

Liquid chromatography at the critical conditions in pure eluent: An efficient tool for the characterization of functional polystyrenes

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Abstract

Functional polymers are usually separated by liquid chromatography at critical conditions (LC-CC) using a desorli/adsorli mixture as eluent. In this paper, we describe LC-CC using dimethylformamide (DMF) as pure eluent at 72 °C and its application to the analysis of functional polystyrenes. The critical adsorption point is reached by tuning the temperature so that the lack of repeatability is no longer a problem. We analysed several batches of polystyrenes, exhibiting different molecular weights and functionalities. We were able to differentiate di-, mono- and non-functional polystyrenes, bearing carboxylic acid, hydroxyl or nitroxide moieties. The behaviour of these polystyrenes expressed by the experimental results was compared with their behaviour described by the LC-CC theory through the calculation of the effective interaction parameter of each end group. The technique also makes it possible to quantify the fractions of different functional polymers in a blend.
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1. Introduction

The development of living radical polymerization techniques (Nitroxide Mediated Polymerization (NMP), ATRP, RAFT) [1] has been accompanied with the extensive study of their mechanisms and kinetics in the past 15 years. These techniques are indeed of great interest, as they provide a much easier access to block copolymers and complex architectures than anionic polymerization techniques, but their major drawback is that “dead” polymer chains form during the course of the polymerization, which can be an obstacle for the synthesis of pure block copolymers. The development of a method that makes it possible to quantify the fraction of dead species in a polymer synthesized by living radical polymerization is therefore essential.

We study here polymers synthesized by Nitroxide Mediated Polymerization (Fig. 1). This process provides living polymers which are α,ω -difunctional species, the α and ω moieties corresponding to the initiating radical and the nitroxide, respectively. The dead species have lost the terminal nitroxide moiety. The

separation of living and dead species should therefore be based on the analysis of the end groups of the polymer.

A powerful method for the study of complex polymers is liquid chromatography at critical conditions (LC-CC). It was first experimentally described by Belenky et al. [2,3] and then theoretically studied by Gorbunov and Skvortsov (see following section) in the 1970s but started being intensively studied a few years ago only. This chromatography mode, halfway between size exclusion chromatography (SEC) and interactive liquid chromatography (iLC) modes, consists in making the entropic and enthalpic interactions between the polymer and the stationary phase compensate each other. In these particular experimental conditions, the polymer chain eluted at the critical conditions becomes chromatographically “invisible” and the elution is independent of the molar mass. LC-CC is applicable to the characterization of block copolymers A-*b*-B: for example, the analysis is performed at the critical conditions of block A and the elution is only governed by the size of block B, or *vice versa*. It is consequently theoretically possible to fully characterize a block copolymer in terms of molar mass distribution of each block *via* LC-CC. A large number of papers have already been published on the subject [4–8]. However, some authors discussed the accuracy of the analysis [9,10].

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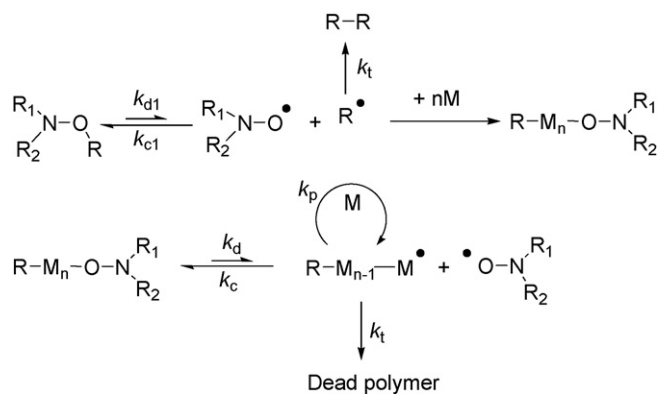


Fig. 1. Nitroxide Mediated Polymerization mechanism.

LC-CC is a powerful technique not only for the characterization of block copolymers but also for the separation of functional polymers. A large number of papers have been published on the separation of functional polymers [11–13], usually focusing on carboxylic acid [14], aldehyde [15] or alcohol [15] functionalised polymers. The critical conditions are usually reached by mixing an adsorbi and a desorbi of the polymer in the appropriate proportions, and using the mixture as an eluent at ambient temperature. Another method consists in working with a pure eluent and tuning the system temperature until the critical adsorption point is reached. Nevertheless, this latter method is rarely used because there are few pure eluents that make it possible to reach critical conditions. Very few examples of use of this method have been published. Macko et al. [16] determined the critical conditions for various polymer/eluent/stationary phase systems. They separated polystyrenes of different tacticities and also blends of polystyrene and poly(methyl methacrylate). Heinz et al. [17] separated polystyrene from blends of polystyrene, polyethylene and polyethylene-*block*-polystyrene, using a normal phase system and decaline at 140 °C as eluent. Lee et al. analysed polystyrene-*b*-polyisoprene block copolymers at the critical conditions of polyisoprene using a reversed phase and 1,4-dioxane at 47.7 °C as eluent [18]. We propose here an original application of LC-CC in pure dimethylformamide (DMF) to the separation of functional polymers synthesized by Nitroxide Mediated Polymerization [1]. We evaluate how the theoretical models describe the chromatographic behaviour of these polymers.

LC-CC was applied to the analysis of several batches of NMP-synthesized polystyrenes exhibiting different molecular weights and functionalities, using pure dimethylformamide as eluent. We were able to differentiate di-, mono- and non-functional polystyrenes, bearing carboxylic acid, hydroxyl or nitroxide moieties. We were also able to quantify the fraction of each end group in a blend of polymers.

2. Theory

In liquid chromatography, the retention of polymers is represented by the distribution coefficient, K_d , which is the ratio between the polymer concentrations in the stationary phase and in the mobile phase. K_d is related to the variation of Gibbs free

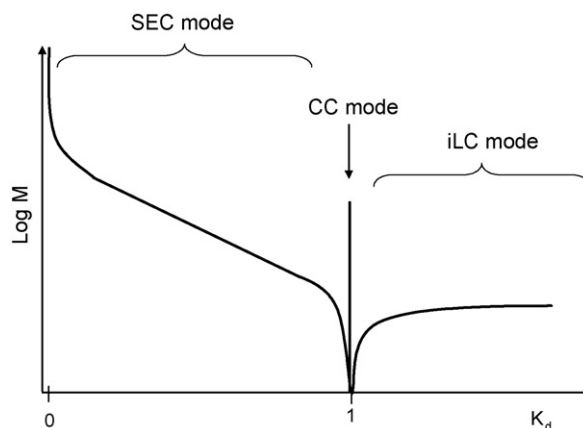


Fig. 2. Schematic representation of the different modes in liquid chromatography.

energy when the macromolecules move from the mobile phase to the stationary phase.

$$K_d = \frac{[\text{polymer}]_{\text{stationary phase}}}{[\text{polymer}]_{\text{mobile phase}}} = \exp\left(-\frac{\Delta G}{RT}\right)$$

$$= \exp\left(-\frac{\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right)$$

The elution volume, V_e , depends on this coefficient:

$$V_e = V_i + K_d V_p \quad (1)$$

where V_i is the interstitial volume, representing the volume outside the particles of the packing and V_p is the pore volume, which is the difference between the total volume of the column and the interstitial volume. The retention phenomenon is thus based on two types of interactions: enthalpic interactions (enthalpic term ΔH) and steric exclusion interactions (entropic term ΔS).

Under particular experimental conditions (stationary phase/eluent/polymer/temperature), it is possible to make the enthalpic and entropic phenomena counterbalance each other. In this case, all non-functional homopolymers are eluted at the same elution volume (total volume), whatever their molar masses (Fig. 2):

$$K_d = 1.$$

This particular chromatographic mode, whose theory was developed in the 1970s by Gorbunov and Skvortsov [19–25], is called liquid chromatography at critical conditions. At critical conditions, a polymer chain becomes chromatographically “invisible”. The retention therefore depends only on the number and nature of the end groups in the case of homopolymers [11,12,14,15] or on the size of the second block in the case of di- or triblock copolymers [4–6,26,27].

Gorbunov et al. developed the theory for mono- and difunctional polymers [28,29]. The effective interaction parameter, q_i was introduced to take into account the interactions of the terminal group i with the column surface.

$$q_i = \frac{\delta}{d} \left[\exp\left(-\frac{\Delta \varepsilon_i}{kT}\right) - 1 \right]$$

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