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Polystyrene-*block*-poly(ethylene oxide) from nitroxide mediated polymerization: detection of minor species by coupled chromatographic techniques

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Abstract

A polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) copolymer is synthesised in an original manner by nitroxide mediated polymerization of styrene from a PEO macroalkoxyamine. Minor amounts of side products are unavoidably present in the final polymer, including: traces of macroalkoxyamine, PEO-*b*-PS-*b*-PEO triblock copolymer—a product of the recombination of PEO-*b*-PS˙ macro-radical during the initial stage of the polymerization—and hPS—a product of thermal initiation. These species do not represent more than a little percentage of the total composition. They are hardly detectable with classical SEC. We use liquid chromatography at critical conditions (LC-CC), 2D chromatography and LC-CC-NMR to get an exhaustive description of the chemical composition distributions (CCD) and of the molar mass distributions (MMD) of all the minor species quoted above. The results are consistent with the synthesis route and prove the accuracy of the LC-CC based techniques in analysing even very small amounts of species.
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Keywords: PS-*b*-PEO block copolymer; Liquid chromatography; Critical conditions

1. Introduction

Block copolymers are very promising materials because of their ambivalent properties. They have many industrial applications: impact-resistant polymers, consisting of a soft and a hard group, conducting polymers including a non-conducting, more easily processable segment, associative polymers containing a hydrophilic and a hydrophobic group, among others. One of the most important applications of block copolymers at the industrial scale is their use as surfactants for the pharmaceutical industry, oil industry, agriculture and paper and detergent industries [1]. The PEO-*b*-PPO block copolymer family has often been described but more recently attention has focused on PEO-*b*-PS [2]. As far as characterization is concerned, block copolymers are complex materials that exhibit heterogeneities regarding molar masses, chemical compositions of the different blocks, architectures and so on. As a result, it is difficult to obtain a clear, precise characterisation of these molecules. For example, size exclusion chromatography (SEC) is poorly efficient as a means of determining the molar masses and molar mass distribution of copolymers, because two species of different molar masses and different chemical compositions may have the same hydrodynamic volume. That is why, over the last few years, new techniques have been developed to be used as more relevant tools [3,4]. Among them, a very promising one is liquid chromatography at critical conditions, LC-CC [4,5]. It is a high performance liquid chromatography (HPLC) procedure in which a certain type of polymer is eluted independently of its molar mass. LC-CC is one among various chromatographic procedures with the generic name liquid chromatography at the point of exclusion–adsorption transition (LC-PEAT) in which the exclusion and adsorption effects counterbalance each other [5–9]. LC-CC is called liquid chromatography at critical adsorption point, LC-CAP, when there are interactions between a polymer and a solid phase (e.g. silica) and liquid chromatography at critical partition point, LC-CPP, when there are interactions (solubilisation) between a polymer and a liquid bonded phase (e.g. C18 hydrophobic layer onto silica). The behaviour of a polymer in such peculiar conditions, when

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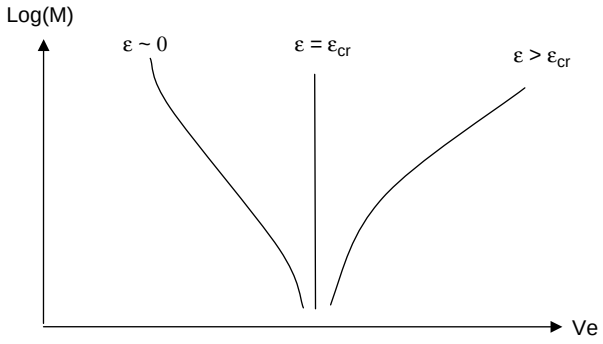


Fig. 1. Different elution conditions depending on the polymer–column interaction energy (ε). When ε is close to zero, the polymer is eluted in an exclusion mode. If ε is higher than a critical value ε_{cr}, the polymer is eluted in an adsorption mode. For a specific value ε_{cr} is the critical elution mode.

exclusion and adsorption (or partition) compensate each other, has been described theoretically for linear [10–18], ring [19] and star [20] polymers. As illustrated in Fig. 1, LC-PEAT corresponds to a very peculiar polymer–adsorbant interaction energy, called ε_{cr}, sufficient enough so that the entropic effect—due to the polymer size—is compensated by the enthalpic effect—due to the interactions between the polymer and the stationary phase. Under such conditions, for a linear non-functionalized homopolymer, the distribution coefficient between the pores and the interstitial volume of the column is equal to one. Practically, this occurs only within a limited molar mass range, as exclusion and adsorption may not compensate rigorously each other over a very broad molar mass range. The LC-CC conditions require a specific 'critical' eluent, that is a mixture of a strong desorption-promoting eluent, and a weak, adsorption-promoting one. The mixture composition depends on the nature of the polymer and on the nature of the stationary phase, but also critically on the temperature, column packing and porosity [21–23]. Other limitations are related to the thermodynamical quality of the eluent mixture, which should be a good solvent in the adsorption mode for all species. Let us notice at this point that the partition mode is very different from the adsorption mode, as the polymer interacts with a liquid instead of a solid stationary phase [24,25] (C_{18} grafted silica for example). In such a separation mode, the liquid stationary phase has indeed to be a better solvent than the mobile phase. Separation does not depend on the eluent strength of the mobile phase any longer, but on the differences between mobile and liquid stationary phase solvent quality.

As far as LC-CC of block copolymers is concerned, one block should be eluted at critical conditions. Very often for the other blocks the exclusion mode is preferred to the adsorption one, in order to prevent complete adsorption of high molar masses onto the column surface. Nevertheless, for a controlled molar mass and a specific eluent mixture, separation by adsorption mode is also possible for the second block, thanks to its very narrow molar mass distribution. LC-CC of segmented copolymers has been successfully performed with several block or grafted structures [4,26]. These included commercial PS-*b*-PEO, whose separation was performed with regard to the PEO block length [27]. Nevertheless, even in that case, a few points remain unclear. The peak of lower polarity was attributed to the residual PEO homopolymer. This does not seem obvious, as this polymer does not absorb at the 261 nm wavelength of the UV detector. However, this very interesting work gives valuable information, such as the LC-CC conditions with regard to the eluent composition and column porosity.

Like all LC-PEAT procedures, LC-CC works in isocratic mode. The main advantages of such isocratic mode are that a RI detector could easily be used, and that LC-CC could easily be coupled to a second analytical technique, as discussed below. Another interesting separation procedure is gradient LAC (gradient liquid adsorption chromatography). A gradient from weak to strong eluent is applied during elution in order to separate macromolecules with regard to their chemical compositions, again independently of their molar masses [28–31]. This latter technique, even though it does not have the above mentioned advantages, has been applied successfully to many polymer systems, including PS-*g*-PEO [32].

Coupling LC-CC with a second dimension SEC yields more information [33–35]. This technique, called 2D chromatography, gives a 2D map, with the chemical composition on one axis and the hydrodynamic volume on the other axis. It has been developed and performed on various functional polymers and block copolymers, including PS-*b*-PMMA, PS-*b*-PB, PEO-*b*-PPO-*b*-PEO and others [2,4,36–40].

Coupling LC-CC with NMR instead of SEC in the second dimension gives interesting information, especially on the chemical structure of the species.

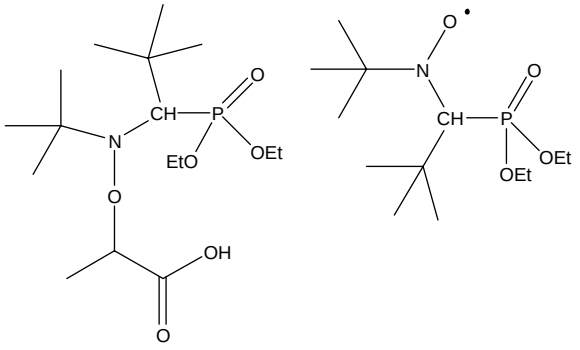
Our goal is not the classical separation of a polymer mixture (different polymers and copolymers in significant proportions). Here, LC-CC is used to detect the very small amounts of by-products of a NMP polymerization [41,42]. These minor species include the PEO-*b*-PS-*b*-PEO triblock copolymer, the PS homopolymer and the un-reacted PEO macroinitiator, as described in Section 2.

2. Experimental

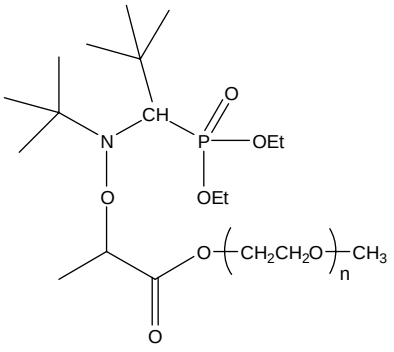
2.1. Polymer preparation

Full synthetic details of the preparation and characterization of PS-*b*-PEO will be provided in a forthcoming paper [43]. Briefly, 1 was esterified with PEO 2000 in the presence of DCC (*N*,*N*-dicyclohexylcarbodiimide) and DMAP (4-dimethylaminopyridine) to yield alkoxyamine 2, which was used as a macro initiator for the polymerization of styrene (Scheme 1).

This macro-alkoxyamine was purified once in ether in order to remove the residual alkoxyamine 1. The final purity, analysed by ^{1}H NMR, was close to 99% and confirmed the absence of homopolyoxyethylene. 2 was then used as a macro-initiator for the radical polymerization of styrene in a controlled manner (120 °C, 2.5 h). As a result, a copolymer PS-*b*-PEO (Scheme 2) in which the PEO and PS blocks have a narrow molar mass distribution was obtained. From the synthesis route, this product was expected to exhibit at least



1 SG1



2 (macro alkoxyamine)

Scheme 1. Precursors for the styrene polymerization.

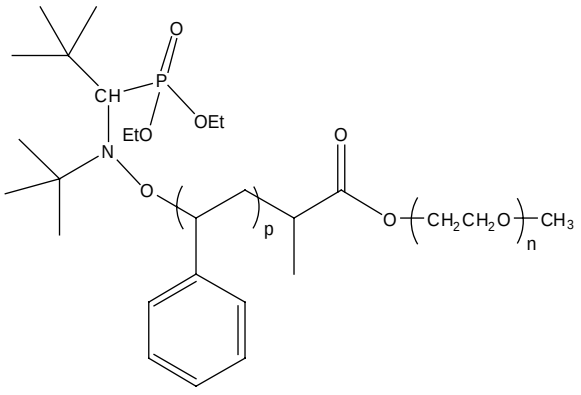
90% purity based on previous results for the NMP of styrene in the presence of SG1 [41].

2.1.1. Expected by-products

2.1.1.1. Macro alkoxyamine 2. Traces of unreacted macro alkoxyamine may be found in the final copolymer.

2.1.1.2. PEO-b-PS-b-PEO. At the very beginning of the reaction, due to the persistent radical effect (PRE), growing macroradicals recombine to produce a dead polymer 3 [44].

At the beginning of the nitroxide mediated polymerization of styrene at 120 °C, a little percentage of dead product 3 is formed by recombination of the growing PEO-*b*-PS· macroradicals as presented on Scheme 3. From the kinetical studies developed by Fisher [44], the theoretical molar mass of the middle PS block should be close to 5000 g mol^{-1} [44].



Scheme 2. PEO-*b*-PS block copolymer.

2.1.1.3. Homo-polystyrene (hPS). Styrene is well known for self-initiating at high temperature. The free SG1 present in the medium ensures control of this homopolymerization [41]. Thus, the expected molar mass is the same as that of the PS block in the copolymer: 12,000 g mol^{-1}. The expected amount of thermal PS is only a little percentage of the total copolymer [41].

2.2. Chromatographic eluents

THF (99.7% purity) from SDS chemical company was filtered on 0.2 μm Alltech filters and used without further purification. Water was distilled once before being filtered on 0.2 μm Alltech filters. The eluent mixture was prepared by weighing (±0.1%).

2.3. Size exclusion chromatography experiments

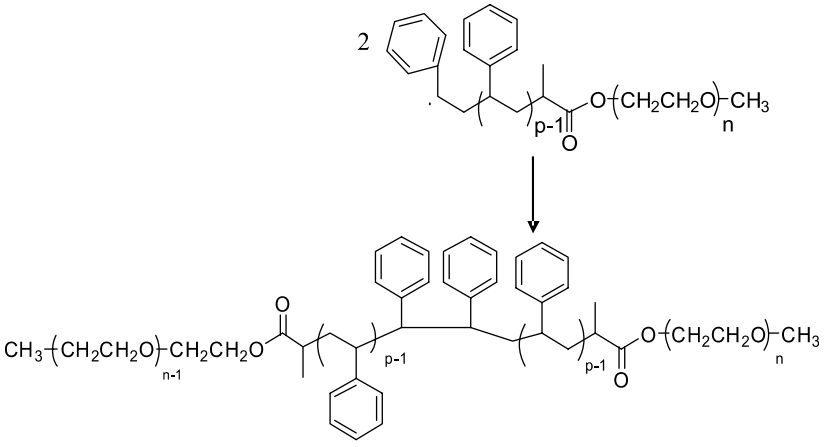
Size exclusion chromatography was performed with a Waters 515 isocratic pump. Eluent was pure THF. Samples were dissolved in pure THF at 0.5% wt concentration for several hours before being filtered on 0.2 μm Alltech filters. The injection volume was 20 μL. A Waters Styragel HR 3 column or a combination of HR 3 and HR 4 was used. The columns were thermostated in a Waters column heater at 40 °C. The flow rate was 1 mL min^{-1}. A differential refractometer RI 2414 from Waters was used for simple detection and an additional UV detector 2486 was used for double detection. Results were collected and analysed with PSS WinGPC 7 software.

Relative calibration was made using either PS standards (Aldrich) or PEO standards (PL laboratories), depending of the nature of the polymer to analyse.

2.4. Liquid chromatography at critical condition

LC-CC experiments were performed using a Waters 600E pump with degasser, equipped with a manual Rheodyne valve. The injection volume was 20 μL. A Si–C18 reverse-phase, 250 mm×4.6 mm, 5 μm, 300 Å pore size, Macrosphere RP 300 Alltech column, thermostated at 25 °C, was used for PS critical conditions. A 300 mm×7.5 mm, 20 μm, PL Gel Mixed A Polymer Laboratory column, thermostated at 25 °C, was used for PEO critical conditions. The Waters 2487 UV detector signal set at 254 nm, as well as the Waters differential refractometer RI 2414 detector signal, was collected with polymer standards service PSS WinGPC-7 software.

We used LC-CC was to separate the diblock PS-*b*-PEO copolymer from other components, independently of the length of one of the two blocks. PEO critical conditions were obtained with a THF (71.5% wt)–hexane (28.5% wt) mixture and were close to the conditions determined by Murgasova et al. [26] for a PS-DVB column and at similar temperature. PS critical



Scheme 3. PEO-*b*-PS-*b*-PEO triblock copolymer.

conditions were obtained with a THF (87.4% wt)–water (12.6% wt) mixture and were similar to those determined by Baran et al. [27] for similar column and temperature. These two mixtures had been freshly prepared beforehand in a sealed bottle, in order to prevent preferential evaporation. The flow rate was 1 mL min^{-1} for both experiments. The sample solvent was always rigorously the same as the critical eluent. When determining the critical conditions, even a 0.1% change in the critical eluant composition implied the preparation of a new sample solvent composition.

2.5. Bidimensional (2D) chromatography experiments

For the first dimension we used the same LC-CC system described above, at critical conditions for PS. A Waters 515 isocratic pump, pumping pure THF as eluent, a Waters Styragel HR3 column and a Waters RI 2414 differential refractometer were used for the 2nd dimension SEC. The connection between LC-CC and SEC was ensured by a two 200 μL loop, 8 injection port, Vici valve from PSS. In this automated procedure, one loop was filled with the polymer coming from the first dimension (LC-CC system) while the second loop injected its content into the SEC second dimension. Valve switches were controlled and recorded with a polymer standards service (PSS) WinGPC-7 software, and signals from both detectors were recorded using the same software. Fractions were collected and injected without any loss. Because of the 10 min recording time necessary to obtain one SEC chromatogram, the flow rates were 0.02 and 1 mL min^{-1} for LC-CC and SEC, respectively, meaning valve switches occurred every 10 min. The loop volume, 200 μL, was our limiting resolution on the LC-CC axis of a 2D chromatogram.

2.6. NMR on fractioned samples

The LC-CC system was the one described above except that an agilent 1100 series pump was used. Identical samples were injected repeatedly into the LC-CC system in order to collect several 100 μL fractions corresponding to the same elution peak. These identical fractions were concentrated into one single fraction in order to record a more intense NMR signal in the second dimension. The eluent was evaporated under argon flow and the residual solid was dissolved in $CDCl_3$. ^1H NMR analyses were performed on a Brucker 500 MHz spectrometer equipped with a cryosonde.

3. Results and discussion

3.1. SEC experiments

The chromatogram of the copolymer mixture is reported in Fig. 2. The UV detector revealed only one sharp peak. PS calibration applied to the main peak gave a polydispersity index of 1.15. This value is not rigorous, because of the relative calibration used, but informs on the control of the polymerization. In addition to the above mentioned peak, the DRI detector showed another small peak at a higher elution volume. PS calibration gave $M_n = 2000$ g mol^{-1}. In the copolymer mixture, the only species which did not absorb in the UV and which had this order of molar mass magnitude was the residual macroalkoxyamine. This macroalkoxyamine, which was the

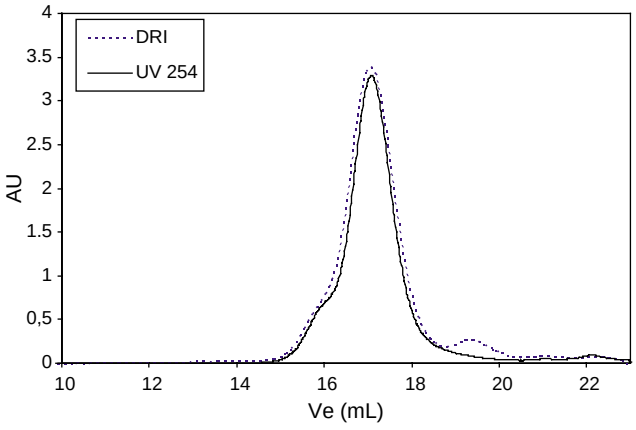


Fig. 2. SEC chromatograms from UV detector (—) and RI detector (- - -). No significant difference is seen in the shape of the copolymer peak. Nevertheless, a minor species with a low hydrodynamic volume, which does not absorb in UV, is identified at high elution volume.

smallest polymer species in the mixture, gave rise to the highest SEC elution peak. Thus, it was well observable from SEC. Because of the higher molar masses of hPS and PEO-*b*-PS-*b*-PEO, their corresponding peaks could not be distinguished from the main PS-*b*-PEO peak. Indeed, the hydrodynamic volumes of these three species were too close to one another for SEC to distinguish them. We stretched the RI signal so that its maximum reached the same intensity as that of the UV, in order to compare the shape of the main peak from both detectors. No change in the ratio RI/UV (Fig. 2) across the peak was observed, despite the different responses of the hPS, of the diblock copolymer (one PEO block) and of the triblock copolymer (two PEO blocks) to these detectors. Traces of the hPS and of the triblock copolymer were hidden by the diblock copolymer. These species were seen as only one mixture in SEC mode. This would have not been the case if these three species were in the same order of magnitude of concentration. But because one of them was very preponderant, and because the two others were only traces, the change in composition across the main peak could not be observed. This is why LC-CC appears as a necessary tool to investigate our sample when one product is preponderant over the others.

3.2. LC-CC experiments

In order to separate the other minor species from the copolymer, LC-CC was tested successively on PEO and PS.

The chromatogram obtained with LC-CC at PEO critical conditions is presented in Fig. 3. It contains one main peak plus a very small one at the total volume of the column. The main peak on Fig. 3 is attributed to the copolymer. The very small peak at the total volume is a solvent peak, and corresponds to any small species, including possible traces of residual styrene monomer—which strongly absorbs in UV even at very low concentration—or solvent stabilizers. PEO critical conditions are illustrated on Fig. 4. At the critical conditions used, PS was in exclusion mode: on Fig. 4, the peaks are displaced towards

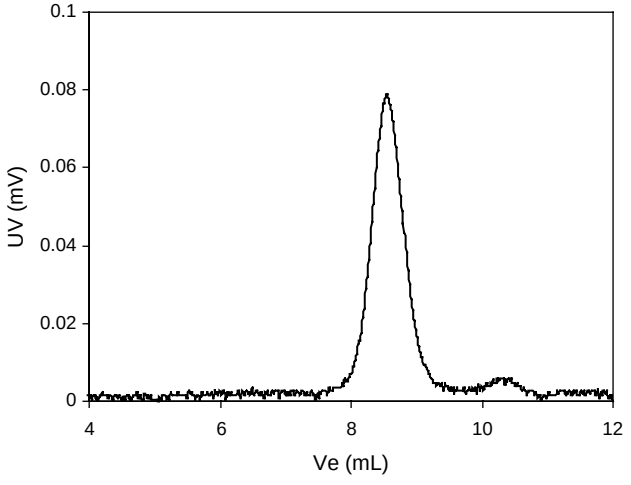


Fig. 3. LC-CC chromatogram (UV detector) of the PS-*b*-PEO copolymer studied in this work, for PEO critical conditions. Only one main peak is visible. The shoulder at higher elution volume is attributed to the styrene monomer.

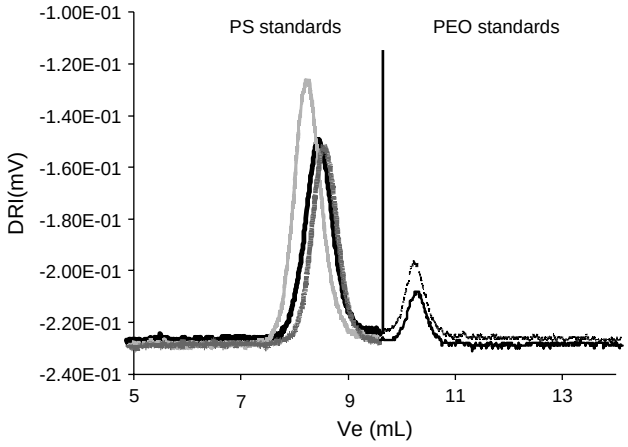


Fig. 4. Calibration of the column for critical conditions of PEO (DRI detector). Left part: PS standards. Dashed grey: PS 7600 g mol^{-1}. Black: PS 12,000 g mol^{-1}. Grey: PS 15,000 g mol^{-1}. Right part: PEO standards. Dashed line: PEO 2000 g mol^{-1}. Full line: PEO 10,000 g mol^{-1}.

lower elution volumes as the molar mass of PS increases. Let us notice that the 12,000 g mol^{-1} PS standard (same order of molar mass as the expected hPS by-product) had the closest elution volume to that of the mixture. A separation of hPS from the diblock copolymer was not expected to occur, since hPS and the polystyrene block in the block copolymer were expected to have identical molar masses.

LC-CC at the critical conditions of PS was applied to the copolymer mixture. The LC-CC chromatogram is shown in Fig. 5. Two shoulders plus two distinct peaks can be observed, denoted (1)–(4) with increasing elution volumes. As a reverse phase was used, peak (1) is the most polar. It is not well defined and appears as a shoulder. Peak (2) is not well defined either and appears as a smaller and less resolved shoulder. Peak (3) is attributed to the PS-*b*-PEO copolymer, because of its intensity. Peak (4), which characterizes the less polar species, is not sharp. Interpretation is as follows:

3.2.1. Peak (1)

The first peak corresponds to the most polar species. Its UV intensity is low compared to that of the main fraction. A quantification is not possible, as we do not know its content in

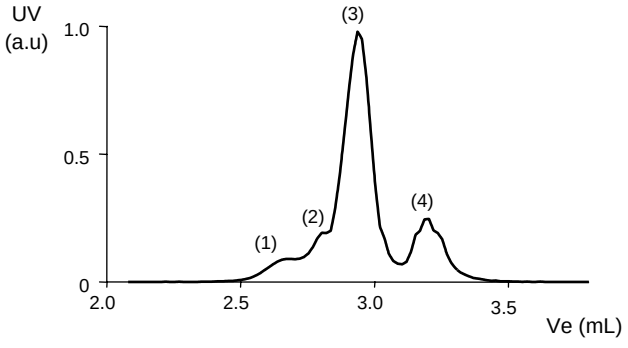


Fig. 5. LC-CC chromatogram (UV detector) of the PS-*b*-PEO copolymer, in PS critical conditions. Three peaks and one shoulder are observed, at distinct elution volumes, denoted (1)–(4). See text for the attribution of these peaks.

PEO, which is not UV sensitive. Regarding polarity, peak (1) may correspond to a PEO rich polymer. The high polarity observed would fit the expected PEO-*b*-PS-*b*-PEO triblock copolymer. Yet, 2D chromatography and LC NMR will be helpful to confirm this.

3.2.2. Peak (2)

This peak is not well defined and low in intensity compared to the main one. Moreover, this shoulder, which does not appear on Fig. 7, may simply be an apparatus artefact. Its attribution is difficult, and 2D chromatography will be needed before concluding.

3.2.3. Peak (3)

This is by far the most intense peak. As the synthesis route followed by the purification yields quite a pure copolymer, this fraction corresponds to the desired PS-*b*-PEO. At the present time, we could wonder whether peak (2) could correspond to a living copolymer (SG1-PS-*b*-PEO), and peak (3) to a dead copolymer. Because of its very strong polarity, the extra SG1 group could account for the presence of two separate peaks. Nevertheless, it is very unlikely for the dead PS to be formed alongside the living PS, because of the small target masses of the PS blocks. Indeed, in the range of masses expected (about 12,000 g mol^{-1} for the PS block), polymerization always leads to an almost fully living polymer [42]. This was confirmed in our laboratory, by means of LC-CC and ^{31}P NMR.

3.2.4. Peak (4)

The last peak is attributed to polystyrene: hPS samples injected for comparison were eluted at the same volume whatever their molar masses (critical conditions for PS). This peak has a stair-like shape, which is unusual for PS critical conditions. This may be put down to LC-CC experimental drawbacks: lack of resolution, preferential solvation, radial diffusion and so on. Different end-chains for the dead or living homo PSs could also account for the thickness of this peak, but PS should essentially be SG1 end functionalized (living species), for the same reason as explained above for the third fraction. The presence of styrene monomer, yielding a peak that could interfere with the hPS peak in PS critical conditions, is also worth considering. However, the expected hPS minor species is clearly identified.

3.3. 2D-Chromatography

The 2D chromatogram presented in Fig. 6 is, to the best of our knowledge, the first one obtained for a PS-*b*-PEO copolymer. First dimension was at critical conditions for PS. By looking along the LC-CC axis, one can find the classical chromatogram shown in Fig. 5. This was a good thing as the decrease in flow rate (from 1 to 0.02 mL min^{-1}) did not change the critical conditions. On the SEC axis, the LC-CC fractions are separated as a function of the hydrodynamic volume. We assume that the values of the elution times and hydrodynamic volumes are reliable for all species.

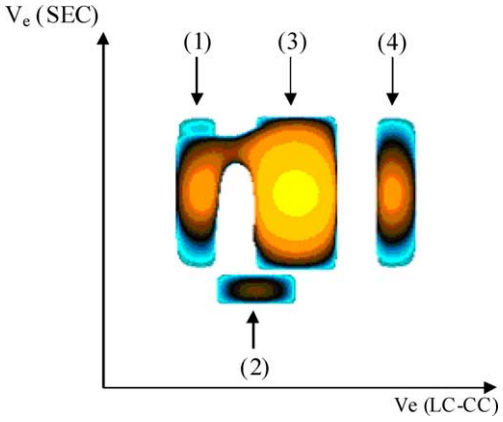


Fig. 6. 2D Chromatogram of the PS-*b*-PEO copolymer, built from the second dimension RI detector signal. Four peaks can be seen, denoted (1)–(4). Identification of these peaks is explained in the text.

Four peaks are to be identified on Fig. 6.

3.3.1. Peak (1)

The first peak has the same hydrodynamic volume as the copolymer peak (3), whose targeted mass is 14,000 g mol^{-1}. Assuming peak (1) corresponds to the PEO-*b*-PS-*b*-PEO triblock polymer from LC-CC, this means a molar mass order of 10,000 g mol^{-1} for the central PS block. This value is slightly higher than the Fischer prediction [40] in the case of a well controlled reaction: DP close to 50, $M_n = 5000$ g mol^{-1}. It is not easy to conclude whether the problem was either a poor NMP control or a lack of reliability of the SEC assessment of the block copolymer. Indeed, a strong repulsion between the central PS block and the two PEO blocks can increase significantly the hydrodynamic volume, leading to a strong overestimation of the real mass.

3.3.2. Peak (2)

The second peak is small but very distinct, with a much higher SEC elution volume. Both the polarity and THE hydrodynamic volume correspond precisely to the macroalkoxyamine 2 injected in the 2D chromatography system for comparison. This peak confirms the presence of some residual macroalkoxyamine, as already supposed from SEC experiments.

The fact that (2) and (3) do not exactly have the same elution volume on the LC-CC axis, despite the invisibility of PS, can be explained by the possible difference in conformation of the PEO. The PEO of the macroalkoxyamine and the PEO of the diblock copolymer do not necessarily have the same conformation, because of the strong incompatibility between PS and PEO. The hydrodynamic volume of a PEO chain alone and of a PEO chain attached to an incompatible PS block may be different, which would explain the small shift in the elution volume in the LC-CC dimension (PEO in exclusion mode).

3.3.3. Peak (3)

The main peak has already been attributed to the copolymer. M_n and M_w are not easily obtained because of the very different natures of its two blocks. Yet, the elution curve is gaussian and

sharp, which means that the polydispersity is low, as already observed with classical SEC.

3.3.4. Peak (4)

The 2D chromatogram enables us to compare the hydrodynamic volume of the homopolystyrene minor species with that of the main copolymer. As seen on Fig. 6, these fractions have almost the same elution volume in the SEC dimension. This may be surprising at first, as self initiation of styrene usually leads to high masses. But let us point out that the free SG1 nitroxide, released in the course of the polymerization, also controls the macroradicals from self initiation. As a result, all the products obtained are mass-controlled.

The UV detector used for LC-CC did not enable us to compare the peak areas. Indeed, while PS strongly absorbed in UV, the PEO block did not absorb. Traces of a styrene monomer could also change the quantification completely, because of its very high UV absorption. 2D chromatography gave more quantitative results, since the SEC dimension, used to build 2D chromatograms, was performed with a RI detector. We verified that identical concentrations of homo PS and PEO give almost similar DRI peak amplitudes. The fractions could be quantified and were found to be 2.5% for the first peak (1) (PEO-*b*-PS-*b*-PEO dead copolymer); less than 1% for the second peak (2) (residual macroalkoxyamine); 95% for the main peak (3) (PS-*b*-PEO copolymer) and 1.5% for the fourth peak (4) (homopolystyrene). These ratios are consistent with the synthesis route and show the accuracy of the technique, not only in identifying but also in quantifying minor species mixed with a highly pure copolymer.

3.4. NMR

Peaks (1), (3) and (4) of the LC-CC chromatogram were isolated, as shown on Fig. 7, and analysed separately. Peak (2) was not isolated, but had already been identified as initiator using 2D chromatography.

3.4.1. Peak (1)

As seen on Fig. 8(a), the first fraction reveals PS aromatic peaks around 6.5–7 ppm and a strong PEO signature at 3.6 ppm. This supports the assumption that this first fraction contained the PEO-*b*-PS-*b*-PEO copolymer. Attributing an intensity of 362 to the peak corresponding to the two PEO blocks (intensity of 1 per hydrogen) leads to a PS molar mass value of 6600 g mol^{-1}. This result is more in agreement with Fischer's model than the result of 2D chromatography, and confirms the overestimation of molar masses when using SEC for triblock amphiphilic copolymers. From this experiment, enough evidence has been collected, allowing us to attribute the first LC-CC peak to the expected PEO–PS–PEO minor species.

3.4.2. Peak (2)

The main fraction reveals the PEO and PS signals in ^{1}H NMR (Fig. 8(b)). This fraction corresponds to the pure copolymer. As the PEO block length is well defined (M_n = 2000 g mol^{-1}), attributing an intensity of 181 to its peak gives an intensity of 1 per hydrogen. Thereby, we can calculate the PS block length. PS integration is equal to 584, leading to a molar mass of M_n = 12,000 g mol^{-1}. This is exactly the value targeted during synthesis, leading to a total mass of 14,000 g mol^{-1} for the copolymer, in very good agreement with our SEC results.

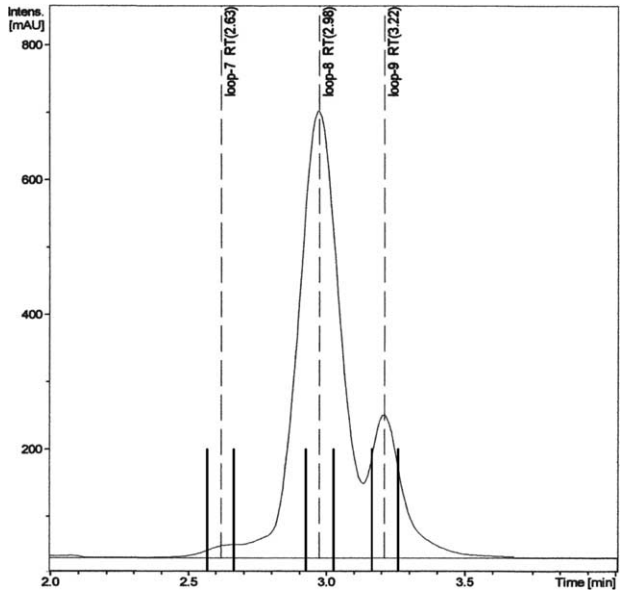


Fig. 7. LC-CC–^{1}H NMR coupling is a discontinuous process, in which the fractions are collected at the exit of the HPLC column. The 100 μL fraction collections centered on LC-CC peaks (dot lines) are represented with vertical lines.

3.4.3. Peak (4)

The last fraction has already been attributed to pure homopolystyrene when using LC-CC. Fig. 8(c) shows that PS is the main species, but PEO is also present. Because of the ratio of the intensities of the two species, we cannot attribute this signal to the presence of a copolymer. Indeed, this copolymer would have a very high PS block molar mass, which is in agreement neither with the controlled polymerization, nor with the 2D chromatogram. As seen on Fig. 7, it is not possible, with 100 μL loops, to fully isolate the third chromatographic peak, which is too close to the main peak. A simple explanation for the presence of PEO in the ^{1}H NMR spectrum of peak 4 is that a small part of the copolymer was trapped into separating loops during the separation process.

4. Conclusion

We characterized a PS-*b*-PEO copolymer synthesised in our laboratory by initiating styrene with a modified PEO-based macroalkoxyamine. Liquid chromatography at critical conditions (LC-CC) proved to be a powerful tool for identifying and isolating minor species formed during NMP synthesis. At the point of exclusion adsorption transition (PEAT) of polystyrene, thanks to a very narrow mass distribution PEO

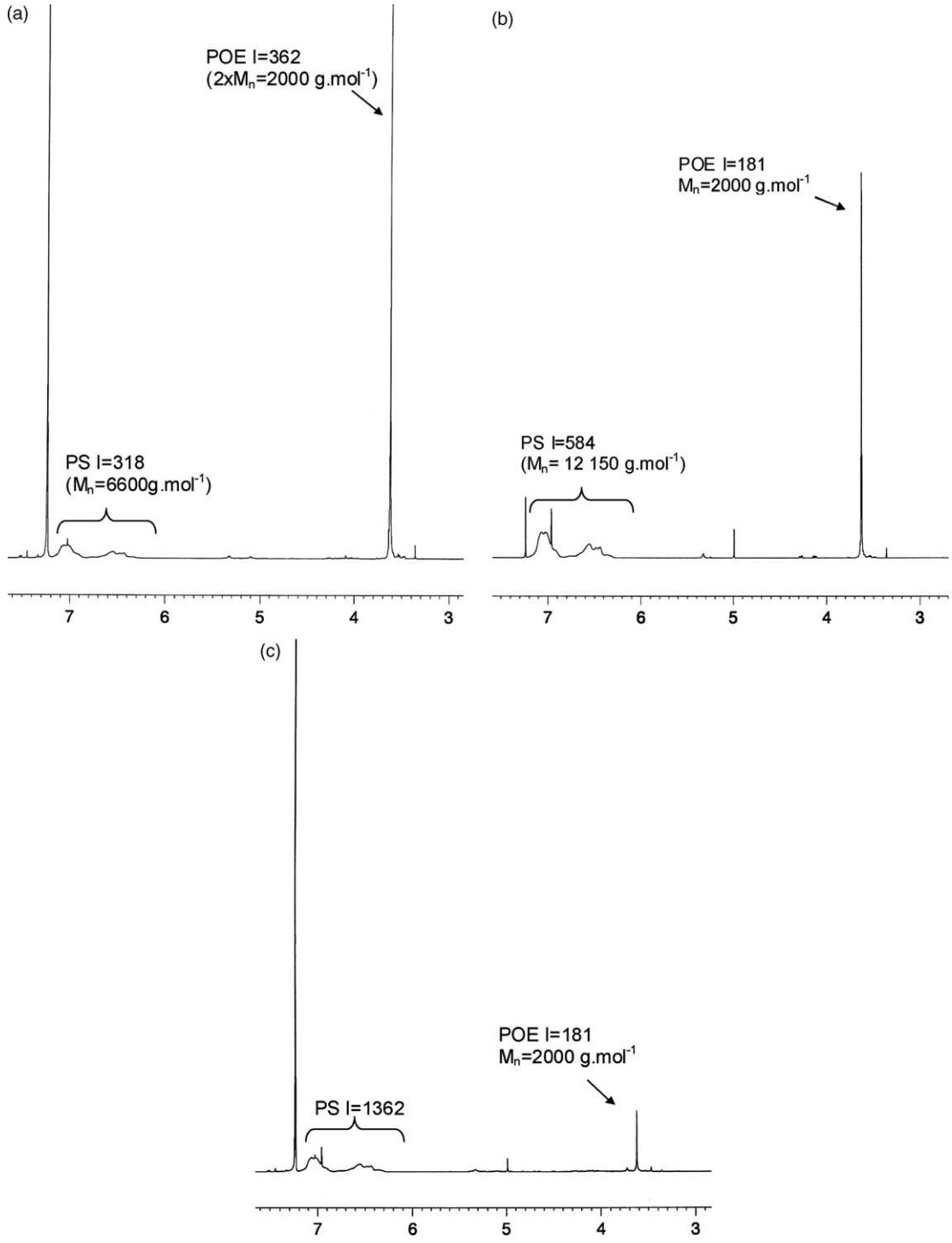


Fig. 8. (a) ^{1}H NMR spectrum of the first LC-CC peak. Protons from the PEO backbone are seen at 3.6 ppm, whereas aromatic protons from polystyrene appear between 6.5 and 7 ppm, depending on their position on the cycle. This fraction has a high PEO content. (b) ^{1}H NMR spectrum of the main fraction (peak (3)). Comparison of the intensities, as the PEO number molar mass is well known, leads to a number molar mass for PS close to 12,000 g mol^{-1}, which confirms the target mass for this block. (c) ^{1}H NMR spectrum of peak (4). This fraction is not supposed to contain PEO, which is a polar species. However, 100 μL collecting loops are too big for a perfect separation: a small amount of copolymer from the second peak is present in the collecting loops.

block, we were able to separate species independently of the copolymer molar mass. This latter parameter was studied independently in the second dimension of 2D chromatography. The expected minor species were well separated. Let us point out that not all LC-CC techniques have the same resolving power. Indeed, LC-CC for PEO did not permit the identification of any by-product. LC-CC for PS was more sensitive and yielded good results. The most polar by-product was identified as a PEO-*b*-PS-*b*-PEO triblock copolymer. Its molar mass determined using LC NMR was in agreement with theoretical predictions. The residual macroalkoxyamine was clearly identified using 2D chromatography. The presence of

self initiated PS was also in agreement with theory. Using coupled LC-CC techniques, we were able to quantify minor species representing only a small percentage of the total composition. Finally, the critical conditions, which may sometimes appear very hard to obtain for broad molar mass distributions, were easily applied to our system, with good reproducibility. This was facilitated by the synthesis route developed in our laboratory—nitroxide mediated polymerization (NMP)—which yielded polymers with narrow molar mass distribution.

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