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Macromonomers and Coordination Polymerization

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Summary: The present work discusses the synthesis of well-defined comb-shaped polymers or graft copolymer structures based on coordination (co)polymerization of macromonomers. Polystyrene macromonomers with various polymerizable entities were synthesized first by induced deactivation reactions. The homopolymerization of these macromonomers in the presence of selected early or late transition metal catalysts was examined. Comb-shaped polymers could be obtained over a large range of DP values. The results were compared to those obtained by anionic homopolymerization. Some results on the copolymerization of these PS macromonomers with ethylene in the presence of VERSIPOL^{TM} type catalysts were presented.

Keywords: branched polymers; coordination polymerization; copolymerization; macromonomers; polymacromonomers; polystyrene

Introduction

Macromonomers, macromolecules (usually short) with polymerizable entities at one or both chain ends, have opened new perspectives in graft or comb-shaped polymers controlled synthesis. Random radical (controlled or free) or ionic copolymerization of macromonomers with a vinyl or acrylic monomer yields graft copolymers.[1,2] Homopolymerization of macromonomers, based on a polymer-polymer reaction, has been successfully used to design a new type of comb-shaped polymer. Well defined macromolecules characterized by unusually high segment densities could be obtained either by radical or by anionic polymerization processes.[3-8] Coordination (co-)polymerization of macromonomers has attracted recently increasing interest due to its two decisive advantages: the intrinsic possibility to control the tacticity of the backbone and the ability to polymerize allylic monomers i.e. macromonomers with allylic polymerizable end groups.[9-15]

The first part of the present work deals with the synthesis of well-defined polystyrene (PS) macromonomers by induced deactivation reactions. Once characterized, these PS macromonomers will be homopolymerized in the presence of selected early or late transition

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metal catalysts and the results compared to those obtained by anionic homopolymerization. The copolymerization of these PS macromonomers with ethylene in the presence of VERSIPOL^{TM} type catalysts will be presented and discussed in the final section.

Experimental

Synthesis of ω-allyl, ω-undecenyl, ω,ω-undecenyl or ω-vinylbenzyl Polystyrene Macromonomers. The polystyrene macromonomers with allylic, undecenyl or styrenyl end groups were prepared by induced anionic deactivation reactions as already described in several previous publications.[1,8,12]

Homopolymerization of Polystyrene Macromonomers. A Schlenk flask was charged with 1 g of PS macromonomer, dried and purged with several vacuum/argon cycles. The desired amount of methylaluminoxane (MAO) in solution in toluene was added with a syringe and the volume completed with toluene up to 10 mL. The mixture was heated to the desired temperature and the catalyst (in solution in toluene) was added. The sample was kept at that temperature for the selected polymerization time and quenched with a mixture of methanol and hydrochloric acid. The sample was recovered according to well-established procedures[12] and analyzed as indicated below.

Copolymerization of ethylene with ω-allyl, ω-undecenyl, ω,ω-undecenyl or ω-vinylbenzyl 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 three times 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.

Characterization. Molar mass determinations were made by SEC 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 (λ = 254 nm), and a multi-angle laser light scattering detector Wyatt DAWN DSP (laser λ = 632.8 nm). Calibration was performed using linear PS standards. The ^{1}H NMR spectra were recorded on a Brüker AC200 apparatus.

Results and Discussion

Various methods have been developed to yield polymers quantitatively fitted with polymerizable units.[1] Among the end-functionalization reactions, those based on induced deactivation are usually efficient, provided the double bonds are not involved in side reactions. Several PS macromonomers have been prepared by quenching, under adapted experimental conditions,[12] living PS either directly with allyl bromide, 11-bromo-undecene, 4-vinylbenzyl chloride, or 4-vinylbenzyl chloride after intermediate addition of 1,1-diphenylethylene (DPE). Some data on the ω-vinylbenzyl PS macromonomers are given in Table 1. The characteristics of the ω-allyl, ω-undecenyl, and ω,ω-undecenyl macromonomers were already published.[14]

Table 1. Molecular characteristics of ω-vinylbenzyl polystyrene macromonomers prepared by induced deactivation.

Run	Method[a)]	$M_{n\,th}$[b)] ($g.mol^{-1}$)	$M_{n\,exp}$[c)] ($g.mol^{-1}$)	MWD[d)]	Funct.[e)] (%)
1	A	1100	1120	1.05	97
2	A	1200	1200	1.04	97
3	A	5000	4800	1.05	85
4	B	1200	1150	1.05	98
5	B	1100	1120	1.05	98
6	B	2000	1980	1.06	90
7	B	5000	5000	1.04	95
8	B	10000	10300	1.05	95

Typical polymerization conditions ($M_{n,\,th}$=1100g.mol^{-1}): toluene=100mL, styrene=15g (16.7mL, 0.144mol), BuLi [0.6N]=25 mL. Initiation at 10°C, propagation at 35°C, addition of 100mL of THF at −70°C, termination by addition of the functionalization agent (0.144 mol).

a) A refers to a sample prepared with intermediate addition of DPE, B without DPE.

b) Theoretical molar mass calculated from ratio monomer converted to initiator concentration.

c) Experimental molar mass measured in THF by SEC, calibration with linear PS.

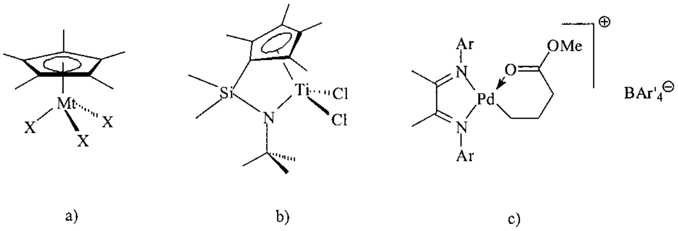
d) Molecular Weight Distribution.

e) Functionalization yield determined by chemical titration (Johnson and Fletcher reaction[16]).

Well-defined macromonomers with narrow molar mass distributions and free of coupling products (no shoulder detected on the SEC diagram peak) could be obtained for molar masses ranging from 1000 to 10 000 g.mol^{-1}. Experimental and theoretical molar masses are in good agreement. The functionalization yields determined by chemical titration, ^{1}H NMR analysis, and Maldi-TOF[12] are almost quantitative whatever the chain end.

Homopolymerization of ω-functionalized PS macromonomers via coordination polymerization

The homopolymerization of PS macromonomers has been investigated using hemi-metallocene catalysts: (CpTiCl$_3$, Cp*TiCl$_3$, CpZrCl$_3$, CpTiF$_3$, CGC-Ti) or the following palladium complex $[(ArN{=}C(Me){-}C(Me){=}NAr)Pd(CH_2)_3(COOMe)]^+$ BAr'$_4^-$ (VERSIPOL^{TM})



Scheme 1. Catalysts used for the polymerization of macromonomers: a) hemi-metallocene catalyst with various substituents, b) CGC catalyst (Dow), c) VERSIPOL^{TM} catalyst.

From these attempts the following conclusions could be drawn:

- It could be confirmed that the homopolymerization of ω-vinylbenzyl PS macromonomers with CpTiCl$_3$/MAO or Cp*TiCl$_3$/MAO is possible and provides access to highly compact branched polymers as revealed by SEC with online LS characterization. In most cases, homopolymerization yields are yet far from being quantitative.
- The DP depends on the polymerization conditions. Higher molar masses have been obtained at low temperature and with low catalyst and cocatalyst concentrations. The suppression of the DPE unit in the ω-vinylbenzyl PS macromonomers has improved the homopolymerization. Best results, DP values up to 50, were obtained with CpTiF$_3$ complexes introduced by the group of Kaminsky.[17]
- CGC- (Constrained Geometry Catalyst) complexes are known to be much more efficient for the coordination polymerization of styrene. Some results obtained by homopolymerization of ω-vinylbenzyl PS macromonomers in the presence of these catalysts, under conditions almost identical to those employed with CpTiCl$_3$/MAO or Cp*TiCl$_3$/MAO, are listed in Table 2. A typical SEC diagram of the raw reaction product is given on Figure 1 together

with the SEC of the polymacromonomer resulting from the polymerization of a ω-undecenyl PS macromonomer in presence of the same catalyst.

As it can be seen from these SEC diagrams, in both cases homopolymerization was possible, but the homopolymerization yields are far from being quantitative. In addition, the molecular weight distribution is rather large for the polymacromonomers resulting from the homopolymerization of ω-vinylbenzyl PS macromonomers. A possible explanation may be the occurrence of increasing transfer reactions during the polymerization process.

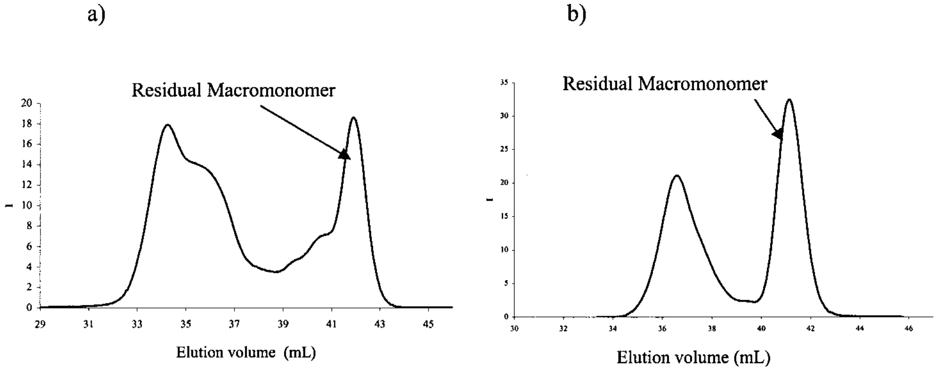


Figure 1. Typical SEC diagrams of the raw reaction product of the homopolymerization PS macromonomers in the presence of CGC catalysts: (a) ω-vinylbenzyl PS macromonomer, (b) ω-undecenyl PS macromonomer.

When compared to earlier results observed for the anionic homopolymerization of ω-vinylbenzyl PS macromonomers,[8] the following comments can be made: for identical molar masses of the macromonomer precursor, anionic homopolymerization yields were almost quantitative and sharp molar mass distributions of the resulting polymacromonomers were noted. This is explained by the specific characteristics of the anionic polymerization (long life time of the active sites and absence of transfer reactions under appropriate conditions). On the contrary the maximum DP values are lowered by 40 for polymacromonomers originating from macromonomers of almost identical molar masses. Anionic polymerization is well known to be much more sensitive to the presence of remaining impurities.

Table 2. Polymerization of ω-vinylbenzyl PS macromonomers (with DPE) in the presence of the CGC catalyst and characteristics of the resulting polymacromonomers.

Run	Macro a) (g)	CGC-Ti (µmol)	$M_{n,SEC}$ b) (g.mol^{-1})	$M_{w,SEC}$ b) (g.mol^{-1})	M_{wLS} c) (g.mol^{-1})	MWD d)	DP	Conv. e) (%)
9	0.25	1	20500	36600	74000	1.8	74	70
10	0.5	1	62000	148000	420000	2.4	420	35
11	0.5	2	33000	81000	175000	2.4	175	42
12	1	2	53000	103000	290000	1.9	290	24
13	0.5	5	44000	87000	258000	2.0	258	53
14*	1	2	75000	126000	500000	1,7	100	8

Typical polymerization conditions: toluene 2ml (excepted for samples 9 and 10: 1.5 ml), [Al]/[Ti]=1000, T=50°C, polymerization time = 16 hours.

a) Molar mass of the macromonomer: 1000 g.mol^{-1} (except sample 14* molar mass 5000 g.mol^{-1})

b) Molar mass measured by SEC in THF, calibration with linear PS.

c) Molar mass measured by SEC with online LS.

d) Molecular Weight Distribution.

e) Macromonomer conversion.

In conclusion, for the ω-vinylbenzyl PS macromonomers, the highest polymerization degrees have been obtained using the CGC-Ti complexes. For ω-vinylbenzyl PS macromonomers, free of the bulky DPE unit, homopolymerization yield and molar mass of the resulting polymacromonomer significantly increased.

Among these catalysts, the CGC-Ti catalyst was the only one able to homopolymerize ω-undecenyl PS macromonomers, giving access to a new type of graft copolymer ethylene-*g*-(ethylene-*b*-styrene). No homopolymerization of ω-allyl PS macromonomer was detected with the same CGC catalyst. As it could be anticipated, no homopolymerization at all was observed with VERSIPOL™ catalysts whatever the polymerizable entity at the PS chain end.

$CpTiCl_3$/MAO catalytic system has been reported to provide access to highly syndiotactic polystyrenes.[17] The presence of a substituent in the para position of the styrene unit does not modify the syndiotactic polymerization process. Therefore there is no reason why the backbone of polymacromonomers resulting from coordination processes should not be syndiotactic. On the contrary, these polymacromonomers with basically a syndiotactic backbone and atactic grafts are well soluble at room temperature in usual solvents (THF, toluene). They remained soluble even at rather high polymerization degrees of the main chain.

Therefore we attempted some solution NMR experiments to attest the syndiotactic nature of the backbone. In fact, the concentration of syndiotactic styrene units is too low to be really determined. As mentioned in the introduction, Senoo et al.[9] polymerized vinyl-terminated polyisoprene macromonomers in the presence of $CpTiCl_3$/MAO to high molar mass polymacromonomers. In a subsequent step, ozonolysis was achieved. The resulting polymer was no more soluble in usual solvents at room temperature and its syndiotactic character could be confirmed by NMR spectroscopy.

The solution properties of these different polymacromonomers were investigated and their compactness with respect to the linear equivalent could be confirmed. The relation between the polymerization degree of the polymacromonomers and their structures has been established. That point will be discussed in details in a forthcoming paper.

Copolymerization of PS macromonomers with ethylene

As mentioned in the introduction, radical (controlled or free) or ionic copolymerization of macromonomers with a vinyl or acrylic monomer are very efficient pathways to design graft copolymers. Only little work in this domain referred to coordination polymerization processes. On another hand higher alpha olefins can be incorporated in polyolefins via Ziegler Natta or metallocene catalysts. In addition, a part of long chains branches formed in Pd catalyzed polymerization of ethylene,[19,20] could be explained by the incorporation of higher alpha olefins i.e. of macromonomers formed during the polymerization. This led us to examine the copolymerization of ω-allyl, ω-undecenyl or ω,ω-undecenyl PS macromonomers with ethylene in the presence of the Pd dimiine catalyst introduced by Brookhart.[19]

In preliminary experiments,[11,12] copolymerization experiments of PS macromonomers with ethylene in the presence of the above mentioned Pd catalyst were performed. The reaction products were characterized by SEC with online LS. From the raw product containing unreacted macromonomer, graft copolymer species had to be isolated by repeated selective precipitation. FTIR and ^1H NMR confirmed unambiguously the presence of the macromonomer in the graft copolymer. This prompted us to perform a systematic investigation of that copolymerization reaction.

ω-allyl or ω–undecenyl PS macromonomers of different molar mass were copolymerized with ethylene using the VERSIPOL™ catalyst under various experimental conditions with the aim of increasing the content of PS in poly(ethylene) based materials. In most cases, the average molar masses of the isolated copolymers are lower than those observed for polyethylene prepared under identical conditions. In the case of ω-allyl PS macromonomers, whatever the experimental conditions, the degree of incorporation remained low. This can be explained by the restricted accessibility of the polymerizable group. For macromonomers containing an alkyl spacer, taking the polystyrene chain away from the terminal double bond, the macromonomer content in the copolymer increases notably. In addition, higher molar mass copolymers have been obtained with average molar masses up to 158 000 $g.mol^{-1}$. This confirms the observations made in homopolymerization attempts on the same type of PS macromonomers. Besides the macromonomer weight percent content decreases with increasing ethylene pressure whereas the molar masses of the copolymer increases with ethylene pressure. That point will be discussed more in details in a forthcoming paper. An increase in macromonomer molar mass corresponds to a decrease of the conversion. Similar observations, were made in the case of free radical copolymerization of macromonomers with micromolecular polymerizable compounds.

To try to still increase that macromonomer content i.e the styrene content, copolymerization experiments with bifunctional PS macromonomers were performed. We examined again the influence of several factors (polymerization solvent, ethylene pressure, molar mass of the macromonomer and reaction time) on the conversion, the molar mass of the graft copolymers and the number of grafts incorporated. Some of these results are presented in Tables 3 and 4.

Table 3. Evolution of the macromonomer incorporation yield and the molar masses of the graft copolymers for the copolymerization of ethylene and ω,ω-undecenyl PS macromonomers in the presence of VERSIPOL™ as a function of reaction time.

Run	Time (h)	M_{wLS} [a)] $g.mol^{-1}$	Wt.-% of styrene	Number of grafts per chain	Yield (g)	Conv. [b)] (%)
15	1	81000	21	3	0.5	11
16	2,5	210000	6.3	3	1.7	11
17	5	625000	6.8	8	4.7	27
18	7,5	673000	5.5	8	4.7	26
19	10	860000	7	12	5.5	39
20	18	gel	-	-	5.8	-

Typical polymerization conditions Ethylene pressure = 3 bars, Molar mass of the macromonomer used in copolymerization: 5000 $g.mol^{-1}$, amount macromonomer = 1g, cata= 10 µmol, T=25°C, toluene= 30 mL

a) measured by SEC in THF with online LS. b) Macromonomer conversion.

The weight average molar mass of the copolymer, measured by light scattering, increases with increasing reaction time. After 18 hours totally insoluble materials resulted. On the contrary the samples 15-19 are well soluble in THF or toluene and do not contain significant amounts of microgel. This was confirmed by molar mass determinations on sample 19 before and after filtration: no difference in weight average molar masses was observed. The number of macromonomers units incorporated in the graft copolymer increases with reaction time. It is interesting to note that these graft copolymers still contain unsaturations. This was confirmed by copolymerization experiments between ethylene and these graft copolymers in the presence of VERSIPOL^{TM} catalysts. The molar mass of the resulting product measured by SEC with online LS still increased and the presence of the styrene units could be confirmed unambiguously by SEC with UV detection.

For a given reaction time, the molar mass of the graft copolymer increases with increasing ethylene pressure (Table 4). The molar mass distribution gets larger with increasing reaction

Table 4. Evolution of the macromonomer incorporation yield and the resulting graft copolymer molar masses for the copolymerization of ethylene and ω,ω-undecenyl PS macromonomers in the presence of VERSIPOL^{TM} with ethylene pressure.

Run	Time (h)	P (bar)	M_{wLS} a) g.mol^{-1}	M_{wLS} b) g.mol^{-1}	MWD c)	Wt% of styrene	Number of grafts per chain
21	20	0.2	470000	510000	1.6	15.0	14
22	20	0.5	980000	1000000	3.8	10.6	21
23	20	1	1560000	1600000	4.9	8.0	26
24	20	2	1620000	4500000	4.3	8.2	26
25	20	3	gel	-	-	-	-
26	5	1	270000	300000	1.6	10.0	5
27	5	2	570000	-	2.1	7.2	9
17	5	3	620000	670000	2.0	6.8	8
28	5	4	490000	-	2.2	6.0	6
29	5	5	480000	-	1.9	5.2	5
30	3	6	430000	540000	1.9	5.0	4

Typical polymerization conditions: Catalyst = 10 μmol, Molar mass of the macromonomer used in copolymerization 5000 g.mol^{-1}, amout of macromonomer = 1g, cata= 10 μmol, T=25°C, toluene= 30 mL

a) Molar mass measured by SEC in THF with online LS.

b) Molar mass measured by static light scattering.

c) Molecular weight distribution.

time due probably to increasing transfer reactions. At low ethylene pressure the macromonomer content in the copolymer is much higher.

The different samples resulting from copolymerization of ethylene with PS macromonomers were submitted to detailed investigations of their dilute solution and solid state properties. The results were compared to those obtained for polyethylenes prepared under the same conditions. The discussion of the different results is out of the scope of the present work.

Conclusion

The homopolymerization of well-defined ω-allyl, ω-undecenyl, and ω-vinylbenzyl PS macromonomers in the presence of selected early or late transition metal catalysts was examined with respect to the influence of several experimental parameters on the homopolymerization yield and the homopolymerization degree. The polymerization degrees of the resulting polymacromonomers depend strongly on the polymerization conditions. Higher molar masses have been obtained with low temperature and low catalyst and cocatalyst concentrations. The absence of the DPE unit in the ω-vinylbenzyl PS macromonomers has improved the homopolymerization results. Best results were obtained with CGC catalysts whatever the polymerizable chain end.

The Pd catalyst (VERSIPOL^{TM}) allows the incorporation of ω-allyl or ω-undecenyl PS macromonomers into PE chains giving access to a new type of copolymer structure, potential compatibilizers. The introduction of the alkyl spacer in PS macromonomers increases the macromonomer incorporation yield, which could still be improved while using bifunctional PS macromonomers.

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