# Estimation of critical conditions of polymers based on monitoring the polymer recovery

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## ARTICLE INFO

## ABSTRACT

Liquid chromatography at critical conditions (LCCC) is a very attractive chromatographic technique on the border between the size exclusion and liquid adsorption mode of the liquid chromatography. The strong interest in LCCC arises from the fact that it is well suited to analyze the block lengths in segmented copolymers or the heterogeneities with regard to end groups present, for example, in functionalized polymers e.g., telechelics. In this paper a new method for identification of the critical conditions of synthetic polymers is proposed, which requires only one polymer sample with higher molar mass. The method is based on monitoring the recovery of the polymer sample from a column. The composition of the mobile phase is modified until the polymer sample is fully recovered from the column. The corresponding composition of the mobile phase is composition corresponding to LCCC. This new method was applied for the determination of critical conditions for polyethylene, syndiotactic polypropylene and isotactic polypropylene. The results of the new method will be compared to those of classical approaches and advantages will be pointed out.

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## 1. Introduction

The concept of liquid chromatography at critical conditions (LCCC) was for the first time proposed by Belenky et al. [1] and Entelis et al. [2]. The LCCC is an intermediate mode of chromatography between size exclusion chromatography (SEC) and liquid adsorption chromatography (LAC). In SEC mode polymers are separated according to their hydrodynamic volume in solution, while in LAC mode they are separated on the basis of their enthalpic interactions with the stationary phase in a mobile phase system. At LCCC the entropic effects of size exclusion and the enthalpic effects of adsorption compensate each other and macromolecules of a given polymer elute at the same elution volume from the stationary phase irrespective of their molar mass.

LCCC is a practically important chromatographic method, because it enables to achieve separations, which are not realizable with other chromatographic methods. For example, LCCC has been applied for separations of block copolymers [3–11], to determine the average molar mass of constituent blocks in di- and tri-block copolymer (type A–B and A–B–A) [12,13] as well as for

selective separations of end-functionalized polymers according to their functional groups [2,3,14,15]. Several groups have described successful separations of macromolecules according to their architecture (for example, linear from star shaped or linear from rings) [16–19] or their tacticity [20–25] with LCCC.

In the majority of the papers, the critical conditions are determined by evaluating the dependence between the elution volumes and the molar mass of a series of samples for a polymer of interest (SEC-LAC-plots) [1–23]. Namely, at a specific composition of a mixed mobile phase and at a given temperature, the polymer samples with different molar mass elute at the same elution volume. This specific composition of the mobile phase is the critical point for the polymer at the applied temperature in this chromatographic system. This method of determining the critical point may be laborious due to the fact that a series of a polymer with different molar masses needs to be injected in series of a mobile phase with different composition. This may be a particular impediment due to the fact that the required series of polymers are not easily accessible.

Cools et al. [26] proposed a graphical extrapolation of the critical composition from the dependence between the elution volume at peak maximum $[E_{pmax}]$ and the composition of a binary mobile phase. Cools' method also requires a significant number of measurements similar to the classical procedure (i.e., SEC-LAC plots) at different compositions of a selected mobile phase with analogous

**Table 1**
Polymer samples used for the experiments.

| Sample code | $M_w$ [kg/mol] | Đ |
|---|---|---|
| it-PP[348] | 348.3 | 8.01 |
| st-PP[196] | 196.8 | 2.44 |
| PE[181] | 181 | 1.59 |

drawbacks. These are avoided by the method proposed by Brun et al. [27,28] and used by Bashir et al. [29], which requires a single polymer sample of high molar mass and a gradient pump to generate a linear gradient. The critical conditions are then determined as the composition of a mobile phase when the polymer is just desorbed and eluted from the column in the solvent gradient. $E_{pmax}$ for a polymer sample of high molar mass is then used as a basis to refine the critical point for that polymer further using Bashir's method. Bashir's method requires two measurements i.e., one injection of the polymer sample in a solvent gradient and one experiment to determine the composition of the mobile phase in the detector used i.e., the delay volume.

Berek et al. pointed out a serious problem of limited recovery of the sample from the column, connected with LCCC in some polymer/solvent/sorbent systems. The sample recovery from the column rapidly decreases with increasing weight average molar mass and approaches zero for macromolecules between 100,000 and 500,000 g/mol molar mass [4,30–32]. The dependence of sample recovery on its molar mass also means that the high molar mass fractions of a broadly distributed polymer sample might be selectively retained within the column, which then may lead to an error in the determination of the critical point. Consequently, the determined molar masses and molar mass distributions values of polymers obtained from two-dimensional chromatography by coupling LCCC with SEC (LCCC × SEC) will be erroneous also for that part of macromolecules which is otherwise separated in the SEC mode [4,32].

Although polyolefins have been industrially produced for 70 years, LCCC of polyethylene (PE) or polypropylene (PP) could not have been realized until recently, because experimental conditions for their reversible adsorption were not known. The breakthrough came with the application of porous graphitic carbon (PGC) as stationary phase material i.e., when Macko et al. described the separation of PE, PP and ethylene/1-alkene copolymers using porous graphitic carbon (PGC) [33,34]. This has enabled to realize LCCC for linear polyethylene (PE) by Mekap et al. [25] and of PP by Bhati et al. [24] using the SEC-LAC method as well as the method according to Cools and Bashir.

Commercially available polyolefins regularly contain high or even ultra-high molar mass fractions, which may be eventually adsorbed at critical conditions. Therefore, a new method for determination the critical point will be described in this paper, which is based on monitoring the recovery of a single polymer sample with high average molar mass from a column. This method will be tested to determine the LCCC of Isotactic Polypropylene (it-PP), Syndiotactic Polypropylene (st-PP) and PE.

## 2. Experimental

### 2.1. Polymer samples

An it-PP standard (catalogue number: PP350K) was obtained from American Polymer Standards Corporation (Mentor, Ohio, USA). An st-PP standard (catalogue number: 452149) was obtained from Sigma-Aldrich (Milwaukee, USA). A linear PE standard (catalogue number: PSS-pe181k) was obtained from Polymer Standards Service, Mainz, Germany. The characteristics of the polymer samples used are shown in Table 1. The data about the weight average
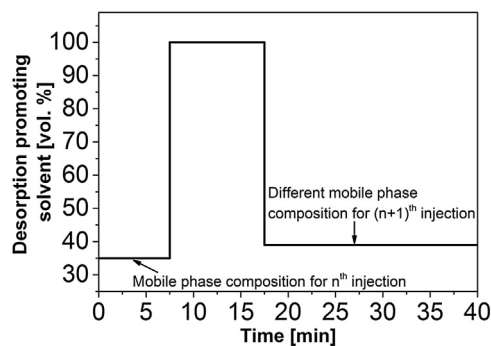


**Fig. 1.** Composition of the mobile phase for nth and (n + 1)th injection versus time.

molar mass ($M_w$) and the dispersity index (Đ) of these samples were provided by the suppliers.

The polymer standards were dissolved (∼2–3 mg/mL) at 160 °C for ∼2 h in a pure adsorption promoting solvent. The adsorption promoting solvent is usually a thermodynamically poor solvent for the polymer of interest, which promotes it's adsorption on the stationary phase.

### 2.2. Mobile phase and stationary phase

1,2-Dichlorobenzene (ODCB), 1,2,4-trichlorobenzene (TCB), 2-octanol and 2-ethyl-1-hexanol (2E1H) were obtained from Merck KGaA, Darmstadt, Germany. ODCB and TCB were distilled prior to use, the remaining mobile phases were used as received. A Hypercarb™ column 4.6 (mm) × 250 (mm) I.D. × L. containing porous graphitic carbon with an average particle diameter of 5 μm, a surface area of 122 m²/g and a pore diameter of 250 Å was purchased from ThermoFisher Scientific, Dreieich, Germany.

### 2.3. High temperature high performance liquid chromatography

A high temperature liquid chromatograph (PL-XTR 220, Polymer Laboratories, Church Stretton, England) was used for the experiments. The temperatures of the sample oven, transfer line, injector and the column oven were set on 160 °C. The sample loop had a volume of 50 μL. An evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used to monitor the composition of the effluent. Temperatures of the nebulizer and evaporator were set to 160 °C and 260 °C, respectively, whereas a nitrogen flow rate of 1.5 L/min was used for nebulization of the effluent. Data collection (1 point/s) and processing were done with WinGPC-software (Polymer Standards Service, Mainz, Germany).

A high-pressure binary gradient pump (Agilent, Heilbronn, Germany) was used for mixing and pumping of the binary mobile phases. The mobile phase flow rate was maintained constant at 1 mL/min. Total delay volume of the system was determined according to Ginzburg et al. [35]. The delay volume of the system was 5.1 mL.

The following programme was used for pumping of the mobile phase (Fig. 1).

The polymer was injected into such a mobile phase composition (first step in Fig. 1) that it was fully or partially adsorbed in the column. Subsequently, the retained polymer was desorbed and eluted after pumping a desorption promoting solvent i.e., TCB or ODCB (second step in Fig. 1). For the next injection the column was purged with the new mobile phase (final step in Fig. 1), which contained an increased concentration of the desorption promoting solvent. This procedure was repeated until no peak of the polymer appeared on the chromatogram after purging the column with TCB or ODCB.