Synthesis of PS Star Polymers from Tetracarbanionic Initiators

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Summary: A novel tetracarbanionic initiator as designed and used to obtain star polymers. Well-defined four-arm polystyrene stars exhibiting expected molar masses and low polydispersity indexes have been obtained in this way.

Keywords: anionic polymerization; core-first method; pluricarbanionic initiator; polystyrene; star polymers

Introduction

Star-type polymers attract interest because of their intrinsic features [1], namely, high segment density and low viscosity. In spite of severe experimental constraints, anionic polymerization is still one of the best routes to synthesize well-defined star-type polymers. Thanks to the long lifetime of active anionic species, features such as the functionality of the core, the polymolecularity and molar mass of branches can be precisely controlled in the stars obtained. There are two strategies [2] to produce star-type polymers, either the so-called "arm-first" or "core-first" methods. The arm-first approach entails the coupling of linear "living" chains to multifunctional agent such as $SiCl_4$. The second method involves the use of a plurifunctional core that can initiate polymerization in multiple directions. This approach is a major challenge since it requires the prior design of well-defined multifunctional initiators. Examples of such initiators are scarce, specially those that can trigger carbanionic polymerization [3-8].

In a recent addition to the field of anionic polymerization, Tsitsilianis et al. [9] described a novel difunctional initiator. Based on the well-known halogen-lithium exchange reaction that was first investigated by Gilman et al. [10] this initiator affords the synthesis of triblock polymers in a polar solvent.

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In this contribution we have also exploited the possibilities offered by this halogen-lithium chemistry to synthesize well-defined star-type polymers using the "core-first" method. To this end, the synthesis of a carbanionic compound from a dibromoaryl compound was first investigated and its behavior as a difunctional initiator studied. In a second step, a procedure similar to that used for the synthesis of this difunctional initiator was applied to obtain a tetracarbanionic initiator. The conditions that have been applied to obtain four-arm PS star polymers of targeted molar masses, low polydispersity indexes and accurate number of arms are discussed here.

Experimental part

Materials: Benzene was distilled over living polystyryllithium prior to its use. 2-Bromobutane, undecane, N,N,N',N''-tetramethylethylenediamine (TMEDA) were dried over calcium hydride for several days before being distilled. Styrene was dried over CaH_2 for 2 days, then distilled over dibutylmagnesium and redistilled just before use. Commercially available sec-butyllithium was titrated according to a literature method [18]. (1,2,3,4-tetra(p-bromophenyl)-5-phenyl)benzene (II) was synthesized as described [19]. 4, 4'-dibromobiphenyl (ACROS) and compound II were freeze-dried twice with benzene. Methanol was used as received.

All anionic polymerizations were performed under a slight argon overpressure using a tight reactor equipped with a argon inlet, magnetic stirring, a sampling device and burets meant to introduce solvent, sec-BuLi, monomer and deactivator.

Viscosimety measurements were realised using a Ubbelohde-type flow capillary viscosimeter. Intrinsic viscosities were obtained by extrapolation to zero concentration of the reduced and inherent viscosities. Measurements were performed in toluene at 35°C.

The size exclusion chromatography (SEC) equipment consisted of a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns, a Varian refractive index detector and a JASCO 875 UV/VIS absorption detector, THF being the mobile phase. The columns were calibrated with polystyrene standards. The actual molar masses of star samples were calculated from the response of the multiangle laser light scattering detector, Wyatt Technology, that was connected to SEC.

Synthesis of linear PS by pathway A: In a typical reaction, 4, 4'-dibromobiphenyl (0.25g, 0.8 mmol/L) was dissolved in 15 ml of benzene. 1.23 ml of sec-BuLi (1.6 mmol, [sec-BuLi]=1.3

mol/L) was added at once. After 20min at room temperature 1.23 ml of sec-BuLi (1.6 mmol) and 0.5 ml of TMEDA (3.2 mmol) were added. Then, 17ml (0.15 mol) of styrene was slowly added to the previous solution. Deactivation was performed after about 12 h of polymerization by addition of methanol. Precipitation in methanol yielded pure PS.

Synthesis of linear PS by pathway B: In a typical reaction, 4, 4'-dibromobiphenyl (0.25g, 0.8 mmol/L) was dissolved in 15 ml of benzene. Sec-BuLi (1.23 ml, 1.6 mmol) was added at once. After 20 min at room temperature the initiator formed was collected by filtration and then washed with 10 ml of benzene. Three successive filtration-washing processes were carried out. Afterward, initiator was dissolved in 30 ml of benzene prior to the addition of 0.25 ml (1.6 mmol) of TMEDA. Then, 8 ml (0.07 mol) of styrene was slowly added to this solution. Deactivation was performed after about 12 h of polymerization by addition of methanol. Precipitation in methanol yielded pure PS.

Synthesis of PS star: The same procedure as that used for the synthesis of linear PS was followed. Selective precipitation was carried out by slow addition of methanol into the benzene solution containing the star polymer.

Results and discussion

Synthesis of 4, 4'-dilithiobiphenyl from a 4, 4'-dibromobiphenyl:

4, 4'-dilithiobiphenyl was obtained by reaction of 4,4'-dibromobiphenyl with sec-butyllithium (Figure 1) through halogen-lithium exchange reaction [10] ; the latter gives rise to an equilibrium that lies towards the side giving the more stable organolithium compound. This chemistry is particularly useful for preparing aryl lithium. Under similar experimental conditions similar to those described in the literature [11-12], halogen-metal interconversion is complete when carried out in benzene. Likely due to its high degree of aggregation 4,4'-dilithiobiphenyl was found to be insoluble in benzene, but became soluble upon addition of trimethylethylenediamine (TMEDA). It could thus be used to initiate the polymerization of styrene.

(1)

Figure 1. Synthesis of 4,4'-dilithiobiphenyl.

One feature of this halogen-lithium exchange reaction that caused complications was the formation of sec-butylbromide, an alkylbromide that was found to deactivate the growing polystyryllithium. In order to avoid such a deactivation, sec-butyl bromide had to be eliminated and two solutions have been explored (Figure 2) to this end :

A- Before adding styrene an attempt was thus made to neutralize sec-BuBr with sec-BuLi : in fact, this compound reacted quantitatively with the bromide derivative in less than 1 minute in presence of TMEDA,

B- As another means to eliminate sec-BuBr, insoluble 4, 4'-dilithiobiphenyl was isolated by filtration and then dissolved in benzene/TMEDA.

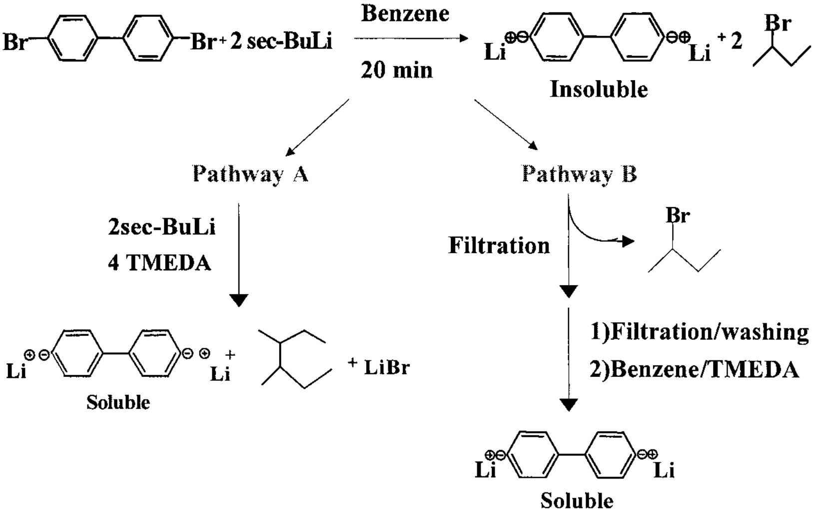


Figure 2. The two pathways used to purify 4,4'-dilithiobiphenyl initiator.

Styrene polymerization:

The anionic polymerization of styrene was triggered upon addition at room temperature of monomer into the flask containing the 4,4'-dilithiobiphenyl initiator obtained by the two pathways (A, B) described above. After complete conversion of styrene, methanol was added to the medium as quenching agent. All samples were characterized by size exclusion chromatography (SEC) (Table 1) and gas chromatography (GC).

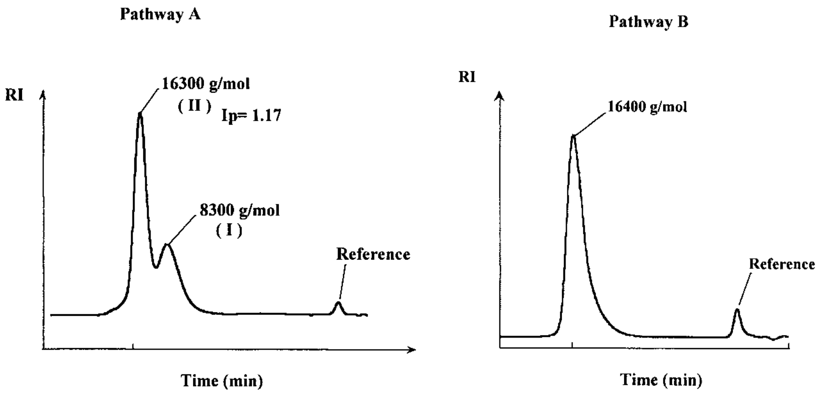
Table 1. Characteristics of polystyrene samples obtained using routes A and B.

Pathways	$\overline{DP}_{n,targ.}$ [a]	$\overline{M}_{n,targ.}$ [b] g/mol	$\overline{M}_{n,exp}$ (SEC) g/mol	$\overline{M}_w / \overline{M}_n$
A	187	19500	19000/9200	bimodal
A	173	18000	16300/8300	bimodal
B	81	8500	9200	1.15
B	107	11200	12000	1.17
B	144	15000	16400	1.12

a) $\overline{DP}_{n,targ.} = 2\times([M]/2\times[LiPhPhLi])$

b) $\overline{M}_{n,targ.} = 104 \times \overline{DP}_{n,targ.}$

Regardless of the experimental conditions used GC analysis showed that 100% of the dilithio compound had been consumed in the initiation of the polymerization of styrene. However, the samples obtained using initiator purified *via* pathway A, exhibited a bimodal molecular weight distribution (Figure 3).



Pathway A

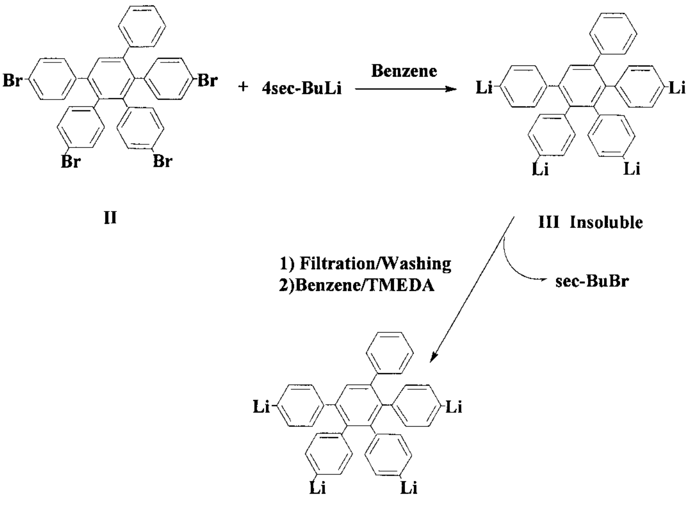
Pathway B

Figure 3. SEC chromatograms of linear polystyrene obtained from pathways A and B.

The population of lower molar mass (I), less than 10% in weight, was identified as resulting from the initiation by residual sec-butyllithium remaining in the reaction medium after neutralization of sec-BuBr. The molar mass of this minor population was about half that of the second population. Unlike the samples generated by route A, those obtained by the pathway B showed a low dispersity index and molar mass in excellent agreement with targeted values attesting to the efficiency of this method (Table 1, Figure 3).

Synthesis of tetracarbanionic initiator from a tetrabromoaryl compound:

The synthesis of tetrabromoaryl compound II was performed according to the procedure described in the literature [13-14]. Under the same conditions as those described above the tetralithioaryl compound III was synthesized in benzene. The yield of the halogen-metal reaction was checked by GC by measuring the quantity of sec-BuBr released. The value obtained was close to 100% attesting to the complete transformation of bromide atom into lithium. Due to its insolubility in benzene prior to the addition of TMEDA and its very good solubility in the presence of the latter additive, only the pathway B has been contemplated (Figure 4).



Soluble

Figure 4. Synthesis of tetracarbanionic initiator.

Synthesis of four-arm star polymers:

The tetralithioaryl compound III obtained under these conditions was used to trigger the polymerization of styrene. After complete monomer conversion the carbanionic species were deactivated by addition of methanol. The resulting polymers were characterized by SEC coupled with laser light scattering so as to determine their actual molar masses. The chromatogram obtained attested to the complete consumption of the tetrafunctional initiator as no signal due to the protonated version of III could be detected in the region of lower masses. However, the SEC chromatograms revealed the presence of two populations of chains : that of largest amount (~90%) exhibited molar mass in agreement with a tetrafunctional initiation and a low molar mass distribution attesting to fast initiation step (Table 2). The second population represented hardly 10% by weight and its molar mass was four time lower than that of the main population. It was identified as linear polystyrene initiated by residual sec-BuLi which was entrapped inside aggregated tetracarbanionic species and could not be removed even after several washings and filtrations. Regardless of the number of washing steps with a dry solvent it was not possible to totally eliminate this second population. Nevertheless, pure polystyrene star polymers could be isolated as shown by SEC analysis upon selective precipitation using a methanol/benzene mixture(Figure 5).

Table 2. Characteristics of the four-arm polystyrene stars obtained.

$\overline{M}_{n,targ.}$ a) g/mol	$\overline{M}_{w,DDL}$ b)(B) g/mol	$\overline{M}_{n,SEC}$ (A) g/mol	$\overline{M}_w / \overline{M}_n$	$[\eta]_{star}$ c) dl/g	$[\eta]_{linear}$ c) dl/g	g’
39500	38400	9800	1.08	0.166	0.222	0.75
55000	49500	12500	1.09	-	-	-
120000	98600	25200	1.08	0.297	0.430	0.69

a) $\overline{M}_{n,targ.} = 104 \times ([M]/[PhLi]) \times 4$

b) Molar masses determined from SEC equipped with a laser light detector

c) Determined in toluene at 35°C

The branched nature of the samples obtained was demonstrated by viscometry and more particularly through the determination of g' which represents the ratio $[\eta]_{star}/[\eta]_{linear}$. As can be seen in Table 2, the g' values exhibited by all samples are very close to the theoretical values ($0.71<g'<0.79$) predicted by the theoretical models of Zimm [15] and Stockmayer [16]. Quite a bit large values had been previously reported by Roovers [17] for four-arm polystyrene stars in good solvent ($g' = 0.86$). These results substantiate the four-arm structure of the stars obtained.

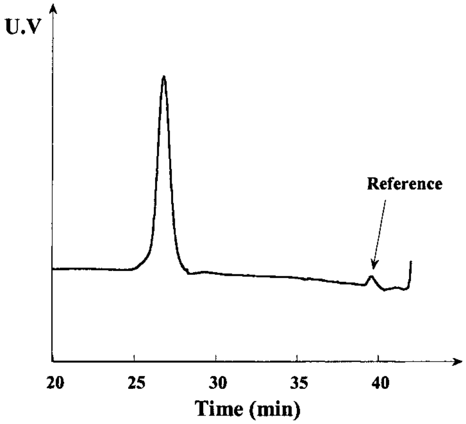


Figure 5. SEC chromatogram of a four-arm polystyrene star after purification.

Conclusion

In this study, it was demonstrated that phenyllithium species can be used to initiate the "living" anionic polymerization of styrene; a novel tetracarbanionic initiator carrying four phenyl lithium sites was synthesized and used to trigger the polymerization of styrene. Four-arm polystyrene star exhibiting the expected macromolecular architecture could be obtained in this way. The synthesis of PS-b-PB star block copolymers is currently in progress in our laboratory and will be described in a future contribution.

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