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Two-dimensional liquid chromatography of polystyrene–polyethylene oxide block copolymers

Muhammad Imran Malik[a,b,*], Gareth W. Harding[a], Monika Elvira Grabowsky[a], Harald Pasch[a]

[a] Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch, South Africa
[b] H.E.J. Research Institute of Chemistry, International Centre for Chemical and Biological Sciences (ICCBS), University of Karachi, Karachi, Pakistan

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ABSTRACT

In this study, liquid chromatography at critical conditions of polystyrene (PS) and polyethylene oxide (PEO) is used as the first dimension for the two-dimensional analysis of PS-b-PEO copolymers. Comprehensive two-dimensional liquid chromatography, with size exclusion chromatography as the second dimension, reveals information about the molar mass distributions of all separated fractions from the first dimension. Furthermore, fractions eluting at the critical conditions of one block were collected and subjected to analysis in the second dimension at the critical conditions of the other block. These fractions were analysed by FTIR to determine their chemical compositions. The combination of the above approaches and the calibration of the evaporative light scattering (ELS) detector for the first-dimensional analysis yield deep insights into the molecular heterogeneity of the block copolymer samples. The composition of the samples and the chemical composition of the real block copolymer are also calculated by combining results obtained at both critical conditions.

1. Introduction

Amphiphilic copolymers generally consist of covalently bonded hydrophilic and hydrophobic blocks. Due to the incompatibility of these blocks with each other and their different affinities for different solvents, they exhibit surface activity. Recently, these materials have attracted considerable attention due to their applications in several different fields: for the modification of surfaces to control protein adsorption, nano- and biomaterials, controlled release, nanofiltration membranes, surface modification of biomaterials, synthetic lubricants, emulsifiers, and for biomedical applications [1–4].

In most cases polyoxyethylene is the hydrophilic block, while alkyl, aryl alkyl, poly(ether), poly(ester), poly(styrene), etc. are the hydrophobic blocks. The block copolymers consisting of ethylene oxide and styrene are amphiphilic in nature. The amphiphilic nature of PS-b-PEO has been exploited for many different industrial applications such as polymeric surfactants in the oil, pharmaceutical, agriculture, paper and detergent industries, as well as compatibilisers in polymer blending, dispersions, stabilisers, and templates for the preparation of inorganic nanoparticles [5]. Exploiting the self-assembly of PS-b-PEO and PS-b-PEO-b-PS to ordered nanostructures, novel applications such as the preparation of mesoporous silica films with different pore sizes [6] and electrolytes for rechargeable batteries have been developed [7]. Darling demonstrated in a review that the size and shape of self-assembled amphiphilic block copolymers are tuneable through the synthetic chemistry of the constituent molecules [8].

During the synthesis of PS-b-PEO copolymers, side reactions can take place leading to the formation of homopolymers with different functionalities of both types of monomers involved, along with the targeted block copolymers. The presence of homopolymers and the size of the different blocks have a significant effect on the final properties of these materials [8]. Therefore, characterisation of these block copolymers is vital to develop the structure–property relationships and to improve synthesis procedures. The application of spectroscopic methods such as NMR, MS, and FTIR to the bulk products only yields the average composition of the sample, which is not always conclusive with regard to information about all the components. These methods are, however, very often informative when used after fractionation by HPLC or other fractionation techniques.

Liquid chromatography is one of the most powerful methods for the characterisation of the molecular heterogeneity of complex polymers and liquid chromatography at critical conditions (LCCC) has been employed successfully for the fractionation of many different types of polymer blends, block copolymers, and polymers with different functionalities, etc. LCCC is one of the major modes of liquid chromatography employed as the first dimension in multidimensional liquid chromatography [9–31].

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[*] Corresponding author at: H.E.J. Research Institute of Chemistry, International Centre for Chemical and Biological Sciences (ICCBS), University of Karachi, Karachi, Pakistan. Fax: +92 21 34819018 9.

E-mail address: mimran.malik@iccs.edu (M.I. Malik).

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In this study, liquid chromatography at the critical conditions of PS and PEO is used to separate the block copolymers from respective homopolymers. In one of our previous papers, the critical conditions of PS were established using a tetrahydrofuran (THF)–water mobile phase. However, due to the limited solubility of the polymers being investigated, this system only works for chains with a molar mass of up to 10 kg/mol of each block [32]. In this study we used a different mobile phase system in order to extend the molar mass range. This approach should provide information on the molar mass distribution of the non-critical block in the block copolymer and allows separation of critical homopolymers from the rest of the sample if there are any. An ELS detector is calibrated under the above conditions and the homopolymer content is quantified. Comprehensive two-dimensional liquid chromatography is used to obtain the molar mass distribution of the fractions separated at the critical conditions of both PS and PEO. As a next step, fractions are collected and subjected to further analysis at the critical conditions of the other block, as well as by FTIR for qualitative as well as quantitative analysis. The study is further extended by combining the results obtained at both critical conditions to quantify the homopolymer content as well as the chemical composition distribution of the real block copolymers. Recently, this approach has been demonstrated for PDMS-b-PS copolymers [33,34] to obtain valuable information regarding the complex polymer system. In this study, we applied a similar approach to other commercially important PS-b-PEO copolymers.

2. HPLC of polymers

The separation mechanism in liquid chromatography of polymers depends on the size/pore size ratio and on the so-called interaction parameter *c*, which describes the interaction of the structural unit with the stationary phase [35]. This parameter is negative in size exclusion chromatography (SEC), in which retention decreases with an increase in molar mass, and is positive in liquid adsorption chromatography (LAC) where retention increases exponentially with the number of repeat units.

In both cases, the elution volume V_e depends upon the distribution coefficient *K* of the polymer between the interstitial volume V_i and the pore volume V_p:

$$V_e = V_i + K \cdot V_p \tag{1}$$

This equation is well known in SEC (where *K* can assume values between 0 and 1): a polymer of very high molar mass (above the exclusion limit) elutes at V_i (as $K = 0$), while small molecules (which have access to the entire pore volume) elute at the void volume $V_0 = V_i + V_p$ (as $K = 1$).

In LAC, the distribution coefficient can assume very high values (much larger than 1). The distribution coefficient is related to the free energy change related to the transition of the polymer from the interstitial volume into the pores of the stationary phase:

$$\ln K = \Delta G = \Delta H - T \cdot \Delta S \tag{2}$$

In general, the driving force in SEC is the entropy change, while in LAC retention is governed by the enthalpic interaction of the repeat unit with the stationary phase.

For a given system (polymer–stationary phase–mobile phase) there may be a mobile phase composition (and temperature), where entropic and enthalpic contributions compensate each other ($\Delta H = T\Delta S$), hence $\Delta G = 0$ and $K = 1$.

The transition point between SEC and LAC is often termed as the “critical conditions” or the critical adsorption point (CAP). At the CAP, the interaction parameter has a value of zero: under such conditions, a non-functional homopolymer elutes – independent of its molar mass – at the void volume of the column. In other words, the polymer chain becomes chromatographically invisible [36–39], hence it is possible to separate a complex polymer according to other structural units (different from the repeat unit), such as end groups or other blocks.

The selection of suitable column, mobile phase, and temperature is very important for establishing critical conditions for a particular type of polymer. The critical conditions at a given temperature are characteristic of polymer–adsorbant–eluent system. The ideal critical conditions for high polymers are those, which result in size exclusion elution of the non-critical components. Generally, critical conditions for nonpolar polymers can be established on a RP column in low mobile phase polarity. Under these conditions, polymers which are more polar than the critical ones elute in the size exclusion regime. Similarly, in high mobile phase polarity on a NP column, critical conditions for polar polymers can be established and nonpolar polymers elute in the size exclusion regime under these conditions [17]. The classic way of establishment of critical conditions is to select carefully column, mobile phase, and temperature for a particular polymer type and perform some isocratic runs of homopolymer standards in different mobile phase compositions. Of course this approach requires many isocratic runs to reach the critical point. Bashir et al., proposed a strategy for the fast determination of the CAP by gradient chromatography. For high molar mass polymers, the composition at elution is close to the critical composition [40]. This approach leads to considerable reduction in the number of experiments for establishing critical conditions.

These three modes of liquid chromatography can be combined in the analysis of functional polymers and copolymers by two-dimensional chromatography.

In the case of block copolymers the interaction parameters c_A and c_B of the individual structural units (A and B) may have different values. In a mobile phase, where both c_A and c_B are strongly negative, the molar mass distribution (MMD) can be determined by SEC, with retention decreasing with increasing molar mass. In SEC, the influence of chemical composition is often rather small. SEC yields the MMD of the entire molecule (provided that the calibration functions for A and B are comparable).

SEC is, however, not capable of discriminating mixtures of homopolymers with different repeat unit or polymers with the same repeat unit, but different functionality. This can be achieved by LCCC.

At the CAP of the repeat unit A, the elution volume is independent of the chain length of block A. In this case, AB copolymers can be separated according to block B.

Basically, there are two possible situations, which may be utilised:

1. If the interaction parameter c_B of block B is negative, the block copolymer will elute earlier than the homopolymer A (in SEC order). Obviously, situation 1 will only be useful if block B is sufficiently large: it can be used for the separation of homopolymers from block copolymers [23,24,37,41–44].
2. If c_B is positive, the block copolymer elutes later than the homopolymer A (in LAC order) [16,45]. Situation 2 is limited to short blocks in the case of strong interaction (i.e. large c_B). It can be very useful, if the non-critical block is monodisperse [44].

3. Experimental

3.1. Synthesis of PS-b-PEO diblock copolymers

PS-b-PEO diblock copolymers were produced by Polymer Standards Service GmbH (Mainz, Germany) by sequential living anionic polymerisation of styrene and ethylene oxide [46]. Briefly, styrene was polymerised at −78 °C in THF using cumylpotassium as