



# Controlled block-polymerization of styrene, divinylbenzene and ethylene oxide. Intermolecular cross-linking towards well-defined miktoarm copolymer stars

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## ABSTRACT

A novel approach for the synthesis of miktoarm copolymer stars with divinylbenzene cross-linked core, via anionic polymerization is reported. This synthetic route gives access to polymers, characterized by low dispersity values and improved structural homogeneity for both arm species. Specifically, miktoarm copolymer stars of  $A_nB_n$  type, with cross-linked divinylbenzene (DVB) core and arms of polystyrene (PS) and poly(ethylene oxide) (PEO), are synthesized via anionic polymerization and sequential monomer addition, employing high vacuum techniques. Analytically, the first step involves the synthesis of a triblock terpolymer PS-*b*-PDVB-*b*-PEO. Then, in the presence of a free radical initiator the pending vinyl groups of the middle DVB block cross-link intermolecularly, leading to the final miktoarm copolymer star. The novelty of the proposed synthetic route, lies in the potassium alkoxide *co*-initiator, which is responsible for the controlled polymerization of both DVB and EO in one pot, without the need for end group modification between the two steps. Concerning the final polymer, there are numerous benefits advancing from this synthetic protocol, such as the control of the molecular characteristics of both arms, as well as the easily confirmed structural integrity of the precursor triblock which is inherited to the resulting miktoarm star. For comparison reasons, another batch of (PS)(PEO) miktoarm copolymers was synthesized, following the “in-out” synthetic route. For this reason, styrene was polymerized using *s*-BuLi, which is used as macroinitiator for the polymerization/cross-linking of DVB, resulting PS star with DVB cross-linked core. With the addition of EO, in the presence of *p*4 *t*-Bu phosphazene base, PEO arms are polymerized, initiating from the core's active sites outwards.

## 1. Introduction

The utilization of DVB in the synthesis of cross-linked, mostly styrenic polymers, has been extensively reported in literature [1–3]. Such copolymer gels find a wide range of applications in industry among others, i.e. as packing material in Gel Permeation Chromatography columns [4]. The synthesis of cross-linked PS-DVB nanoparticles with varying weight fraction of cross-linker has been also reported, and the effect of their surface morphology and their rigidity have been well studied over the polymer chain diffusion and dynamics in their blends with linear polymers [5–7]. DVB microspheres have been prepared, with subsequent surface modification and coupling with poly(*N*-isopropylacrylamide) via thiol-ene reaction and click-chemistry [8]. Also, the synthesis of a highly cross-linked polystyrene with

interpenetrating nanodomains of poly(ethylene oxide)/ionic liquid, achieving high ionic conductivities as well as high elastic modulus, has been reported [9]. In recent publications from our group, blends of linear liquid PEO with PS-PEO miktoarm, and PMMA stars with DVB cross-linked core has been reported to greatly improve the mechanical properties, while maintaining the ionic conductivity of pure PEO [10,11].

Star shaped polymer synthesis employing bis-unsaturated monomers such as DVB, can be categorized into the “Arm first” [12] and “Core first” [13,14] methods. More specifically by the “Arm first” method, where a “living” chain acts as a macroinitiator for the polymerization/cross-link of the DVB core, increasing the MW of the macroinitiator and/or decreasing the polymerization concentration and the degree of DVB polymerization, improves significantly the distribution of the arms’

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population and the overall MW distribution. Reversing any of the above parameters, the population of the arms increases, arms and core size distribution widen and core becomes bulkier. Pushing even further, extended cross-linking takes place and as a result insoluble particles occur, whereas the morphology tends to “hairy” microgels [15,16]. “Core first” method where active sites on a cross-linked core acts as a multifunctional initiator for the radiating arms, is capable to yield stars with up to a few hundred arms, but lacks in functionality control along with arms’ molecular characteristics [14].

In order to prepare star polymers with well-defined structure, the method of “coupling onto” by reacting anionically polymerized “living” polymer chains with precisely functionalized chlorosilane dendrimer cores, is the most appealing, with stars bearing up to more than one hundred arms being reported [17]. Nevertheless, “Arm first” and “Core first” methods significantly augment reagents complexity, cost, and reaction time.

The two methods can be combined in a technique known as “in-out”, giving the ability to develop a second population of chemically same or different arms [2,3,18]. Ideally, the two populations will be equal, as the concentration of active sites does not change throughout the synthesis, but in fact the involvement of cross-linking as intermediate step, is expected to introduce “trapped” active sites inside the core, inaccessible for the second monomer. During the reaction of the cross-linking and the formation of the stars, two variables appear. One is the size of cores, and the other is the number of the arms. These two characteristics are not expected to be exactly the same throughout the polymer volume, as they are determined by the steric hindrance of the arms on the active sites of each polymer molecule independently. This effect initially broadens the distribution of the homopolymer star, and as a result creates a hindrance gradient among the active sites on the core’s surface. Moreover, the larger the core size, the more active sites get trapped inside. As a result, the consumption of the second monomer during the “out” polymerization is expected to be inhomogeneous throughout the product. Finally, considering a percentage of unreacted vinyl groups, star-star coupling may occur in case two cores collide, during the cross-linking stage or in case a carbanion growing arm reaches another core during the second arms’ population polymerization [15,19]. All the above, result in distribution broadening and inconsistent composition of the arms over each star and among the stars of a sample.

It has been lately reported, that linear, controlled polymerization of DVB has been achieved, not only in homopolymers, but also in higher architectures, such as diblock copolymers and miktoarm stars. The pending vinyl groups from the DVB block, gives access to a whole field of post polymerization reactions. The key for the controlled polymerization of DVB lies in the fact that the vinyl groups do not share the same reactivity. Since the first one has reacted, the reactivity of the remaining vinyl groups decreases, due to the alteration in the ion stabilization system (resonance, induction) [20]. In that way, designing an initiator system with fine-tuned nucleophilicity, selective attack only on the free monomer is possible. This can be achieved with the addition of potassium alkoxides excess in respect to the *sec*-BuLi. According to the proposed theory, the main events that take place with the potassium alkoxide addition, are the substitution of  $\text{Li}^+$  in the active site to  $\text{K}^+$ , and the coordination of the excess salt around the chain end ion-pair. As a result, the dissociation equilibrium shifts from a solvent-separated ion pair of well soluble  $\text{Li}^+$  active sites, to a contact ion pair, as the solubility decreases. Also, the polar salt molecules coordinate around the active site due to their ionic interactions, and provide steric hindrance, further reducing its reactivity [20–22].

Herein, we report a novel approach for the synthesis of well-defined miktoarm copolymer stars with cross-linked divinylbenzene (DVB) core, arms of polystyrene (PS) and poly(ethylene oxide) (PEO). Initially, a triblock terpolymer PS-*b*-PDVB-*b*-PEO was synthesized by anionic polymerization, and then, in the presence of a free radical initiator the pending vinyl groups of the middle DVB block cross-link intermolecularly, leading to the final miktoarm copolymer star. This synthetic

protocol offers control over the molecular characteristics of both arm species, such as, molecular weight and composition, as well as, chemical homogeneity, which is not possible to achieve by any other synthetic route.

## 2. Experimental

### 2.1. Chemicals and materials

All monomers and solvents involved in polymerization as well as cross-linking reactions were purified, dried and degassed, according to standard anionic polymerization procedures, as described in literature [23,24].

*Sec*-BuLi, was synthesized by reacting its precursor, *s*-BuCl with tenfold excess of Lithium (4% Na w/w) in *n*-hexane. The resulting initiator was filtered, transferred to calibrated ampules and stored at  $-20\text{ }^\circ\text{C}$ . Triphenylmethyl potassium and potassium *tert*-butoxide were synthesized starting from triphenylmethane and *tert*-butanol respectively, using a twofold excess of potassium mirror. These initiators were synthesized in THF due to their low solubility in non-polar solvents and stored at room temperature. Potassium 2,6 di-*tert*-butyl-4-methylphenoxide was activated with potassium naphthalene instead of potassium mirror due to the acidity of the methyl groups. For that reason, naphthalene was purified by triple sublimation and finally collected to a calibrated ampule alongside THF solvent. The solution was then added dropwise to a twofold excess of potassium mirror obtaining a characteristic green color, filtered and transferred to a round bottom flask. In the meantime, an *n*-hexane solution of cresol was dried under  $\text{CaH}_2$ , filtered, concentrated and recrystallized. *n*-Hexane was removed under vacuum and the cresol crystals were weighted, collected in a calibrated ampule, degassed and THF was distilled. The cresol solution was then titrated with the potassium naphthalene obtaining a persistent deep red color at first, followed by a sharp transition to a clear colorless solution. The final product was collected to calibrated ampules and stored at room temperature. AIBN was recrystallized from methanol, dried under vacuum and stored at  $-20\text{ }^\circ\text{C}$ .

The above anionic initiators were titrated with standard HCl solution, using phenolphthalein indicator, in order to determine their exact concentration.

### 2.2. Synthesis procedure

All polymer samples were synthesized employing anionic polymerization under high vacuum, with sequential monomer addition, in all-glass, joint-less apparatuses. In order to achieve a degassed and free of impurities environment, prior to polymerization reactions apparatuses were degassed and purged with a solution of *n*-BuLi in benzene (or diphenylhexyl lithium in THF). For that reason, an apparatus consisting of the main reactor equipped with the reagents’ ampules as well as a purge section, was connected to the high vacuum and degassed thoroughly while flamed with a hand torch. Subsequently, 3 mL of *n*-BuLi (2.5 M in Hexane) was injected, and *n*-hexane was evaporated to the vacuum line. The desired amount of solvent was introduced via distillation and the apparatus was sealed off the vacuum line. Then, the *n*-BuLi solution was transferred around, in order to react with the impurities on the apparatus walls, collected to the purge section and refluxed in order to rinse the remained *n*-BuLi and impurities. The refluxed solvent was drained to the purge section. Then, the desired amount of solvent was distilled back to the reactor and the purge section was sealed off. Following the polymerization of each monomer, a small sample was collected for molecular characterization, when it was possible.

#### 2.2.1. Synthesis of miktoarm copolymer star from star precursor vs linear precursor

Two different sets of polymers were synthesized with respect to the cross-linking procedure. For both sets, sequential addition of monomers

(Styrene → DVB → Ethylene Oxide) was followed. In the case of the first set (Synthesis 1), both vinyl groups of DVB were attacked from the macroinitiator, resulting a PS star precursor bearing a “living” cross-linked core. Following, by the EO addition PEO arms radiated from the core outwards, leading to the final PS-PEO miktoarm copolymer star. For the second set (Synthesis 2), controlled polymerization of DVB took place, leading to a triblock precursor with vinyl groups pending from the middle block. Subsequently, these groups were cross-linked in a post polymerization reaction, thus obtaining the final miktoarm copolymer star.

### 2.2.2. Synthesis of miktoarm copolymer star from star precursor (Synthesis 1)

For the PS<sub>n</sub>-PEO<sub>m</sub> miktoarm star, initially the macroinitiator of PS-Li was synthesized. The reaction took place in an apparatus equipped with two ampules, containing styrene and *s*-BuLi respectively, and calibrated ampules to collect the desired amount of macroinitiator. Following the purging procedure described above and the distillation of benzene solvent into the apparatus, styrene and *s*-BuLi were added to the main reactor and left to polymerize for 24 h at room temperature, in monomer concentration of 10% (w/v).

The next day, the “living” PSLi was collected in the calibrated ampules and sealed off. For the polymerization of DVB and EO, a new apparatus was constructed, carrying an ampule with the PSLi macroinitiator, two ampules containing the DVB and EO monomers, one ampule of P<sub>4</sub> *t*-Bu phosphazene base and one ampule with methanol. This apparatus was purged and rinsed as well, and an extra amount of benzene was distilled in order to achieve a total polymer concentration (Styrene and DVB) of 5% (w/v) during DVB polymerization.

The macroinitiator was introduced to the main reactor, followed by addition of the DVB monomer and allowed to react for 24 h at RT, then for another 24 h at 40 °C, and finally for 48 h at RT, under vigorous stirring. Following, EO was added and left under stirring until discoloration to pale orange. Then the phosphazene was added, the temperature raised to 50 °C and reacted under stirring for 3 days. After completion, methanol was added, the reactor was ruptured and a few drops of fuming HCl (aq) were added to terminate the polymerization. The polymer solution was then concentrated to ~10% (w/v) and precipitated in a large amount of cold *n*-hexane. The precipitate was collected through filtration and dried under vacuum. Polymerization conditions and reagent quantities are listed in Table 1.

### 2.2.3. Synthesis of miktoarm copolymer star from linear precursor (Synthesis 2)

At first, a PSLi<sup>+</sup> macroinitiator was synthesized according to the previously reported procedure, using an apparatus equipped with three ampules containing *s*-BuLi, styrene and DPE, respectively. DPE was added at the chain end and finally, the macroinitiator was collected to calibrated ampules. Due to its high steric hinderance, DPE cannot homopolymerize, so a twofold excess in respect to the anionic sites ensures a quantitative end-capping.

For the preparation of PDVB and PEO blocks, ampules of macroinitiator (PSLi<sup>+</sup>), DVB, EO, potassium oxyanion *co*-initiator and methanol were attached on an apparatus equipped with a magnetic stirrer as

**Table 1**  
Synthesis 1 polymerization conditions.

SAMPLE	n <sub>Initiator</sub> (mmol)	n <sub>Styrene</sub> (mmol)	n <sub>EO</sub> (mmol)	[DVB]: [LE]	C <sub>polymer,crosslink</sub> (g/ml)
Star 1	0.388	33.89	120.32	30:1	5%
Star2	1.09	41.86	158.9	30:1	5%
Star 3	0.624	35.91	14.98	7:1	5%
Star 4	0.651	37.45	29.51	7:1	5%
Star 5	0.533	30.63	39.05	7:1	5%
Star 6	0.364	21.03	40.64	7:1	5%
Star 7	0.3	17.28	75.82	7:1	5%

well. The solvent used in this polymerization was THF, therefore DPHLi was employed for purging instead of *n*-BuLi. Following the apparatus degassing and purging, the potassium oxyanion was added and stirred for a couple of minutes. Afterwards, the solvent was slightly cooled, the macroinitiator was introduced to the main reactor and the apparatus was immediately placed in a –80 °C dry ice/isopropanol bath and left under stirring for 10 min. Then, the DVB ampule was cooled as well, and DVB was added at once, with vigorous shaking. Then, the apparatus was placed back to the isopropanol bath for 25 more minutes under stirring and the EO was added. The reactor was left in the bath until discoloration of the solution and since no further change in color was observed, the reactor was removed from the bath to RT, and after 10 min was placed in 50 °C water bath and left under stirring for 3 days. Finally, the polymerization was terminated by methanol addition, and a few drops of fuming HCl (aq). Then, the solution was filtered, all solvents were removed through the vacuum line, and the polymer was redissolved in chloroform, washed three times with distilled water in a separatory funnel, dried with magnesium sulfate, filtered and quenched in a large amount of cold *n*-hexane. Finally, the precipitate was collected through filtration, dried under vacuum and stored at –20 °C. Polymerization parameters are listed in Table 2.

### 2.3. Cross-linking procedure of the linear triblock terpolymer precursor of Synthesis 2

This reaction takes place in high concentration, 50 % (w/v) (2 g of polymer in 4 mL of solvent), in order to promote the intermolecular cross-linking of the linear precursor. Dry solvent, polymer powder and cross-linker (Free radical initiator, AIBN) were added in an ampule, degassed under high vacuum and sealed. Then, the ampule was immersed in oil bath at elevated temperature and left to react for three days. The details of all cross-linking reactions are listed in Table 3.

### 2.4. Characterization methods

Size exclusion chromatography (SEC) was used to determine molecular weights and molecular weight distributions ( $M_w/M_n$ ) of the polymer samples with respect to polystyrene standards. The unit was equipped with an isotactic pump (Knauer K-501), UV detector (Knauer UV-K2501), and RI detector (Knauer RI-K2301). Polymer samples were analyzed using Polymer Standard Service (PSS, Germany) 1 × 100 Å and 1 × linear SDV5 µm gel columns (60 cm) set or with Polymer Laboratories 2 × mixed-BSDV gel columns (30 cm). THF was used as the mobile phase at a flow rate of 1 mL min<sup>-1</sup> at 30 °C. PSS WinGPC software was used to acquire and analyze the chromatograms. In some cases, SEC was performed on an SEC-LS system consisting of an RI detector (Polymer Laboratories), light scattering 15° and 90° (Precision Detectors, λ = 685 nm, 30 Mw), and viscosity (Viscotec) detectors. <sup>1</sup>H NMR (400 MHz) spectrum was recorded on a Bruker AC-400 spectrometer. The thermal properties of the triblock copolymers and the corresponding crosslinking stars of Table 5 were determined with a Discovery DSC 250 (TA Instruments) differential scanning calorimetry (DSC). The temperature range was from –110 °C to 130 °C.

## 3. Results and discussion

### 3.1. Initiator effect in sequential addition

It is known, that an alkyl lithium initiator is able to initiate the ring opening of EO, but the resulting alkoxy lithium active site is not able to propagate its polymerization, due to the higher aggregation that decreases its nucleophilicity. To overcome this obstacle, in order to synthesize block copolymers of PEO following a carbanion propagating monomer such as styrene, the reactivity can be increased in various ways, such as the addition of P<sub>4</sub>-*tert*-Bu phosphazene base. This cryptand molecule, bonds to and encapsulates the Li<sup>+</sup>, therefore the unpaired

**Table 2**

Polymerization conditions for the triblock precursor of Synthesis 2.

Samples	$n_{\text{Styrene}}$ (mmol)	$n_{\text{EO}}$ (mmol)	[DVB]:[LE]	$C_{\text{polymer}}$ (g/mL)	$n_{\text{Initiator}}$ (mmol)	co-initiator	$n_{\text{co-initiator}}$ (mmol)
Triblock 1	25.35	60.16	15:1	3%	0.44	<i>tert</i> -BuOK	0.88
Triblock 2	25.44	60.16	15:1	3%	0.41	cresol	4.1
Triblock 3	17.28	95.35	15:1	3%	0.3	cresol	3.0
Triblock 4	27.84	24.06	15:1	3%	0.48	cresol	4.8

**Table 3**

Synthesis 2 cross-linking conditions.

Sample	$n_{\text{polymer}}$ (mmol)	$n_{\text{AIBN}}$ (mmol)	[polymer]:[DVB]: [AIBN]* mol:mol: mol	$V_{\text{solvent}}$ (mL)	T (°C), Time
Triblock 1	0.085	0.11	1:15:1.3	4	80 °C, 3 days
Triblock 2	0.140	0.35	1:15:2.5	4	80 °C, 3 days
Triblock 3	0.128	0.32	1:15:2.5	9	80 °C, 3 days
Triblock 4	0.176	0.44	1:15:2.5	6	80 °C, 3 days

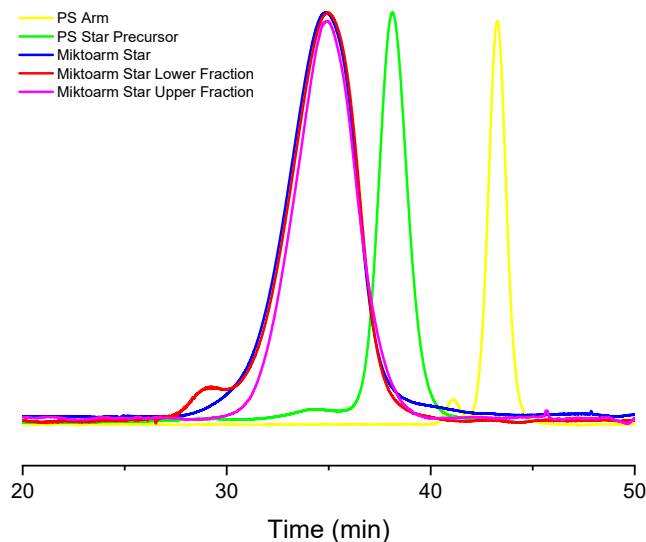
free oxyanion is reactive enough to propagate the ring opening polymerization [25]. Alternatively, the utilization of  $\text{K}^+$  instead of  $\text{Li}^+$  gives a much more soluble ion pair in polar solvents, that is able to propagate the living polymerization of EO anionic polymerization. This can be accomplished with the addition of potassium alkoxides as soon as the EO monomer is added to the polystyryl lithium macroinitiator. Because unhindered potassium alkoxides such as potassium *tert*-butoxide can act as initiators, giving linear PEO homopolymer alongside the desired diblock, more sterically hindered compounds such as potassium 2,6-*tert*-butyl-4-methylphenoxide are preferred [26].

### 3.2. Synthesis of the miktoarm copolymer star from star precursor (Synthesis 1)

(Scheme 1) The molecular characteristics of these polymers were confirmed from GPC chromatography of the final polymer and the PS arm and PS star precursors. Also, from  $^1\text{H-NMR}$  spectroscopy, the chemical composition of the miktoarm copolymer star was calculated (Fig. 1).

As confirmed from the chromatogram, PS arms have narrow and symmetric molecular weight distribution. The distribution appears to be broader for the polymers resulting from each step of the synthesis and shifting to lower elution volumes, as expected. Nevertheless, all distributions remain monomodal and symmetrical (Fig. 2).

From the  $^1\text{H NMR}$  spectrum, integrating the peaks corresponding to



**Fig. 1.** GPC chromatograms during the Synthesis 1 for the PS arm, PS star precursor, miktoarm star and fractionation upper and lower phase.

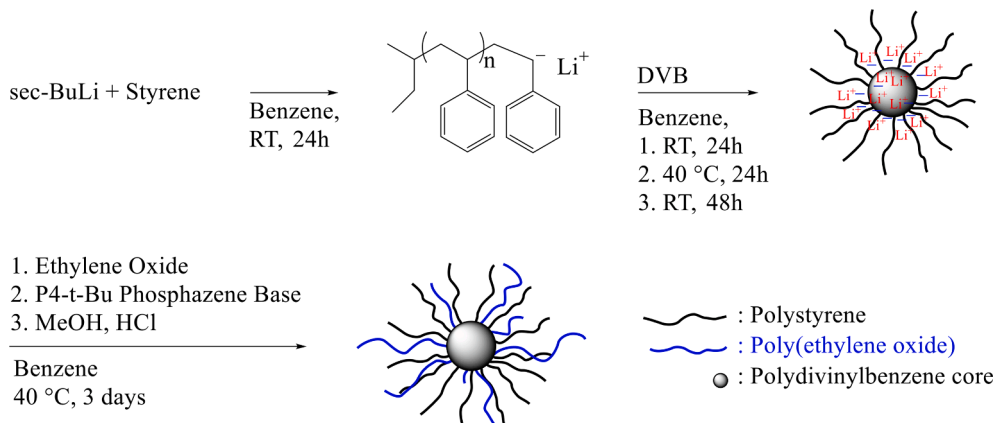
the aromatic protons of PS and the protons of the PEO ether bonds, the experimental composition was found to be close to the theoretical, as all monomers reacted quantitatively.

The mean number of arms for the homopolymer PS star precursor has been calculated by the formula:

$$\frac{\overline{M}_{w,star}}{\overline{M}_{w,linear} + m_0[DVB]/[LE]}$$

where  $M_{n,Star}$ ,  $M_{n,Linear}$  and  $m_0$ , correspond to the molecular weight for the star, the arm and the DVB monomer [27].

Attempting to split each sample to multiple narrower distributions by fractionation, we were surprised to find out that while the GPC traces remained almost identical after the fractionation, the composition percentage in PS and PEO in the resulting fractions were altered as shown in Table 4. This result can be explained by inconsistent composition in PS



**Scheme 1.** Synthesis of PSLi macroinitiator,  $\text{PS}_n$  star precursor and final Miktoarm Star Copolymer  $\text{PS}_n\text{PEO}_m$  following Synthesis 1.

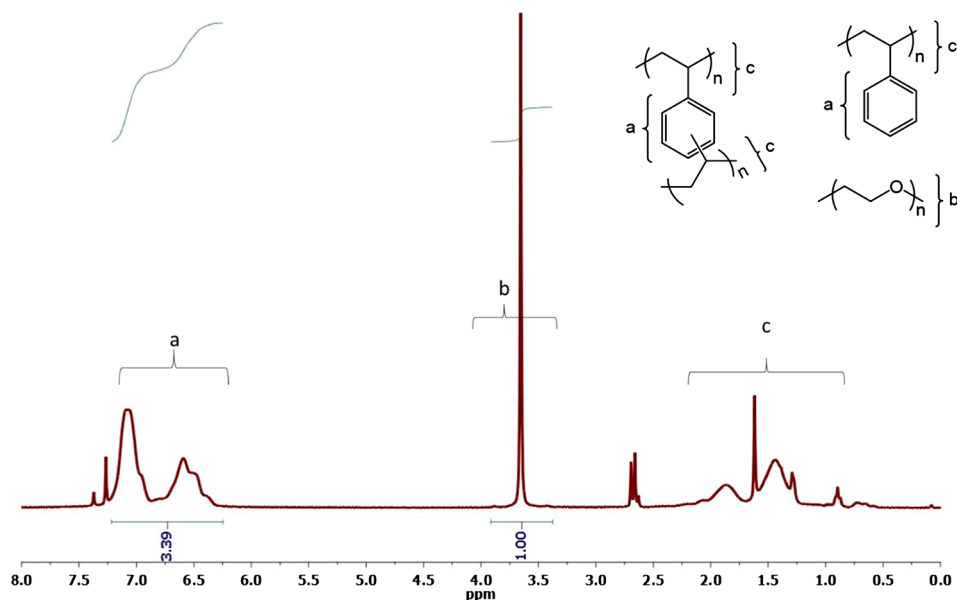


Fig. 2.  $^1\text{H}$  NMR spectrum of  $\text{PS}_n\text{-PEO}_m$  miktoarm star of Synthesis 1.

**Table 4**  
Molecular characteristics of star Synthesis 1.

SAMPLE	PS Arm <sup>a</sup> $M_w$ (g/mol)	PS <sub>n</sub> Star <sup>b</sup> $M_w$ (g/mol)	[DVB]: [LE]	PS weight fraction (%) (% w/w) <sup>c</sup>	PEO weight fraction (%) (%w/w) <sup>c</sup>	PS <sub>n</sub> -PEO <sub>m</sub> <sup>c</sup> $M_w$ (g/mol)	f PS <sup>d</sup>
Star 1	8.5K	gel	30:1	46	54	gel	
Star 1U	8.5K	gel	30:1	82	18	gel	
Star 2	4K	gel	30:1	32	68	gel	
Star 2L	4K	gel	30:1	20	80	gel	
Star 2U	4K	gel	30:1			gel	
Star 3	7K	1.15M	7:1	87	13	1.32M	145
Star 3L	7K	1.15M	7:1	18	82	–	
Star 3U	7K	1.15M	7:1	96	4	–	
Star 4	7K	1.15M	7:1	65	35	1.77M	145
Star 5	7K	1.15M	7:1	66	34	1.74M	145
Star 5L	7K	1.15M	7:1	43	57	–	
Star 5U	7K	1.15M	7:1	98	2	–	
Star 6	7K	1.15M	7:1	54	46	2.13M	145
Star 6L	7K	1.15M	7:1	21	79	–	
Star 6U	7K	1.15M	7:1	97	3	–	
Star 7	7K	1.15M	7:1	36	64	3.19M	145
Star 7L	7K	1.15M	7:1	14	86	–	
Star 7U	7K	1.15M	7:1	97	3	–	

Notation L and U refers to lower and upper fraction respectively, after a fractionation that took place to the samples. <sup>a</sup> Determined by GPC in  $\text{CHCl}_3$  at 25 °C, <sup>b</sup> determined by Static Light Scattering in toluene at 25 °C, <sup>c</sup> calculated from  $^1\text{H}$  NMR, <sup>d</sup>f: functionality number of PS arms.

**Table 5**  
Molecular characteristics for PS-*b*-PDVB-*b*-PEO terpolymers and the corresponding cross-link miktoarm star copolymers.

	Total $M_w$ <sup>a</sup> (Kg/mol)	$M_w/M_n$ <sup>b</sup>	$M_n$ PS Arm (Kg/mol) <sup>b</sup>	$M_w/M_n$ <sup>b</sup> PS Arm	% w.t. PEO <sup>c</sup>	$R_h$ (nm) <sup>d</sup>	Arms functionality (f)
Triblock1	13	1.10	7	1.06	38.0	–	–
Crosslink1	1,685	1.20	7	1.06	38.0	13.5	260
Triblock2	16.6	1.24	7	1.06	51.8	–	–
Crosslink2	1,318	1.30	7	1.06	51.8	15.0	160
Triblock3	28	1.08	7	1.06	71.6	–	–
Crosslink3	686	1.20	7	1.06	71.6	14.0	50
Triblock4	11	1.18	7	1.06	29.6	–	–
Crosslink4	1,155	1.27	7	1.06	29.6	16.0	210

<sup>a</sup> Determined by Static Light Scattering in  $\text{CHCl}_3$  at 25 °C, <sup>b</sup> determined by GPC in  $\text{CHCl}_3$  at 25 °C, <sup>c</sup> determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$ , <sup>d</sup> determined by Dynamic Light Scattering in  $\text{CHCl}_3$  at 25 °C.

and PEO, causing a solubility gradient of the sample in the solvent/non-solvent mixture.

The fact that separation inside GPC columns depends on the molecule's hydrodynamic volume tends to narrow the obtained distribution

for star polymers, as the population of arms has a minor effect over the radius, which is primarily affected by the core size, and the arms extension caused by osmotic pressure. As a result, the actual distribution of the precursor star is broader and the active sites on the core's surface

are subject to an uneven steric hindrance, proportionate to the star's size. Thus, EO conversion is greater at the smaller stars, as they are more accessible to free monomer, growing faster towards the star's corona where shielding effect is even smaller, giving positive feedback to the effect. Accordingly, the resulting miktoarm star will be consisting of densely packed PS stars with short PEO arms, that grow larger for the precursor starts with lesser PS arms.

### 3.3. Synthesis of the miktoarm copolymer star from linear precursor (Synthesis 2)

(Scheme 2) The advantage of separating the polymerization from the cross-linking of DVB to two independent steps is the essence of this synthetic approach, as it gives a more consistent product with well characterized structure. In detail, better characterization of both arm species is possible in the linear precursor as the molecular weight growth corresponds solely to monomer addition and not intermolecular cross-linking reactions. Also, the polymerization of PEO initiates from living chain ends, that offer an unhindered and homogenous environment in comparison to "in-out" method discussed in introduction. (Scheme 3) Finally, the PS to PEO arms ratio is "locked" to 1:1 in the miktoarm star, as it is predetermined in the triblock precursor and inherited to the final miktoarm star after the post polymerization cross-linking reaction.

As seen in the GPC trace, the PS block is characterized by a sharp, symmetrical distribution, that shifts to shorter elution time after the addition of PDVB and PEO blocks. The shoulder following the main peak is attributed to PEO homopolymer initiated from the *t*-BuOK co-initiator. The chromatogram after the cross-link reaction reveals only a partial cross-linking of the triblock, with a broadening to the molecular weight

distribution, while the unreacted triblock as well as the PEO homopolymer were effectively removed by fractionation (Fig. 3).

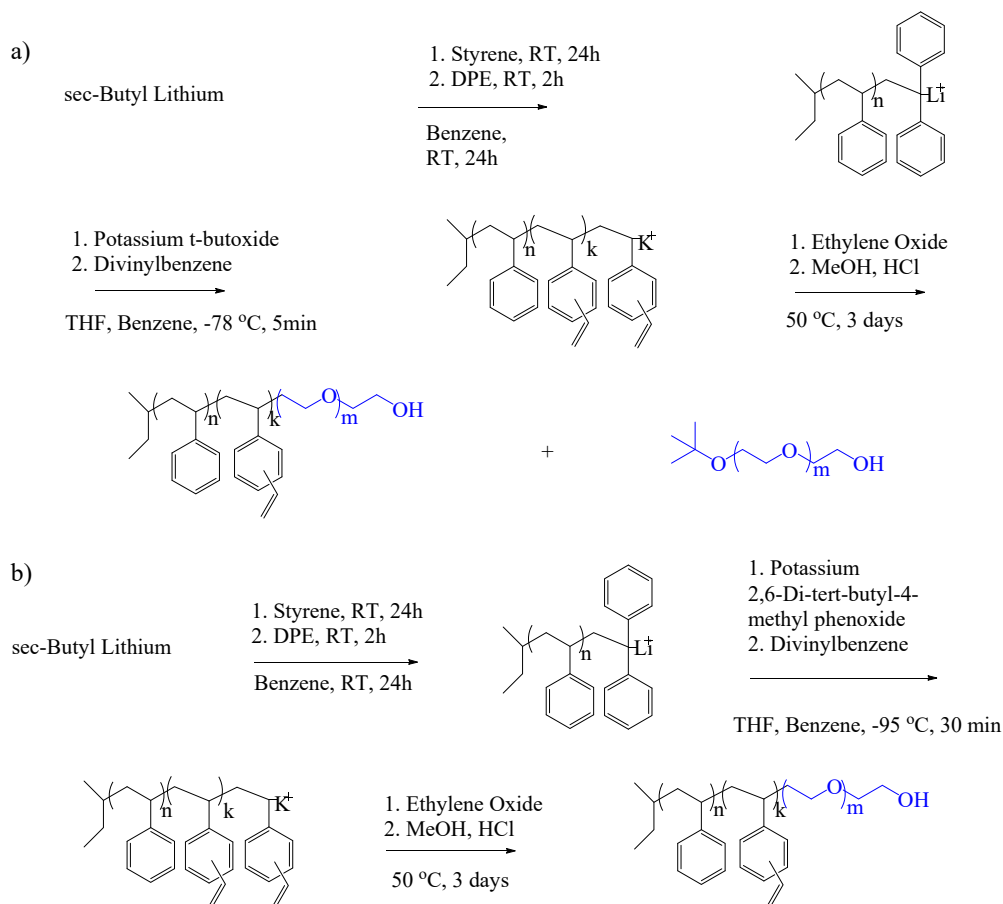
The existence of the pending vinyl groups is seen in <sup>1</sup>H-MNR spectrum before the cross-linking reaction 5–6 ppm indicating the controlled polymerization of DVB, but cannot be quantified due to their low signal. In <sup>1</sup>H NMR spectrum after the cross-linking, these peaks have been eliminated, proving the cross-link reaction. The relative area of aromatic and etheric protons has been changed due to the removal of PEO homopolymer (Fig. 4, Fig. 5).

The addition of potassium 2,6 di-*tert*-butyl-4-methylphenoxide instead of potassium *tert*-butoxide also promotes the controlled polymerization of both DVB and EO, and additionally due to the two *t*-butyl groups it is incapable of initiating EO homopolymerization as seen in the GPC trace (Fig. 6).

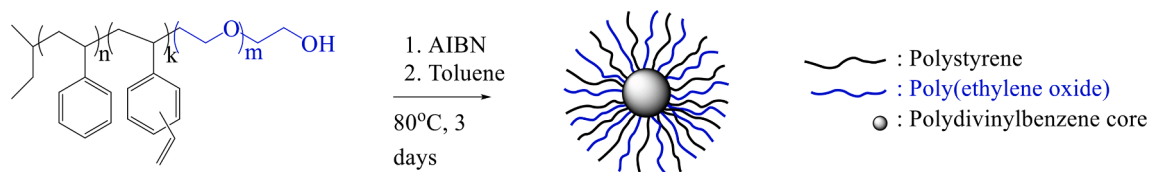
As seen in Table 1, polydispersity indexes broaden systematically after the cross-linking reaction, as expected. Nevertheless, compared to the Synthesis 1, the distributions are significantly narrower, and the mean number of arms can be calculated from the formula:

$$f = \frac{M_{n,Star}}{M_{n,Linear}} \times 2$$

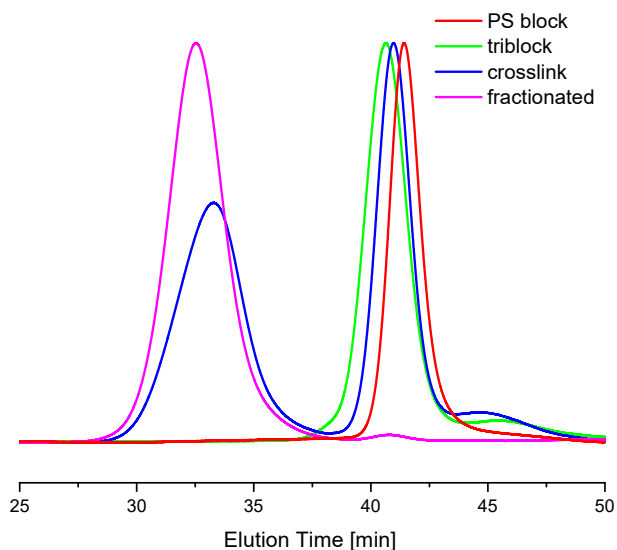
where  $M_{n,Star}$  and  $M_{n,Linear}$  represents the molecular weight of the star and linear polymer, respectively. Also, increasing the PEO content, thus enlarging the overall size of the linear precursor, the resulting star tend to have fewer arms, as the cross-linking reaches faster to saturation due to higher steric hindrance.



**Scheme 2.** Synthesis of PS-*b*-PDVB-*b*-PEO triblock terpolymer precursor (Synthesis 2), a) co-initiator gives PEO homopolymer side product, and b) co-initiator does not give side-products.



**Scheme 3.** Cross-linking reaction of the PS-*b*-PDVB-*b*-PEO triblock tripolymer for Synthesis 2.



**Fig. 3.** GPC chromatograms during the PS-*b*-PDVB-*b*-PEO #1 block terpolymer synthesis, its cross-linking reaction and fractionation.

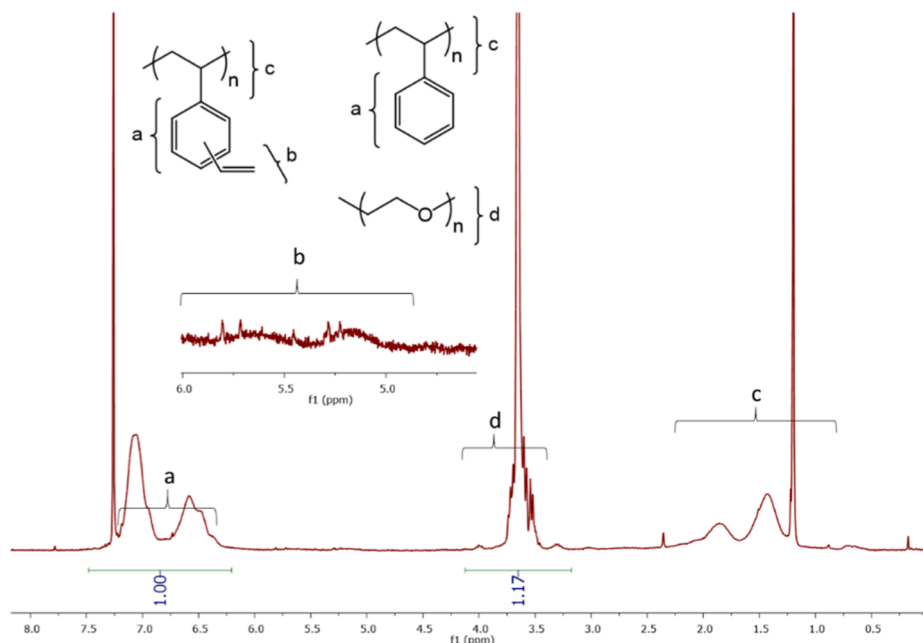
### 3.4. Differential scanning calorimetry results of the linear triblock terpolymers and the corresponding cross-link miktoarm copolymer stars

Two heating/cooling cycles were performed in all cases with a heating/cooling rate of 10 °C/min, under constant nitrogen flow, and the degree of crystallinity, when an endothermic peak was observed in heating, obtained from the second cycle using the equation:

$$\chi_c = \frac{\Delta H}{\Delta H_{cryst}} \cdot 100\%$$

where  $\Delta H$  is the measured enthalpy change during the melting, normalized to the PEO weight fraction of the sample, and  $\Delta H_{cryst}$  is the theoretical heat of fusion of the 100% crystalline PEO and is taken equal to 196.4 J/g [28] (Fig 7).

The differential scanning calorimetry (DSC) data in Fig. 7 correspond to traces taken during heating for the linear terpolymer precursors (solid lines) and the corresponding miktoarm stars (dashed lines), reported at Table 1. While for the Triblocks #2 and #3 an endothermic melting during heating may be seen, due to the melting of PEO, Triblocks 1 and 4 remain amorphous. Due to the low  $M_w$  of Triblocks 1 and 4, 13 and 11 Kg/mol respectively, they are in the disordered state, as it has been reported experimentally [29], and the presence of the glassy PS blocks/chains suppress the ability of the PEO to chains to crystallize; please note the  $T_g$  of PS is larger than the  $T_c$  of PEO. As it is clear from Fig. 7, the area of the melting peak decreases significantly for the cross-link miktoarm stars compared to the corresponding linear triblock copolymer precursors, indicating a strong effect of branching and star-shaped architecture on the crystallization behavior of the PEO blocks/arms, as in known for branched polymers [30,31]. In particular, the degree of crystallinities of the Triblocks 2 and 3 are 46.5% and 69.7% while the corresponding degree of crystallinities for Crosslinks miktoarm stars 2 and 3 are 28.6% and 45.3%, respectively, indicating/verifying the successful branching of the terpolymers to miktoarm star-shaped copolymers.



**Fig. 4.**  $^1\text{H}$  NMR spectrum for triblock tripolymer PS-*b*-PDVB-*b*-PEO #1.

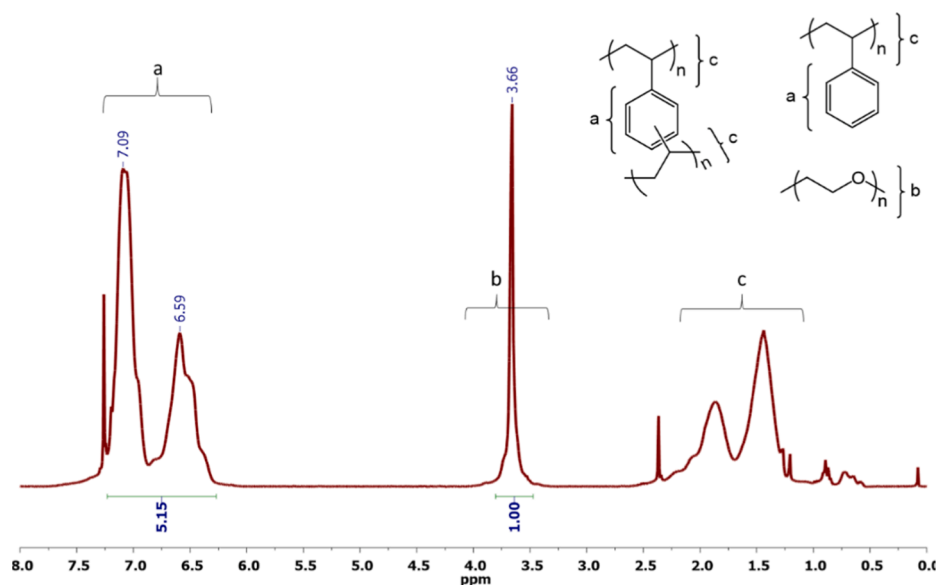


Fig. 5.  $^1\text{H}$  NMR spectrum for cross-linked triblock copolymer PS-*b*-PDVB-*b*-PEO, Triblock #1, after the fractionation.

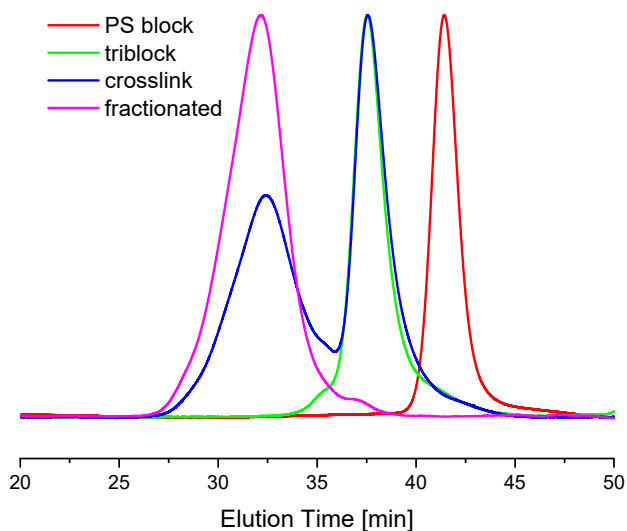


Fig. 6. GPC chromatograms during the PS-*b*-PDVB-*b*-PEO #2 block terpolymer, its cross-linking reaction and fractionation.

#### 4. Conclusions

In this work, two synthetic protocols via anionic polymerization are presented. At first, an initiator-co-initiator system, able to polymerize selectively only the one vinyl-group of divinylbenzene, and sequentially polymerize ethylene oxide. Also, well-defined miktoarm star copolymers of PS and PEO with cross-linked PDVB core have been synthesized by a novel synthetic route. Initially, a triblock terpolymer of PS-*b*-PDVB-*b*-PEO is synthesized. Then, by crosslinking the middle block's pending vinyl groups intermolecularly, the star shaped copolymers are formed (Synthesis 2). For comparison reasons, a second batch of unsymmetrical stars were synthesized, where the miktoarm star is derived from a homopolymer star precursor with PDVB cross-linked core (Synthesis 1).

Synthesis 2 seems to produce symmetric star shaped polymers with consistent PS to PEO ratio, well-defined molecular characteristics over the arms and narrower polydispersity for both the arms and the miktoarm copolymer star. Also, the proposed synthetic route remains simple, fast and inexpensive. In future work, the matter of unreacted triblock copolymer after crosslinking which needs to be removed by

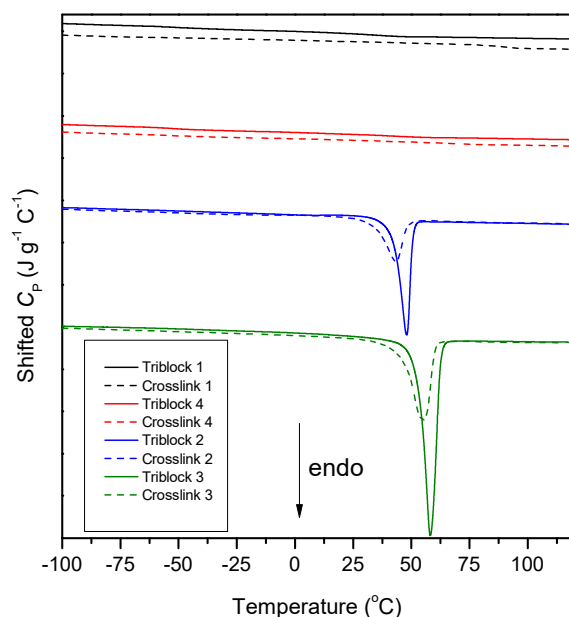


Fig. 7. Heating DSC thermograms of the linear terpolymers (solid lines) and of the corresponding crosslink star-shaped miktoarm stars (dashed lines).

fractionation remains to be addressed. Different reaction conditions will be explored, in order to understand the effect of concentration, reaction time, and the molecular weight of the PDVB block at the cross-linking reaction and at core's size.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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