Macromonomers as Well-Defined Building Blocks in Macromolecular Engineering

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Summary: The present work compares the efficiency of different polymerization methods to design well-defined comb-shaped structures based on macromonomers. Anionic polymerization remains the method of choice and allows the control of polymerization degree of the main chain and the length of the grafts. The presence of an active chain end on the backbone enabled the synthesis of a new type of hyperbranched polymers by reaction with appropriate low molar multifunctional compounds. Free radical polymerization is less efficient for the controlled homopolymerization of macromonomers but less sensitive to the presence of impurities. It requires in most cases long fractionation procedures to access well defined comb-shaped fractions characterized by high molar masses. The controlled free radical polymerization constitutes an interesting alternative. The homopolymerization of macromonomers with late transition metal catalysts was also examined and comb-shaped polymers characterized by a syndiotactic backbone and atactic grafts could be obtained.

Introduction

Macromonomers are polymers of low molar masses with a polymerizable entity at one or both chain ends. The major interest of macromonomers lies by their easy free radical copolymerization with low molar mass monomers to design a large variety of graft copolymers. The homopolymerization of macromonomers affords access to comb-shaped polymers in which each monomer unit contains a graft, the macromonomer. There has been increasing interest over the years for the controlled synthesis of such comb-shaped polymers based on macromonomers, named polymacromonomers[1]. The purpose of the present work is to compare different polymerization processes for the homopolymerization of macromonomers. Indeed, various polymerization processes have already been used efficiently to design well-defined comb shaped or graft copolymers: anionic[2,3], free radical[4-6] or controlled free radical[7,8], ring opening metathesis polymerizations[9,10] and finally metallocenes or late transition metal catalysts[11-15]. The case of anionic polymerization will be discussed first. The

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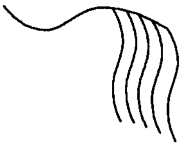
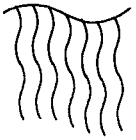
contribution of free radical polymerization to the homopolymerization of macromonomers will be examined based on data taken from the literature. Preliminary results on the use of controlled free radical polymerization for the homopolymerization of macromonomers will be presented briefly. Part of the work deals also with the polymerization of macromonomers in the presence of late transition metal catalysts. Besides, the homopolymerization of bifunctional poly(ethylene oxide) macromonomers have been shown to yield structured hydrogels. That point, out of the scope of the present article, has been reviewed in a recent publication[16]. Some typical structures obtained by polymerization of well-defined macromonomers are given below :

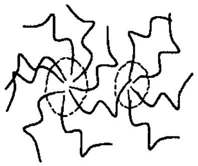
Comb-shaped Polymacromonomer



Palm–tree



Polymacromonomer (with copolymeric branches)



Hydrogel precursor

Synthesis of the ω-functional polystyrene macromonomers

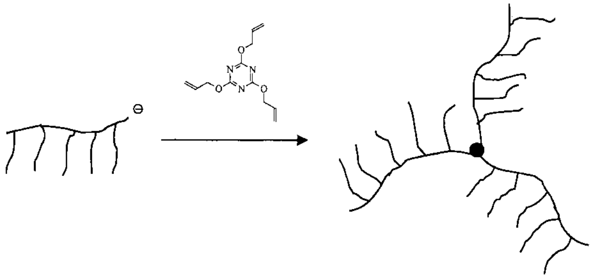
Among the different polymerization processes, anionic polymerization, carried out under proper conditions in aprotic solvents with efficient metal-organic initiators, remains the method of choice to design macromonomers of controlled molar mass and functionality[11]. Therefore, we have synthesized several polystyrene (PS) macromonomers by induced anionic deactivation reactions. They were fitted with polymerizable meth(acrylic) or vinylic monomers. In most cases, an intermediate addition of 1,1-Diphenylethylene (or ethylene oxide) was necessary to limit side reactions during the deactivation procedures. For purpose of comparison PS macromonomers with allylic or undecenyl end groups were also prepared by anionic deactivation reactions. These macromonomers were submitted to detailled characterized as described in previous publications[17-19] (additional characterization was recently made by Maldi-Tof Spectroscopy[11]).

Anionic homopolymerization of ω-functional PS macromonomers

The intrinsic characteristics of anionic polymerization methods especially the long lifetime of the active sites, the absence of transfer reactions provide the best chance for

precise control of the homopolymerization yield and the polymerization degree of the backbone of the polymacromonomer[3]. Here two cases of anionic homopolymerization of PS macromonomers will be exemplified, the macromonomers were either fitted with a polymerizable styrenyl group or with a methylmethacrylate entity. In the first case, the homopolymerization could be controlled over a large domain of temperature and for different solvents. Until degrees of polymerization up to 100, the yields were always quantitative and a good control of the polymacromonomer length could be obtained (Table 1). For PS macromonomers with molar mass higher than 10 000 g.mol^{-1} the situation was more complex. These polymacromonomers are characterized by a backbone and grafts exhibiting the same chemical nature. Their properties were examined on the base of existing theories and compared with other branched structures.
ω-methacryloyloxy polystyrene macromonomers have also been extensively studied[3]. Provided appropriate initiators are used in the presence of LiCl well defined PS polymacromonomers with a PMMA backbone, free of linear precursor could be obtained by anionic polymerization with a good control in advance of the polymerization degree. The kinetics of the homolymerization was followed by SEC and confirmed unambigouesly the influence of the molar mass of the macromonomer on the apparent propagation rate.

The possibility to prepare well defined branched species with active sites at the outer end of the backbone opens new perspectives in the control of macromomolecular architectures. ω-functional polystyrene macromonomers could be homopolymerized in a controlled way and the living polymer was reacted with a stoechiometric amount of deactivators such as tris allyloxytriazines. An increase of the weight average molar mass by a factor 3 with the respect to the weight average molar mass of the polymacromonomer precursor was observed. Further work is going on on that line.



Free radical homopolymerization of ω-functional PS macromonomers

The presence of remaining impurities in the macromonomer limits the domain of applicability of anionic polymerization to rather low DP_n values. In free radical homopolymerization, characterized by short lifetime of the active sites, the growing macroradicals have been shown to be reactive enough to induce polymerization[4,5] but their diffusion is slowed down by the high viscosity of the reaction medium. Consequently, branched polymers with broad or even multimodal molar mass distributions resulted. The homopolymerization yields are not quantitative. Free radical homopolymerization of vinylic or acrylic macromonomers is also far beyond the reach of precise chain-growth control. Provided careful fractionation is performed, comb-shaped PS characterized by high DP_n values can be isolated. The properties and the behavior of species have been extensively studied[6].

The controlled living free radical polymerization process, recently developed may represent an interesting alternative to design polymers of controlled structure[7,8]. The developed idea underlying that polymerization process is to end-cap the macroradical during polymerization. The reversible formation of a σ bond between the growing species and a stable radical may be considered as a special case of chemical stabilization, preventing termination and/or transfer side-reactions by maintaining a low instantaneous concentration of free radicals in the medium. Two initiating systems have been compared: 1-benzoyloxy-2-phenyl-2-(2',2',6',6'-tetramethyl-1-piperidinyloxy) ethane (BPTPE) or a classical initiator (2,2′-azobis(*iso*butyronitrile) (AIBN) or benzoyl peroxide (BPO)), and a stable counter-radical (2,5-dihydro-1,3,5,5-tetraphenyl-1*H*-1,2,4-triazol-2-yl radical). The kinetics of such homopolymerizations was examined and the almost living character of these reactions could be established[7].

Homopolymerization of ω-functional PS macromonomers via coordination polymerization[11-15]

In a preliminary work, we have shown that the homopolymerization of ω-vinyl PS macromonomers by coordination polymerization *i.e.* in the presence of $CpTiCl_3$ or $CpZrCl_3$ is possible, best results being obtained with the titanium compound[15]. These encouraging results prompted us to continue along that line. It has been shown in earlier attempts that the concentration at which the homopolymerization of the PS macromonomers takes place, plays a decisive role. Therefore, we decided to perform the homopolymerization reactions at much higher concentrations. The results obtained are presented on Table 1 together with the experimental conditions. For purpose of comparison we introduced in the same table some characterization data concerning the anionic polymerization of macromonomers exhibiting similar structural characteristics.

Table 1. Experimental conditions for the synthesis and characterization of PS macromonomers prepared with different polymerization process.

Reference		Conversion (%)	M_n (g.mol^{-1})	M_w (g.mol^{-1})	
ω-methacryloyloxy- PS	A	96	1350	64000	48
ω-vinylbenzyl-DPE-PS	A1**	94	1100	13000	11
ω-vinylbenzyl-PS	A1	95	1200	19200	16
ω-vinylbenzyl-DPE-PS	C	48	1100	10500	10
ω-vinylbenzyl PS	C	62	1125	15800	14
ω-allyl PS	C	5*	1200	2400	2
ω-undecenyl PS	C	8*	1600	3200	2

A Initiator 1,1-Diphenyl-3-methyl pentyllithium, [LiCl]/[LE]= 5, THF T : -40°C / 2 hours
A1 Initiator *sec*-BuLi, Toluene, 40°C, 2 hours
C Reaction time: 24 h, T=55°C, $CpTiCl_3$ = 10 µmol, [Al]/[Ti]= 1000, Toluene
*Dimeric species
** This sample is characterized by a perdeuterated backbone
Mn number average molar mass determined by SEC,
Mw weight average molar mass determined by SEC on line light scattering

The following results have been obtained:

- Whatever the experimental conditions the polymerization yield is lower than for styrene alone and for anionic homopolymerization of the same macromonomers
- The homopolymerization yield increases and the molar mass decreases with increasing Al/Ti ratio and seem to stay constant for Al/Ti ratios around 1000 or higher values
- For a given Al/Ti (ratio 1000, the best compromise), the homopolymerization yield increases progressively with the reaction time until 40 hours up to 60 weight % and thus remained unchanged. One has to be aware of the fact that the chain end of the PS macromonomer is fitted with a bulky 1,1-diphenylethylene unit, introduced in order to limit side reactions during the synthesis of the macromonomer. The presence of that bulky group may be a drawback in homopolymerization experiments. To clarify that point, we performed a series of homopolymerization experiments with macromonomers

without that bulky substituent. For these experiments both the homopolymerization yields and the molar masses of the resulting polymacromonomers were higher confirming the steric hindrance due to the DPE unit.

- No homopolymerization of PS ω-allyl and ω-undecenyl PS macromonomers was observed neither via anionic polymerization, nor via polymerization in the presence of metallocene catalysts. The introduction of the alkyl spacer did not affect the results. Far better results were observed for copolymerization with ethylene. These results will be discussed in a forthcoming paper[4].

Conclusion

In the present work, we have examined the performance of various polymerization methods to design well-defined structures based on macromonomers. The controlled living free radical polymerization, less sensitive to impurities, provides an original and efficient approach. The ability of ω-allyl polystyrene and ω-vinylbenzyl polystyrene macromonomers to undergo homopolymerization in the presence of metallocene catalysts was also examined, leading to comb-shaped species with a syndiotactic backbone.

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