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High Performance Poly(styrene-*b*-diene-*b*-styrene) Triblock Copolymers from a Hydrocarbon-Soluble and Additive-Free Dicarbanionic Initiator

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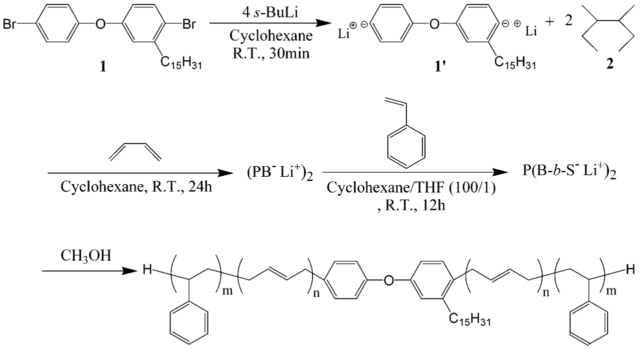
Anionic polymerization is certainly the most reliable and versatile technique for the synthesis of block copolymers due to the absence of transfer and termination reactions.[1] For this reason, it occupies a key position in the industrial production of block copolymers, the most emblematic being SBS triblock copolymers comprising a low Tg polybutadiene (B) block flanked by two glassy polystyrene (S) end blocks. Such triblocks are industrially obtained by butyllithium(BuLi)-initiated sequential polymerization of styrene and butadiene, followed by the deactivation/coupling of growing carbanionic chains by a difunctional electrophilic reagent.[2] Utilized for the last 40 years, this method has, however, a drawback, which is its extreme sensitivity to the stoichiometry of the final dichain coupling; as a result, the triblock copolymers obtained are generally contaminated with diblocks, which is detrimental to excellent stress−strain properties. The use of a dicarbanionic initiator that could trigger polymerization in two directions thus appears as the only viable alternative.[2] One major difficulty met in the latter case is the limited solubility of dicarbanionic initiators in apolar solvents, media that are required for the preparation of a polybutadiene central block with a high content in 1,4-units and elastomers with optimal properties. Whether obtained by reaction of BuLi with appropriate divinylic species[3−8] in 2:1 ratio or by generation of ion radical species which then couple (e-transfer from lithium to α-substituted vinyl monomers),[9] organolithium diinitiators indeed require the presence of active polar additives to efficiently initiate polymerization, which in turn modifies the stereochemistry of the polydiene block and increases its content in 1,2 unsaturations. A dilithiated carbanionic initiator that would be entirely soluble in apolar medium in the absence of any additives or ligands and yet reactive enough is thus very much in demand.

We previously reported the preparation of tri- and tetrafunctional polylithium organic compounds by lithium−halogen exchange and their use as initiators for the synthesis of polystyrene and polybutadiene star polymers.[10] However, the latter polylithiated species formed were found soluble only in the presence of σ/μ-coordinating ligands. Using the same lithium−halogen exchange chemistry, we describe here a new dilithiated initiator that is totally soluble in apolar media in the absence of any additive and is efficient enough to generate well-defined polybutadiene telechelics and SBS triblock copolymers with a high content in 1,4-units and excellent mechanical properties.[11]

3-Pentadecyl phenol, obtained from cashew nut shell liquid,[12] served as the precursor for the dibromo compound, 1-bromo-4-(4′-bromophenoxy)-2-pentadecyl benzene[13] (**1**) (see Scheme S1 in Supporting Information); the latter was subsequently dilithiated and eventually used for difunctional initiation. In this chemistry, advantage is taken of the saturated C_{15} side chain to obtain a soluble dilithiated initiator. **1** was obtained in excellent yields (84%) after bromination in the para position of 1-pentadecyl-3-phenoxy benzene. The structure of the dibromo compound (**1**) was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (see Figures S1 and S2 in Supporting Information). Next, **1** was treated with stoichiometric amounts of *sec*-butyllithium (*s*-BuLi) in cyclohexane which generated **1′** and 2-bromobutane. To prevent the subsequent deactivation of the growing carbanionic chains by 2-bromobutane, another equivalent of *s*-BuLi was added to transform 2-bromobutane into 3,4-dimethylhexane (**2**) (Scheme 1).[10] The product (**1′**) of the reaction of **1** with *s*-BuLi in cyclohexane became a yellow color and a gelly aspect at the concentration of $[\mathrm{Li}^+] = 5.3 \times 10^{-2}$ M. The presence of a C_{15} alkyl side chain in **1′** is responsible for the formation of such a physical gel instead of the irreversible precipitate observed with the dilithiated species formed upon reaction of 4,4′-dibromobenzene with *s*-BuLi.[10]

Scheme 1. Synthesis of SBS Triblock Copolymers



The structure of the dilithium diadduct **1′** was first confirmed by ^{1}H and ^{13}C NMR spectroscopy by analysis of the product isolated after methanol quenching (see Figure S3 in Supporting Information). Mass spectrometry also showed the total disappearance of the peak of the dibromo precursor **1** ($M = 538$ g/mol) in favor of the protonated version of **1′** with a principal peak at $M = 381$ g/mol after methanolysis (see Figure S4 in Supporting Information). **1′** was then used ($[\mathrm{Li}^+] = 5.3 \times 10^{-2}$ M) to initiate the polymerization of styrene or butadiene (Scheme 1). After introduction of a few monomer units, the dilithiated species formed appeared totally soluble in cyclohexane even in the absence of stirring and of any polar additives. On deactivation of the living carbanionic chains by ethylene oxide after complete monomer consumption, α,ω-dihydroxy telechelic polymers were obtained. Analysis by size exclusion chromatography (SEC) indicated the complete consumption of **1′**, the only trace seen being a narrow and monomodal peak corresponding to the expected linear polymer in the high molar mass region (see Figure S5 in Supporting Information). Such an excellent agreement between experimental and targeted values of molar masses and narrow molar mass distributions (M_w/M_n typically

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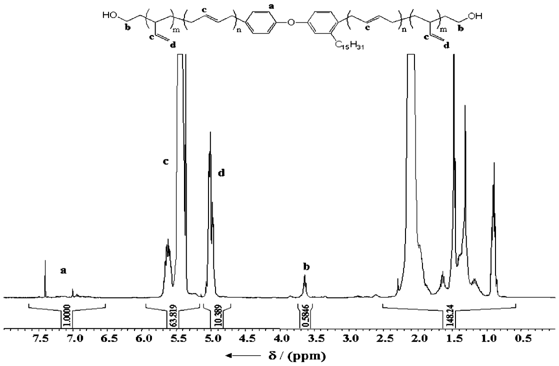

Figure 1. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of a α,ω-dihydroxy-terminated polybutadiene.

Table 1. Characterization of Polystyrene, Polybutadiene, and SBS Samples Synthesized from **1′** as Difunctional Initiator[a]

sample	M_n (g/mol)[b]	M_w/M_n[b]	M_n(expected) (g/mol)[c]	Microstructure (%)[d]		
				1,4-cis	1,4-trans	1,2
S	11400	1.15	12000			
S	43800	1.13	44000			
B	2100	1.2	2000	38	47	15
B	6200	1.13	7000	39	47	14
B	16600	1.07	17000	39	47	14
B	51900	1.08	52000	40	50	10
B	67400	1.1	70000	41	50	9
SBS	110900	1.2	110000	41	50	9

[a] Polymerization of butadiene was initiated in cyclohexane with **1′** ($[Li^+] = 5.3 \times 10^{-2}$ M). [b] Determined by SEC using a refractometric detector; 0.55 was the conversion factor used for the determination of the molar mass of B samples. [c] $M_n(\text{expected}) = M_{\text{butadiene}} \times ([\text{butadiene}]/[-\text{PhLi}]) \times 2$. [d] Calculated by ^{1}H and ^{13}C NMR (see Figure S8 in Supporting Information).

<1.1) reflects a rate of initiation by **1′** comparable to that of propagation (see Supporting Information). The structure of the difunctional polymer formed could be established by ^{1}H NMR using α,ω-dihydroxy telechelic polybutadiene samples of low degrees of polymerization (Figure 1). From the ratio of the integration values due to the signal of the aromatic protons of the difunctional initiator ($\delta = 6.5-7.5$ ppm) to that of $-CH_2-OH$ chain ends ($\delta = 3.7$ ppm), functionality values close to 2 were obtained for the polybutadiene telechelics. The microstructure of the polybutadiene samples determined by ^{1}H and ^{13}C NMR spectroscopy demonstrated a high percentage (86−91%) of 1,4-units (half constituted of 1,4-cis and 1,4-trans) (see Table 1), which is generally the case for polybutadiene synthesized in apolar solvents using butyllithium as initiator.[2]

Next, SBS triblock copolymers were derived by sequential anionic polymerization of butadiene and styrene with **1′** as initiator (Scheme 1). The initiation of styrene by polybutadienyllithium being slow, it was necessary to dilute further the reaction medium with fresh cyclohexane and some THF (cyclohexane/THF, 100/1 in volume). By taking an aliquot before the introduction of styrene, the formation of the SBS samples could be easily followed by SEC (see Figure S7 in Supporting Information).

The absolute molar masses of the SBS triblock copolymers were deduced by ^{1}H NMR spectroscopy knowing that of their polybutadiene precursor from the SEC analysis (see Supporting Information). In all cases, narrow molar mass distributions were observed either for the polybutadiene precursor or for the triblock copolymer structure with a complete consumption of the polybutadiene precursor after polymerization of styrene as attested by SEC (see Supporting Information); this demonstrates that the growth of either the polybutadiene middle block or the two polystyrene glassy end blocks occurred under living conditions. Excellent mechanical properties were measured on these SBS triblock samples—especially on those containing small polystyrene end blocks (wt % (PS) < 35%)—with ultimate tensile strength higher than 30 MPa and elongation at a break of 1000% (see Table 2 in Supporting Information).

In summary, the halogen−lithium exchange reaction has been successfully applied to generate a new dicarbanionic initiator from a dibromoaryl compound. The presence of a C_{15} side alkyl chain in the dibromo precursor is essential to the solubility of the dilithiated initiator in apolar solvent. This is the first example of dilithiated species initiating efficiently anionic polymerization in absence of additive and affording well-defined polybutadiene telechelics with a high percentage of 1,4-units (91%). Accordingly, SBS triblock copolymers with remarkable ultimate tensile strength and elongation at break could eventually be obtained, and in this way, a long-standing issue faced by the industry of styrenic thermoplastic elastomers could be sorted out.

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Supporting Information Available: Experimental details for the synthesis and the characterization of the initiator, homopolymers, and block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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