consequence, the number of grafts per chain will increase.

To conclude on this part, the presence of an alkyl spacer between the terminal double bond and the polystyrene chain of the macromonomer is favourable for the incorporation of higher amounts of styrene into ethylene/PS macromonomer copolymers.

3.3. Copolymerization of ethylene with α,ω-undecenyl PS macromonomers with Versipol™

In order to still increase the percentage of styrene content and the molar mass of the copolymers, the copolymerization of ethylene with α,ω-undecenyl PS macromonomers was investigated. Indeed, the presence of two polymerizable double bonds onto the PS macromonomers should increase the copolymer molar masses as the two double bonds are reactive, and should finally lead to cross-linked materials.

To start with, the influence of the polymerization time was studied. The results are presented in Tables 5 and 6 and in Fig. 4. As indicated in Fig. 4, measured molar masses increase almost linearly with time to lead to a gel after several hours. The same observations are made either in toluene or in dichloromethane. Besides, even if the global weight percentage of styrene decreases with time, the number of grafts per chain increases. In dichloromethane, the content of styrene is higher, but conditions are different.

These results are in agreement with the fact that both terminal double bonds of the PS macromonomers are involved in the process. Indeed, gel formation is due to the polymerization of both double bonds leading to a cross-linking of the copolymer. The increase in the molar mass with time can be thus explained.

Table 4
Copolymerization of ethylene and ω-undecenyl PS macromonomers with Versipol™ in toluene

Run	$M_{n,Macro}$ (g/mol)	$P_{Eth.}$ (bar)	$t_{Pol.}$ (h)	Yield (g)	$M_{w,LS}$ (g/mol)	MMD	S incorp. (wt%)	Macro. conv. (%)	Grafts per chain
13	1410	0.2	5	0.5	58,000	1.6	13.5	6.8	6.5
14	1410	1	5	1.5	140,000	1.6	5.8	8.7	6.8
15	1650	0.2	20	0.7	55,900	1.7	7.1	5.0	2.4
16	1650	0.5	20	0.7	113,400	1.6	4.4	3.1	3.0
17	1650	1	20	1.2	180,100	1.7	4.4	5.3	4.8

Loading Pd, 10 μmol; $T_{Pol.} = 25$ °C; $m_{Macro} = 1$ g; toluene, 30 mL.

Table 5
Influence of the polymerization time on the copolymerization of ethylene and α,ω-undecenyl PS macromonomers with Versipol™ in toluene

Run	t_{Pol} (h)	Yield (g)	$M_{w,LS}$ (g/mol)	MMD	S incorp. (wt%)	Macro. conv. (%)	Grafts per chain
18	1	0.1	81,000	1.2	14.7	1.5	2.4
19	2.5	1.0	209,800	1.5	4.9	4.9	2.1
20	5	3.4	624,800	2.5	4.8	16.3	6.0
21	7.5	4.3	673,000	2.6	3.8	16.2	5.1
22	10	5.5	859,800	2.8	5.2	28.6	9.0
23	18	5.4	Gel	–	–	–	–

Loading Pd, 13.6 μmol; $m_{Macro} = 1$ g; $M_{n,Macro} = 5000$ g/mol; $P_{Eth.} = 3$ bar; $T_{Pol} = 25$ °C; toluene, 30 mL.

Table 6
Influence of the polymerization time on the copolymerization of ethylene and α,ω-undecenyl PS macromonomers with Versipol™ in dichloromethane

Run	t_{Pol} (h)	Yield (g)	$M_{w,LS}$ (g/mol)	MMD	S incorp. (wt%)	Macro. Conv. (%)	Grafts per chain
24	1	0.3	243,700	2.3	15.6	4.7	7.6
25	2.5	0.7	418,200	2.9	11.1	7.8	9.3
26	5	0.9	558,700	2.8	7.4	6.7	8.3
27	7.5	0.8	972,000	3.8	6.3	5.0	12.3

Loading Pd, 13.6 μmol; $m_{Macro}=1$ g; $M_{n,Macro}=5000$ g/mol; $P_{Eth.}=1$ bar; $T_{Pol.}=25$ °C; CH_2Cl_2: 30 mL.

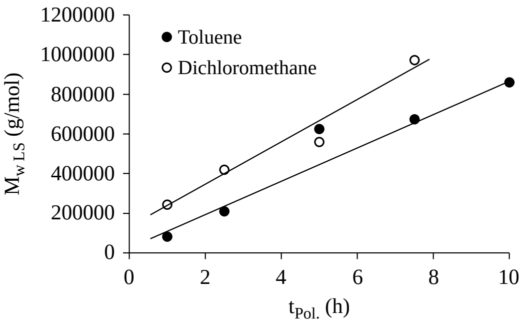


Fig. 4. Influence of the polymerization time on the molar mass of ethylene/α,ω-undecenyl polystyrene macromonomer copolymers.

On a second stage, the influence of the molar mass of the macromonomer on the copolymerization yield, the copolymer molar mass and the styrene copolymer content was studied. The results are summarized in Table 7. The copolymer amount does not depend on the molar mass of the macromonomer, but the macromonomer conversion diminishes strongly. It appears also clearly that the weight percentage of styrene incorporated increases with the molar mass of the macromonomer. The reactivity of the terminal double bonds is thus inversely proportional to the molar mass of the macromonomer. Similar results were already made on monofunctional macromonomers, whatever the polymerization mechanism. It is also noticeable that the molar mass of the copolymer increases with the molar mass of the macromonomer.

The influence of the ethylene pressure was also investigated. Results are presented in Tables 8–10. Whatever the polymerization time, the copolymerization yield increases with ethylene pressure. For short polymerization time (Tables 8 and 9), the copolymerization yield increases also with ethylene pressure. Concerning the evolution of the molar masses, the behavior is a bit more complicated. Indeed, as indicated on Fig. 5, the molar masses of the copolymers increases for the lowest ethylene pressure, goes through a maximum around 2–3 bar and decreases for the highest ethylene pressure. To explain this behavior, it must be considered that the molar mass can increase thanks to chain extension process due to the reaction of both double bonds of the macromonomers. It seems then that the chain extension is favored at low ethylene pressure and disfavored at high ethylene pressure. This is confirmed by the number of grafts per copolymer chain which goes also through a maximum around 2–3 bar. This observation is valid both in toluene and in dichloromethane. Moreover, experimental molar masses are always higher for polymerization performed in dichloromethane compared to toluene. Besides, like for long polymerization time, the weight percentage of styrene content decreases with the ethylene pressure.

For longer polymerization time (Table 10), the copolymerization yield increases with ethylene pressure and whatever the molar mass of the macromonomer, the molar mass of the graft copolymer as well as the molar mass distribution increase with the ethylene pressure, leading to gels for the highest pressures.

Table 7
Influence of the macromonomer molar mass on the copolymerization of ethylene and α,ω-undecenyl PS macromonomers with Versipol™ in toluene

Run	m_{Macro}(g)	$M_{n,Macro}$ (g/mol)	Yield (g)	$M_{w,LS}$ (g/mol)	MMD	S incorp. (wt%)	Macro. Conv. (%)	Grafts per chain
28	0.25	2650	1.0	282,400	1.6	4.3	17.2	4.8
29	0.5	5000	1.0	386,000	1.8	6.9	13.8	5.3
30	1	10,000	0.8	467,000	2.2	10.5	8.4	4.9

Loading Pd, 13.6 μmol; $T_{Pol.}=20$ °C; $t_{Pol.}=5$ h; $P_{Eth.}=1$ bar; $T_{Pol.}=25$ °C; toluene, 15 mL.

Table 8
Influence of the ethylene pressure on the copolymerization of ethylene and α,ω-undecenyl PS macromonomers with Versipol™ in toluene

Run	$P_{Eth.}$ (bar)	Yield (g)	$M_{w,LS}$ (g/mol)	MMD	S incorp. (wt%)	Macro. Conv. (%)	Grafts per chain
39	1	1.4	273,500	1.6	7.2	10.0	3.9
40	2	2.5	567,000	2.1	5.7	14.0	6.4
20	3	3.5	624,800	2.6	4.8	16.4	6.0
41	4	4.1	492,700	2.2	3.9	16.0	3.8
42	5	4.8	482,000	1.9	2.5	11.8	2.4

$m_{Macro}=1$ g; $M_{n,Macro}=5000$ g/mol; $T_{Pol.}=25$ °C; $t_{Pol.}=5$ h; toluene, 30 mL.

Table 9
Influence of the ethylene pressure on the copolymerization of ethylene and α,ω-undecenyl PS macromonomers with Versipol™ in dichloromethane

Run	$P_{Eth.}$ (bar)	Yield (g)	$M_{w,LS}$ (g/mol)	MMD	S incorp. (wt%)	Macro. conv. (%)	Grafts per chain
43	0.5	0.3	132,600	1.3	16.4	4.9	4.4
44	1	1.6	721,100	3.4	7.7	12.3	11.0
45	2	1.2	1,093,000	3.8	3.6	4.3	7.8
46	3	2.3	1,825,000	4.1	2.8	6.4	10.3
47	4	3.8	669,000	2.4	2.4	9.1	3.2
48	5	6.6	783,700	2.7	3.8	25.1	5.9

Loading Pd: 13.6 μmol; $m_{Macro} = 1$ g; $M_{n,Macro} = 5000$ g/mol; $T_{Pol.} = 25$ °C; $t_{Pol.} = 5$ h; CH_2Cl_2: 30 mL.

Table 10
Influence of the ethylene pressure on the copolymerization of ethylene and α,ω-undecenyl PS macromonomers with Versipol™ in toluene

Run	$M_{n,Macro}$ (g/mol)	$P_{Eth.}$ (bar)	Yield (g)	M_{wLS} (g/mol)	MMD	S incorp. (wt%)	Macro. conv. (%)	Grafts per chain
31	2650	0.2	0.6	199,000	2.4	11.4	6.8	21.9
32	2650	0.5	1.4	816,600	3.3	8.5	11.8	27.7
33	2650	1	1.8	1,414,000	3.9	7.1	12.8	42.3
34	2650	3	3.4	Gel	–	–	–	–
35	5000	0.2	1.8	464,100	2.3	10.4	18.7	9.7
36	5000	0.5	2.2	935,600	2.7	7.4	16.2	13.8
37	5000	1	4.1	1,557,000	3.6	6.4	26.0	19.8
38	5000	2	4.7	1,618,000	4.0	5.5	25.9	17.8
23	5000	3	5.2	Gel	–	–	–	–

$T_{Pol.} = 25$ °C; $m_{Macro} = 1$ g; $t_{Pol.} = 20$ h; toluene, 30 mL.

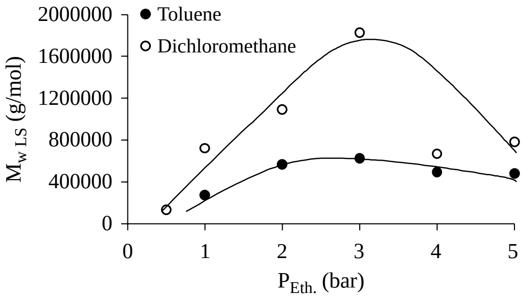


Fig. 5. Influence of the ethylene pressure on the molar mass of ethylene/α,ω-undecenyl polystyrene macromonomer copolymers.

It is assumed that if gel was formed with an increase of ethylene pressure for the same polymerization time, this was probably due to an increase of the global polymerization rate resulting in an increase of the reaction of both double bonds. Moreover, it can be seen that the weight percentage of styrene content diminishes with the ethylene pressure. On the contrary, the macromonomer conversion and the number of grafts per chain increase.

Finally, it was studied the influence of the quantity of solvent, all other reaction parameters being constant. The results are summarized in Table 11. It appears clearly that the molar masses and the styrene content are higher at lower quantity of solvent. Cross-linking is even obtained for low ethylene pressure. Nevertheless, it has to be noticed that yields are higher in more diluted reaction media. This is probably due to higher viscosities in less diluted media (indeed, magnetic stirring was stopped due to too high viscosity), enhancing diffusion problems.

3.4. Characterization of ethylene/α,ω-undecenyl PS macromonomer copolymers

The ethylene/α,ω-undecenyl PS macromonomer copolymers were characterized by several techniques. It was thus measured their intrinsic viscosity in diluted solution. They were also studied by light scattering in order to determine the

Table 11
Influence of the concentration on the copolymerization of ethylene and α,ω-undecenyl PS macromonomers with Versipol™ in toluene

Run	Toluene (mL)	$P_{Eth.}$ (bar)	Yield (g)	M_{wLS} (g/mol)	MMD	S incorp. (wt%)	Macro. conv. (%)	Grafts per chain
35	30	0.2	1.8	464,100	2.3	10.4	18.7	9.7
36	30	0.5	2.2	935,600	2.7	7.4	16.2	13.8
49	30	1	4.1	1,940,000	4.1	6.6	27.1	25.6
50	15	0.2	0.6	502,000	2.4	15.6	9.4	15.6
51	15	0.5	1.5	1,210,000	3.5	13.7	20.6	33.1
52	15	1	2.7	Gel	–	–	–	–

Loading Pd, 13.6 μmol; $m_{Macro} = 1$ g; $M_{n,Macro} = 5000$ g/mol; $T_{Pol.} = 25$ °C; $t_{Pol.} = 20$ h.

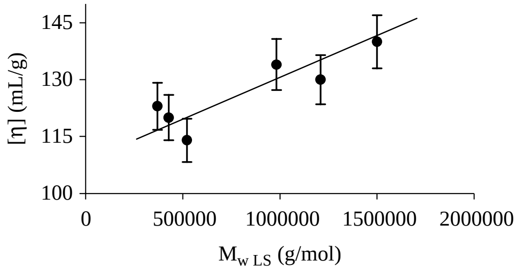


Fig. 6. Influence of the molar mass on the intrinsic viscosity of ethylene/α,ω-undecenyl polystyrene macromonomer copolymers (runs in Table 12).

gyration radii. Finally, rheological measurements were performed and compared to polyethylenes synthesized with the same catalyst.

Concerning the viscosity study, the main results are presented on Fig. 6. For molar masses in the range of 4×10^5–1.5×10^6 g/mol, the viscosity increases slightly with the molar mass, which was expected. Nevertheless, it was impossible to extrapolate these results to determine the coefficients of the Mark–Houwink–Sakurada relationship, probably, because our samples are inhomogeneous in topology. Indeed, these samples were obtained for different ethylene pressure, which mean that they are differently branched as already mentioned for that type of catalyst in the case of PE.

Indeed, it is well-known that with this type of catalyst, when used for the ethylene polymerization, the topology of the resulting polymer is highly dependent on the ethylene pressure. At low ethylene pressure, highly branched PEs are obtained, characterized by long chain branching, whereas at high ethylene pressure, only short chain branching is observed [53–56]. However, the number of $-CH_3/1000\,C$ is roughly the same in both cases (around 100). It was thus studied if for the copolymerization, the structure of the copolymers follows the same behavior. To this end, the copolymers were studied via light scattering, used as a detector for size exclusion chromatography measurements. The evolution of the molar mass versus the elution volume with the ethylene pressure and the polymerization time is represented on Figs. 7 and 8, respectively. In Fig. 7, it can be seen that for a same elution volume, i.e. a same hydrodynamic volume or a same apparent molar mass, the real weight average molar mass of the PE/PS copolymers (determined by LS) synthesized at low pressure is higher. This indicates that the copolymers are more compact when the polymerizations are performed at low ethylene pressure. These observations are in agreement with the ones already made for the homopolymerization of ethylene with such a catalyst. On the contrary, the polymerization time has no influence on the topology of the copolymers, as all the curves are superposable (Fig. 8).

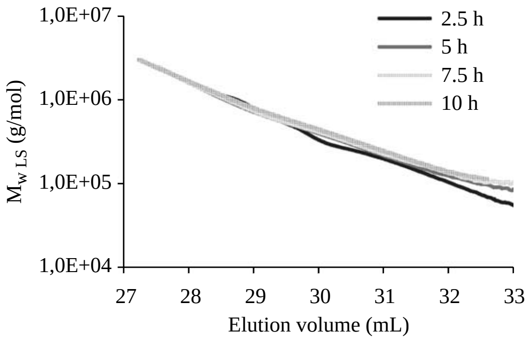


Fig. 8. Influence of the polymerization time onto the molar mass versus elution volume (runs in Table 5).

Nevertheless, it has to be noticed that the topologies of a polyethylene and a copolymer synthesized at a same ethylene pressure are probably slightly different. Indeed, as indicated on Fig. 9, for a same elution volume, the molar mass of the polyethylene is higher, which is again synonymous of more compactness.

Some molar masses, as well as gyration radii, were also estimated by static light scattering and compared to the values obtained by size exclusion chromatography. The results are presented in Table 12. The molar masses measured by both techniques are generally in good agreement, except for run 37. In this case, the huge difference observed with both techniques is probably due to the fact that this sample is partially cross-linked and that for size exclusion chromatography the samples are filtered before injection, which is not done for static light scattering. Indeed, the highest molar masses probably remain on the filter and are thus not detected by SEC.

Finally, preliminary rheological studies were achieved in order to investigate the influence of the presence of polystyrene in the graft copolymers. To this end, measurements were performed also on polyethylene synthesized with the same catalyst [56]. On Fig. 10, the master curves of a polyethylene and a copolymer containing 3.5 wt% of styrene ($M_{n,\mathrm{Macro}}=$

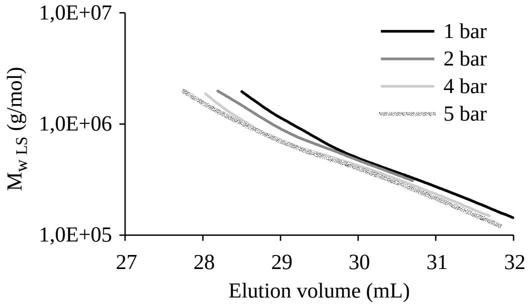


Fig. 7. Influence of ethylene pressure onto the molar mass versus elution volume (runs in Table 9).

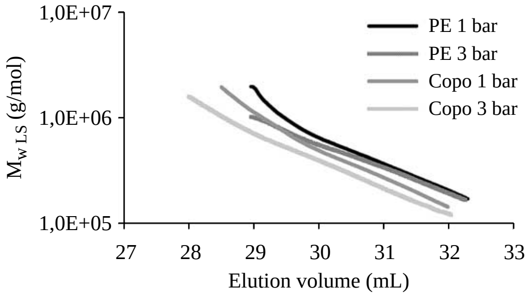


Fig. 9. Comparison of the topology of polyethylene and ethylene/α,ω-undecenyl PS macromonomer copolymer.

Table 12
Light scattering copolymer characterization

Run	$M_{n,Macro}$ (g/mol)	$t_{Pol.}$ (h)	$P_{Eth.}$ (bar)	Yield (g)	S incorp.[a] (wt%)	$M_{w,LS}$[b] (g/mol)	MMD[c]	$M_{w,LS}$[d] (g/mol)	R_g[e] (nm)
53	2650	3	6	1.6	2.7	369,600	1.7	365,200	25.0
54	5000	3	6	5.8	3.6	427,700	1.9	542,400	43.7
55	5000	2	6	2.4	4.9	522,400	2.0	690,300	43.7
36	5000	20	0.5	2.2	7.4	935,600	2.7	1,010,000	47.0
51	5000	20	0.5	1.5	13.7	1,210,000	3.5	1,077,000	52.0
33	2650	20	1	1.8	7.1	1,414,000	3.9	1,584,000	65.2
37	5000	20	1	4.1	6.4	1,557,000	3.6	4,565,000	131.9

[a] Styrene weight percentage in the copolymer determined by UV-SEC.

[b] Weight average molar mass determined by SEC with light scattering online.

[c] Molar mass distribution.

[d] Weight average molar mass determined by static light scattering.

[e] Gyration radii determined by static light scattering.

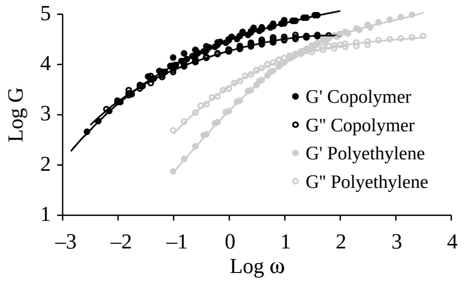


Fig. 10. Master curves of a polyethylene and an ethylene/α,ω-undecenyl polystyrene macromonomer copolymer.

5000 g/mol) are presented. In both cases, the polymerizations were achieved at 6 bar, which means that the topologies are not too far even if they are probably not the same. Besides, molar masses and molar mass distributions are also very close. For the copolymer (black curves), the reference temperature is 100 °C. For the polyethylene (grey curves), the reference temperature is 75 °C. Even if the master curves are not directly comparable because both reference temperatures are different and topologies are also probably a bit different, it can be seen that the incorporation of only 3.5 wt% of styrene modifies strongly the mechanical properties of the polyethylene. This type of modification of polyethylene could be a new route to tune easily polyethylene properties.

4. Conclusion

In this study, ω-allyl, ω-undecenyl and α,ω-undecenyl polystyrene macromonomers were copolymerized with ethylene in the presence of a Versipol™ catalytic system. It was thus demonstrated that the nature and the environment of the terminal chain end has a strong influence. Indeed, macromonomers with an undecenyl end-group were more easily incorporated than macromonomers with an allyl end-group. Moreover, the copolymerization of ethylene with difunctional macromonomers can lead to cross-linking for long polymerization time.

The terminal double bond was not the only parameter to determine the copolymerization behavior. Indeed, the macromonomer molar mass, the polymerization time, the ethylene pressure and the reaction medium concentration have also a strong impact on the copolymer molar mass or structure. Besides, first rheological results showed that a few percentage of polystyrene incorporation can improve drastically the mechanical properties of the copolymers compared to polyethylene.

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References

[1] Bamford CH, White EFT. Trans Faraday Soc 1958;54:268–77.
[2] Ito K. Prog Polym Sci 1998;23:581–620.
[3] Ito K, Kawaguchi S. Adv Polym Sci 1999;142:129–78.
[4] Rempp P, Franta E. Adv Polym Sci 1984;58:1–53.
[5] Hadjichristidis N, Pitsikalis M, Iatrou H, Pispas S. Macromol Rapid Commun 2003;24:979–1013.
[6] Pyun J, Kowalewski T, Matyjaszewski K. Macromol Rapid Commun 2003;24:1043–59.
[7] Börner HG, Matyjaszewski K. Macromol Symp 2002;177:1–15.
[8] Sierra-Vargas J, Franta E, Rempp P. Makromol Chem 1981;182:2603–9.
[9] Takaki M, Asami R, Kuwabara T. Polym Bull 1982;7:521–5.
[10] Rempp P, Lutz P, Masson P, Chaumont P, Franta E. Makromol Chem 1985;13(Suppl):47–66.
[11] Albrecht K, Wunderlich W. Angew Makromol Chem 1986;145/146: 89–100.
[12] Otsu T, Yamashita K, Tsuda K. Macromolecules 1986;19:287–90.
[13] Tsukahara Y, Tsutsumi K, Yamashita Y, Shimada S. Macromolecules 1990;23:5201–8.
[14] Ito K, Tanaka K, Tanaka H, Imai G, Kawaguchi S, Itsuno S. Macromolecules 1991;24:2348–54.
[15] Masson P, Franta E, Rempp P. Makromol Chem. Rapid Commun 1982;3: 499–504.
[16] Ederle Y, Isel F, Grutke S, Lutz PJ. Macromol Symp 1998;132:197–206.
[17] Ryu SW, Hirao A. Macromol Chem Phys 2001;202:1727–36.
[18] Vazaios A, Hadjichristidis N. J Polym Sci, Part A: Polym Chem 2005;43: 1038–48.
[19] Gnanou Y, Lutz P. Makromol Chem 1989;190:577–88.
[20] Breunig S, Héroguez V, Gnanou Y, Fontanille M. Polym Prepr 1994;35: 526–7.

[21] Feast WJ, Gibson VC, Johnson AF, Khosravi E, Mohsin MA. Polymer 1994;35:3542–8.

[22] Breunig S, Héroguez V, Gnanou Y, Fontanille M. Macromol Symp 1995; 95:151–66.

[23] Héroguez V, Breunig S, Gnanou Y, Fontanille M. Macromolecules 1996; 29:4459–64.

[24] Grande D, Six J-L, Breunig S, Héroguez V, Fontanille M, Gnanou Y. Polym Adv Technol 1998;9:601–12.

[25] Héroguez V, Six J-L, Gnanou Y, Fontanille M. Macromol Chem Phys 1998;199:1405–12.

[26] Rizmi ACM, Khosravi E, Feast WJ, Mohsin MA, Johnson AF. Polymer 1998;39:6605–10.

[27] Imanishi Y, Nomura K. J Polym Sci, Part A: Polym Chem 2000;38: 4613–26.

[28] Jha S, Dutta S, Bowden NB. Macromolecules 2004;37:4365–74.

[29] Yamada K, Miyazaki M, Ohno K, Fukuda T, Minoda M. Macromolecules 1999;32:290–3.

[30] Wang X-S, Lascelles SF, Jackson RA, Armes SP. Chem Commun 1999;1817–8.

[31] Haddleton DM, Perrier S, Bon SAF. Macromolecules 2000;33:8246–51.

[32] Shinoda H, Miller PJ, Matyjaszewski K. Macromolecules 2001;34: 3186–94.

[33] Endo K, Senoo K. Macromol Rapid Commun 1998;19:563–6.

[34] Endo K, Senoo K. Polym J 1999;31:817–21.

[35] Endo K, Senoo K. Polymer 1999;40:5977–80.

[36] Endo K, Senoo K. Polym Bull 2000;44:25–30.

[37] Weng J, Markel EJ, Dekmezian AH. Polym Prepr 2000;42:1924–5.

[38] Senoo K, Endo K. Macromol Rapid Commun 2000;21:1244–7.

[39] Batis C, Karanikopoulos G, Pitsikalis M, Hadjichristidis N. Macromolecules 2000;33:8925–30.

[40] Weng W, Markel EJ, Dekmezian AH. Macromol Rapid Commun 2001; 22:1488–92.

[41] Lahitte J-F, Peruch F, Plentz-Meneghetti S, Isel F, Lutz PJ. Macromol Chem Phys 2002;203:2583–9.

[42] Bernard J, Héroguez V, Cramail H. Polymer 2002;43:7251–6.

[43] Schulze U, Fonagy T, Komber H, Pompe G, Pionteck J, Ivan B. Macromolecules 2003;36:4719–26.

[44] Neiser MW, Okuda J, Schmidt M. Macromolecules 2003;36:5437–9.

[45] Kolodka E, Wang W-J, Zhu S, Hamielec A. Macromol Rapid Commun 2003;24:311–5.

[46] Batis C, Karanikopoulos G, Pitsikalis M, Hadjichristidis N. Macromolecules 2003;36:9763–74.

[47] Endo K, Sugita T. J Polym Sci, Part A: Polym Chem 2004;42:2904–10.

[48] Lahitte J-F, Kaminsky W, Stojkovic O, Peruch F, Lutz PJ. Macromol Rapid Commun 2004;25:1010–4.

[49] Ciolino AE, Galland GB, Ferreira ML, Villar MA. J Polym Sci, Part A: Polym Chem 2004;42:2462–73.

[50] Johnson LK, Killian CM, Brookhart MS. J Am Chem Soc 1995;117: 6414–5.

[51] Johnson LK, Mecking S, Brookhart MS. J Am Chem Soc 1996;118: 267–8.

[52] Killian CM, Tempel DJ, Johnson LK, Brookhart MS. J Am Chem Soc 1996;118:11164–5.

[53] Guan Z, Cotts PM. Science 1999;283:2059–62.

[54] Plentz-Meneghetti S, Kress J, Lutz PJ. Macromol Chem Phys 2000;201: 1823–32.

[55] Cotts PM, Guan Z, McCord E, McLain S. Macromolecules 2000;33: 6945–52.

[56] Plentz-Meneghetti S, Kress J, Peruch F, Lapp A, Duval M, Muller R, et al. Polymer 2005;46:8913–25.

[57] Johnson JB, Fletcher JP. Anal Chem 1959;31:1563–4.