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# Two-Dimensional Chromatographic Analysis of Polystyrene-*block*-poly(methyl methacrylate) Copolymers Synthesized by Selective Oxidation of Polystrene-9-borabicyclo[3.3.1]nonane

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**Summary:** The preparation of polystyrene block methyl methacrylate copolymers (PS-b-PMMA) is described. The polystyrene segment was prepared by anionic polymerization and the methylmethacrylate segment was prepared via free radical autoxidation of a borane agent attached to the styrene chain.[1] The chemistry involves a transformation of the anionic polymerization process to borane chemistry by firstly producing polystyrene with chain end unsaturated alkyl functional groups prepared using a *n*-butyllithium initiator and termination with allylchlorodimethylsilane. Secondly, the unsaturated macroinitiator end was hydroborated by 9-borabicyclo-[3.3.1]nonane (9-BBN) to produce a borane terminated PS. Thirdly, the borane group at the chain end was selectively oxidized and converted to polymeric radicals in the presence of methyl methacrylate which then initiated radical polymerization to produce block copolymers. The polymer obtained was characterized using several chromatographic techniques including LC-CC (liquid chromatography under critical conditions) for the polystyrene segments and two-dimensional chromatography with LC-CC in the first dimension and SEC in the second. The results show that block formation was successful although significant homopolymerization of methyl methacrylate is also obtained.

**Keywords:** autoxidation of borane; block copolymer; LCCC; two-dimensional chromatography

## Introduction

It is well known that not all monomers can be polymerized by every available polymerization technique, which limits the possibility of combining various monomers in a block copolymer chain, using only one polymerization method. Living and controlled techniques are useful not only in control of molar mass and molar mass distribution of a polymer but also in the synthesis of block and other structure as well as end functionalized polymers.

Polymerization techniques give several routes for the synthesis of block and other copolymers with well defined structure. Sequential monomer addition as in anionic polymerization has proven useful for the accurate construction of multiblock copolymers with controlled composition and narrow molecular weight distribution[2] by coupling of living polymer chain ends.[3] On the other hand, transformation of a growing chain end to a group capable of initiating polymerization of a second monomer is widely used for synthesis of block copolymers.[4–7]. This methods is especially well suited for block copolymers prepared from monomers which are polymerized by two different techniques. The synthesis of block copolymers usually requires efficient

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controlled and living polymerization. Several papers have reported the synthesis of well defined blocks by combining various techniques using transformation reactions. These include; anionic to cationic,[8,9], anionic polymerization to conventional radical polymerization,[10] anionic to stable free radical polymerization (SFRP)[3,11] to ATRP[4,7,12,13], cationic ring opening polymerization to RAFT,[14] cationic to anionic,[15] ROMP to anionic,[16] ring opening metathesis to ATRP[17] or anionic,[18] and metallocene catalyzed polymerization or degenerative transfer to anionic, RAFT[19] and ATRP,[20,21] RAFT to click chemistry[21] and RAFT to ATRP technique,[22] metallocene catalysts and borane chemistry.[23]

In most cases, block copolymers are synthesized by anionic or coordination polymerization because of the living nature of the polymer chain end. In block synthesis, usually the first monomer is polymerized by anionic techniques followed by conversion of the chain end into functional groups capable of initiating sites for the polymerization of the second monomer via controlled radical techniques.

Chung et al.[20,24–29] in several articles introduced a novel method for the synthesis of polyolefin block or graft copolymers. Polyolefins containing boron as an end or side functional group are used to initiate free radical polymerization to produce block or graft copolymers of polyolefins with another vinyl monomers such as maleic anhydride, methyl methacrylate and styrene. Chung proposed[29] that during oxidation the peroxyborane decomposes homolytically generating an alkoxy radical (C-O•) (I) and borinate radical (B-O•) (II) (see Scheme 1b and 1c). It is suggested that the borinate radical is relatively stable and does not initiate homopolymerization.

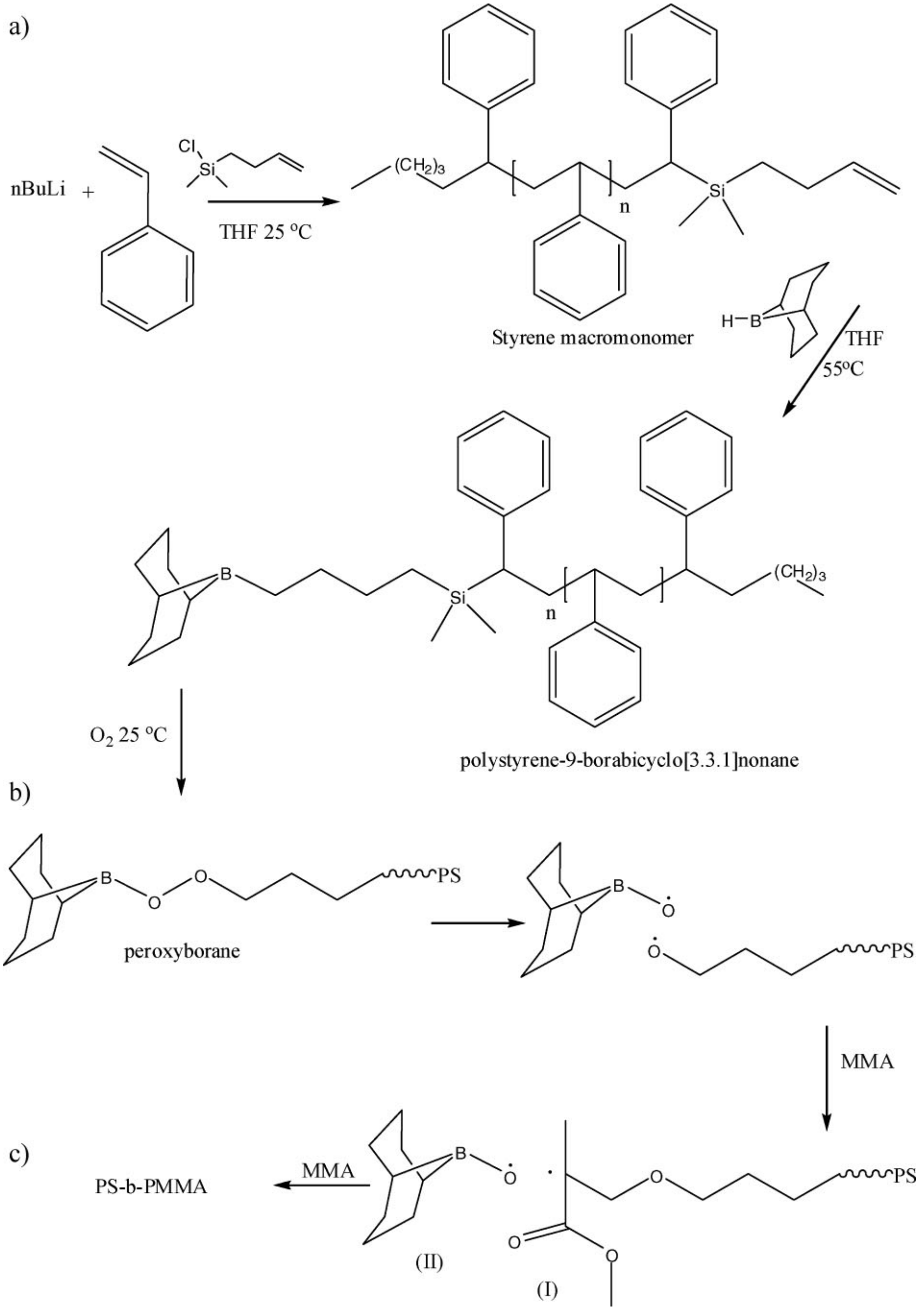
In this work we apply a similar polymerization process to produce polystyrene-block-poly(methyl methacrylate) copolymers. We also present the analysis of the block copolymers to evaluate the efficiency of block formation (efficiency of the chain extension reaction) using this synthetic technique.

In this complex polymer system, with unreacted and partially reacted starting polymer, SEC cannot give a full picture of polymer characterization in terms of chemical composition and distribution of the chemical composition. Liquid chromatography under critical conditions LCCC (which is at the interface between the entropic size exclusion separation and the enthalpy separation liquid adsorption chromatography[30,31]) can be used to characterize the complex polymer mixture. It is possible under these conditions of chromatographic analysis to determine the heterogeneity of the polymer without any influence of the polymer molar mass of one of the blocks of the copolymer. 2-dimensional analysis can be achieved by coupling SEC with LCCC, where in the first dimension the polymer elutes at critical conditions of one of the blocks, and in second dimension elutes in the exclusion mode. This is achieved via a direct coupling technique. This technique is important in the analysis of complex polymers, due to the capability to give distributions of molar mass in one dimension and chemical composition or functionality in the second.[32–35]

## Experimental Part

### Materials

Styrene was purified to remove inhibitors and any impurities by distillation under reduced pressure. Toluene (Analytical reagent, 99.9%), tetrahydrofuran (THF) (Sigma-Aldrich, 99.9%), were distilled over small pieces of sodium metal and benzophenone under an argon atmosphere for several hours. Methanol (Acros, 99.8%), n-butyllithium (Aldrich, 15% in hexane), acetonitrile (ACN) (Sigma-Aldrich, HPLC grade), 0.5 M Bis(9-borabicyclo[3.3.1]nonane) (9-BBN) in THF solution, used as received. Deuterated chloroform ($CDCl_3$, Cambridge Isotope Laboratories) was used as NMR solvent. The Oxygen gas used was AFROX 99.5%. The PMMA standards used in the SEC calibration were from Polymer Laboratories.



***Scheme 1.***

a) Anionic polymerization of styrene, n-BuLi as initiator, terminated via allylchlorodimethylsilane in toluene. b) hydroboration reaction, and c) free radical polymerization via hydroboration reaction (b) and c) based on scheme proposed by Chung et. al. [29])

### Synthesis of Styrene Macromonomers

A general procedure for the preparation of the styrene macroinitiator terminated with allylchlorodimethylsilane is given in the following example. Freshly distilled styrene (40 mmol) and 10 mL of toluene were injected via a syringe into a 100 mL dry round-bottom flask equipped with a magnetic stirrer bar and rubber septum, in an argon atmosphere. n-Butyllithium (0.69 mmol) initiator was added until the characteristic colour (reddish) of the styryl anion was achieved, indicating the initiation of the polymerization reaction. The reaction was allowed to proceed for 50 min at 30 °C before the polystyryllithium solution was terminated by introducing an amount of terminating agent to equimolar n-BuLi, via a syringe, into the reaction mixture. Immediately the reaction mixture became colourless, indicating termination of the polymerization. The macromonomer was then precipitated in methanol, collected by filtration, and dried under vacuum at room temperature overnight to constant weight. The general synthesis route of macromonomers is shown in Scheme 1a. Termination efficiency was calculated from the ratio of the methyl group ($CH_3$) ($\delta = 0.5$–$0.8$ ppm) of n-BuLi and methylene group ($CH_2$) ($\delta = 5$–$6$ ppm) in the $^1$H-NMR spectra of macromonomers. A termination efficiency of 85% was obtained indicating that not all chains were functionalised by the terminating agents. This had an effect on the further copolymerization reactions. The molar mass $M_w$ of the styrene macroinitiator used was 5900 g/mol and had a PDI of 1.2.

### Hydroboration and Autoxidation of Allyl Functional Polystyrene

1.0 g chain-end unsaturated PS was placed in a 100 mL round bottom flask with magnetic stirrer bar, a solution of 30 mL dry, $O_2$-free THF in an argon atmosphere was added. The polymer was hydroborated by the addition of 3.0 mL, 0.5M 9-BBN solution in THF and the mixture was stirred at 55 °C for 2 h. The chain end borane containing polystyrene was then obtained as shown in Scheme 1b).

0.5 g of borane-terminated polystyrene was placed in a solution of 3 g dry uninhibited MMA with 10 mL THF in a sealed bottom flask. The reaction was initiated by injecting $O_2$ gas directly into the solution. A total volume of 0.44 mL dry $O_2$ in was added in 0.10 mL amounts every 2 h. The $O_2$ gas was transferred from a pressure equalized vessel at atmospheric pressure and was therefore assumed to be at atmospheric pressure. The moles added were calculated using the standard gas equation. After 24 h, the reaction was terminated by addition of 10 mL methanol. The polymer mixture precipitated was isolated by filtration and dried in a vacuum oven to constant weight.

In the conversion study, samples were periodically removed and the monomer conversion determined gravimetrically. The molar mass analysis was carried out by SEC.

### Characterization

Molar mass and molar mass distributions were determined by SEC using a dual refractive index and UV 254 nm detector system. The system was calibrated using Polymer Laboratories Easivial PS Standards. THF Chromasolve HPLC grade solvent (0.125% BHT stabilised) was used as the mobile phase at a flow rate of 1ml/min. Samples were dissolved in the stabilised THF at a concentration of 5 mg/ml. 100 μl injection volumes were used. Liquid chromatography under critical conditions (LCCC), experiments were carried out with conventional liquid chromatography equipment. A 300 Si C18 and Nucleosil 120 Si C18 column were used. The column oven temperature was set at 3 °C. The detectors used were the Waters 486 tunable absorbance UV detector at a wavelength of 254 nm and the Polymer Laboratories PL-EMD960 evaporative light scattering detector (ELSD), nebulizer at 80 °C and evaporator at 90 °C with a $N_2$ carrier gas flow rate 1 SLM (standard liters per minute). At the critical conditions the eluent was ACN-THF (51.7-48.3), with a flow rate of 0.5 mL/min. In the first dimension of the two-dimension liquid chromatography experiments, the same setup was used as described for the LCCC analysis of blocks, however the flow rate was set at 0.05 ml/min. Sample fractions from the first dimension were collected in an eight-port valve system (VICI Valco EHC8W), which consisted of two loops, each having a sample capacity of 100 μL. The second dimension consisted of a Waters 510 pump delivering a flow rate of 4 ml/min. The column used was a Polymer Standards Service SDV (styrene divinyl benzene) column (pore size 5 μm, dimensions 300X8 mm i.d.). The same detectors were used as for the analysis of the block at the critical point. For the construction of the contour plots, calibration standards had to be injected. These standards were injected into the second dimension, using Polymer Laboratories Varian PMMA Standards (5 Standards ranging from 2810 g/mol to 342900 g/mol). Sample fractions collected in the first dimension are automatically injected into the second dimension. Data acquisition and processing were automatically performed by the Polymer Standards Service software: WINGPC 7 and PSS-2D-GPC-Software, respectively.

## Results and Discussion

Figure 1. shows the SEC traces of the overlaid normalized RI signal of the molar mass distributions for the copolymerization via 9-BBN of PS-b-PMMA. It is clearly seen that there is a shift from a low molar mass towards a higher molar mass as the reaction proceeds. Some un-reacted styrene or un-functionalized macromonomer is left even after 24 h. The decrease of the styrene macromonomer with time is a good indication of the incorporation of the PS in PMMA to form the block copolymer.

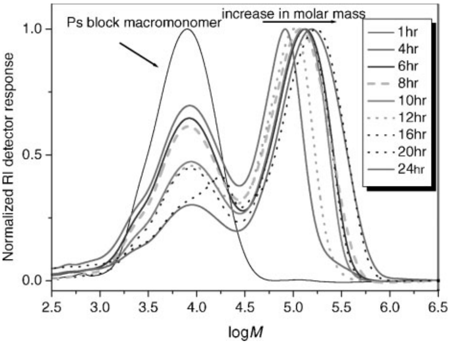


***Figure 1.***
Normalized SEC traces of molar mass distributions with increasing conversion.

Figure 2. shows the monomer conversion versus time for the block copolymer reaction. The figure shows that as conversion increased with time, there was an increase in molar mass of copolymer (Mw of the second peak in Figure 1). After 24 hrs the highest conversion achieved was about 65%.

In order to separate and determine the chemical composition of the block copolymers chromatographic analyses were carried out on the samples at the critical point of adsorption of styrene. It has already been described in literature that mixtures of THF-ACN as mobile phase are well suited for establishing critical conditions of styrene.[36,37] Using a set of nonpolar stationary phase columns (Si C18 300, 100), PS will elute at critical conditions whereas PMMA will elute in the SEC mode.

Figure 3 illustrates the separation of the block copolymer PS-b-PMMA from PS unreacted macroinitiator at the critical conditions of styrene. The analysis is shown for the polymer after 20 h of the second block formation reaction. The critical conditions were the following: stationary phase C18 and mobile phase ACN-THF (51.7-48.3), and flow rate 0.5 ml/min. The block copolymer and methyl methacrylate homo-polymer, if present, elute in SEC mode as explain earlier; the molecules with the longest PMMA block elute first followed by the shorter blocks. This is followed by the elution of the unreacted styrene macroinitiator which elutes at the critical point of styrene. There is a very weak UV detector response for the first elution peak indicating that at least some block formation has occurred. The weak response is reflective of the fact that the

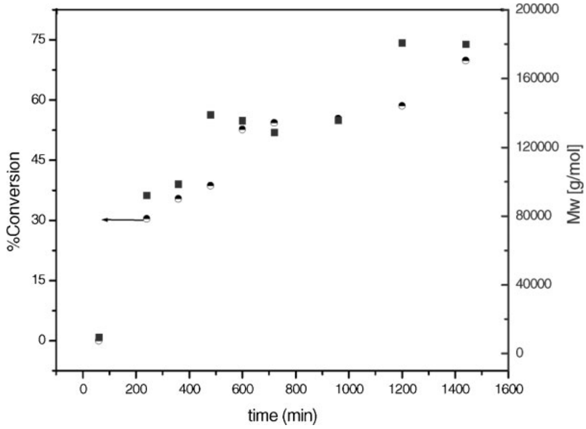


***Figure 2.***
Monomer conversion versus time for block copolymer reaction via the autoxidation hydroboration reaction ($M_w$ reflects the values for high molar mass peak from Figure 1).

styrene block only has a molar mass of 6000 g/mol, while the block molar mass is 120 000 g/mol (20 time higher than the PS macromonomer). In addition to this, the block copolymer co-elutes with any homo-PMMA that forms as a results of initiation by the borinate radical.

Figure 4 shows the contour plot obtained with two dimensional chromatography 2D-LC of the block copolymer. Separation is accomplished in two different directions of molecular heterogeneity. In one direction the separation occurs according to chemical composition, while in the other direction separation occurs according to the molar mass or hydrodynamic volume. Good separation between the styrene macroinitiator and block copolymer is obtained using the LCCC of PS in the first dimension (presented on the y-axis), and SEC in the second dimension (presented on x-axis). The molar mass calibration in the second dimension SEC was carried out using PMMA calibration standards thus; the molar mass of the block can be calculated based on that calibration. In addition to the

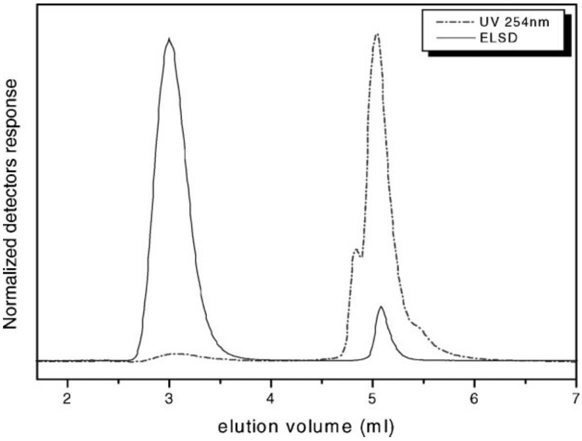


***Figure 3.***
Example of normalized UV and ELSD detector response of the block copolymer PS-b-PMMA at the critical point of styrene after 20h of the second block formation reaction.

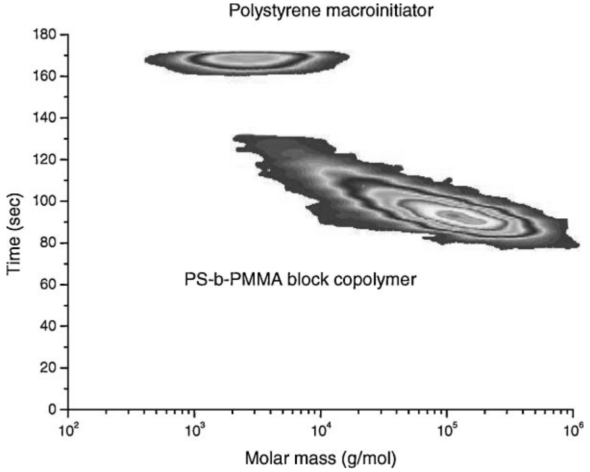


***Figure 4.***
2D-LC contour plots for block copolymer, shows separation of the block copolymer from the un-reacted styrene macroinitiator after 6h of the reactions in the second block formation. First dimension: critical conditions for PS; second dimension: SEC; using experimental conditions as described in the text (ELSD detector).

molar masses, the relative amounts of the components can be determined. The elution of the block copolymer PS-b-PMMA is depended on the chain length of PMMA, with a broader area indicating the different chemical composition of the block (lengths) and the higher molar mass copolymer eluting first flowed by the smaller molar mass polymer (shorter PMMA block length). The un-reacted styrene macroinitiator elutes in a relatively narrow area, no chemical composition distribution should be seen as is expected under critical conditions.

## Conclusion

Synthesis and functionalization of the unsaturated chain end styrene macroinitiator was effectively done. The unsaturated macroinitiator end was hydroborated by 9-borabicyclo[3.3.1]nonane (9-BBN) to produce a borane terminated PS. This was effectively used to produce the block PS-b-PMMA copolymer by free radical polymerization initiated by selective oxidation of polystrene-9-borabicyclo[3.3.1]nonane in the presence of MMA. The results suggest that in addition to block formation some homopolymerization of the MA by the baronate radical is observed. 2D-chromatographic technique where LCCC under the critical conditions of polystyrene is coupled to SEC proved block formation. In addition to the block, the 2-D analysis showed that some of the polystyrene macroinitiator is also present, most probably due to dead chains that where not effectively functionalised or converted to the borane terminated macroinititator.

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