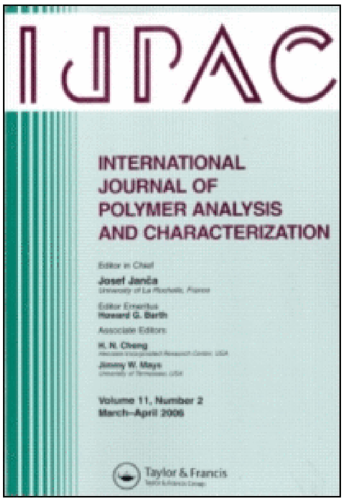

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High-Temperature Liquid Chromatography at Critical Conditions: Separation of Polystyrene from Blends with Polyethylene and Ethylene-Styrene Block Copolymers

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Abstract: Liquid chromatography at critical conditions (LCCC) is an important tool for the separation of complex polymers according to chemical composition. For ambient temperatures more than 150 different LCCC separation systems are known, while at temperatures that are suitable for chromatography of polyolefins (i.e. >130°C) not a single system is known from literature. In this article we present LCCC conditions for polystyrene at a temperature of 140°C and their application to the analysis of polymer blends composed of polystyrene and polyethylene or styrene-ethylene block copolymers.

Keywords: Liquid chomatography; Polyolefins; Ethylene-styrene block copolymers; Liquid chromatography at critical conditions

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INTRODUCTION

Copolymers of ethylene or propylene with other nonpolar and polar monomers possess attractive physical and chemical properties. Their synthesis is an active field of research in academia and industry.[1–3] Out of the large variety of liquid chromatographic techniques, so far only size exclusion chromatography (SEC) has been used for the analysis of polyolefins and their copolymers.[4–8] The corresponding SEC measurements have to be conducted at temperatures of 130–160°C due to the limited solubility of the polyolefin samples at lower temperatures. High-temperature SEC enables obtaining a more or less correct estimation of the molar mass distribution of copolymer samples, while information on chemical composition is not directly available. For amorphous polymers various liquid chromatographic systems are known that enable separating copolymers according to chemical composition,[9,10] including liquid adsorption chromatography (LAC), gradient polymer elution chromatography (GPEC), and liquid chromatography at critical conditions (LCCC).

Interactive liquid chromatography has been used for the characterization of polyolefin copolymers so far only by Lyons et al.[11] The polymer samples were successfully separated according to chemical composition at 30, 50, and 80°C on bare or reversed-phase silica gel packing material by gradient liquid chromatography. The mobile phases consisted of acetonitrile, tetrahydrofuran, n-hexane, chloroform, and cyclohexane. The samples under investigation were of low crystallinity and could be dissolved at temperatures less than 80°C. The separation of semicrystalline copolymer samples with higher crystallinities has not been shown yet, evidently due to the limited solubility of the polymer samples at temperatures below 100°C.

Liquid chromatography at critical conditions enables the separation of macromolecules according to chemical composition or functional groups irrespective of molar mass.[9,10,12]. At ambient working temperatures there are more than 150 LCCC separation systems known,[13] while at temperatures as high as 95°C only one LCCC system has been published.[14] Obviously due to the fact that working temperatures above 100°C cause a number of experimental (and instrumental) problems, interaction chromatography at high temperatures has never been attempted for the separation of olefin copolymers. Recently, our group identified a LCCC system for polymethylmethacrylate operated at 140°C.[15] This chromatographic system was used for separation of ethylene-methylmethacrylate block copolymers according to chemical composition.

In this article we present critical conditions for polystyrene (PS) at a temperature of 140°C and the application of this regime to the analysis of polymer blends. Although adsorption of PS from various solvents is described in the literature,[16] all solvents supporting retention of PS that have been employed so far possess low boiling points. To obtain the critical conditions of adsorption for PS under the conditions of high-temperature chromatography, suitable stationary and mobile phases must be identified and tested.

EXPERIMENTAL SECTION

High-Temperature Chromatograph PL XT-220

A prototype high-temperature gradient chromatograph PL XT-220 with a robotic sample handling system PL-XTR (Polymer Laboratories, Church Stretton, UK) was used for sample preparation, injection, and chromatographic separation. A customized evaporative light-scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, UK) working at a nebulization temperature of 160°C, an evaporation temperature of 270°C, and with an air velocity of 1.5 L/min was used for detection in all tested mobile phases. The eluent flow rate was 1 mL/min. Mobile phases were prepared by mixing the solvents with the gradient pump that is part of chromatograph PL XT-220. A detailed description of the PL XT 220 system will be published separately.[17] For data collection and processing the software package WinGPC-Software (Polymer Standards Service, Mainz, Germany) was used.

Stationary Phases

The following HPLC columns were used:

- Perfectsil 300, 25 × 0.46 cm I.D., particle diameter 5 μm, pore volume 1.05 mL/g (MZ Analysentechnik, Mainz, Germany).
- Nucleosil 500, 25 × 0.46 cm I.D., particle diameter 5 μm, pore volume 0.8 mL/g (Macherey-Nagel, Düren, Germany).
- LiChrosorb 100, 25 × 0.46 cm I.D., irregular particles with an average diameter of 5 μm, pore volume 1.0 mL/g (Merck, Darmstadt, Germany).

Mobile Phases

1,2,4-Trichlorobenzene, 1,2-dichlorobenzene, cyclohexanone, and decalin (Merck, Darmstadt, Germany) were used as mobile phases. The gradient pump that is part of the fast screening system PL XT-220 was used to prepare mixed mobile phases. Through a solvent recycling line leading out of the column oven these mixtures can be collected and used as sample solvents. The polymers were dissolved in the desired mobile phase at 160°C (four hours) at a concentration of around 1 mg/mL and were injected twice.

Polymer Samples

Polyethylenes (PE) with weight-average molar masses between 1.1 and 126 kg/mol and polystyrene (PS) standards (1.75–127 kg/mol) were obtained from Polymer Standards Service (Mainz, Germany).

Samples of ethylene-styrene block copolymers were synthesized at the Freiburg Materials Research Center, Freiburg, Germany, in the group of Rolf Mülhaupt. The average chemical composition of the copolymers was determined by nuclear magnetic resonance (NMR). Some samples of ethylene-styrene block copolymers were extracted using a Soxhlet apparatus with tert.-butylmethylether to remove the polystyrene homopolymer.

RESULTS AND DISCUSSION

For a first screening, the three columns under investigation were attached in parallel to the column-switching valve located in the column compartment of the chromatograph PL XT-220. For the testing, four different mobile phases were used: 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, decalin, and cyclohexanone. These mobile phases are good solvents for both polyethylene and polystyrene at 140°C. The elution behavior of PS and PE standards of different molar masses in different sorbent-solvent systems was screened at a temperature of 140°C, i.e., each column was tested with all four mobile phases. It was found that PE and PS eluted in the size exclusion mode for all sorbent-solvent combinations except for PS in decalin on silica gel LiChrosorb. In this specific system PS was fully retained.

Based on this observation, the other silica gel materials were reinvestigated with decalin as the mobile phase. However, none of them adsorbed polystyrene. Apparently, there are differences in the surface chemistries of the different stationary phases, e.g., the amount of silanol groups at the silica surface, that are responsible for the observed behavior. To identify the critical point of adsorption for PS on the LiChrosorb column at 140°C, decalin as the adsorption promoting eluent was combined with cyclohexanone as a good eluent. The determination of the mobile phase composition corresponding to the critical point was conducted by measuring the elution volumes of PS of different molar masses in mixtures of decalin and cyclohexanone. The PS samples were dissolved in the mobile phase; mixing was done by the binary pump of the PL XT-220 system.

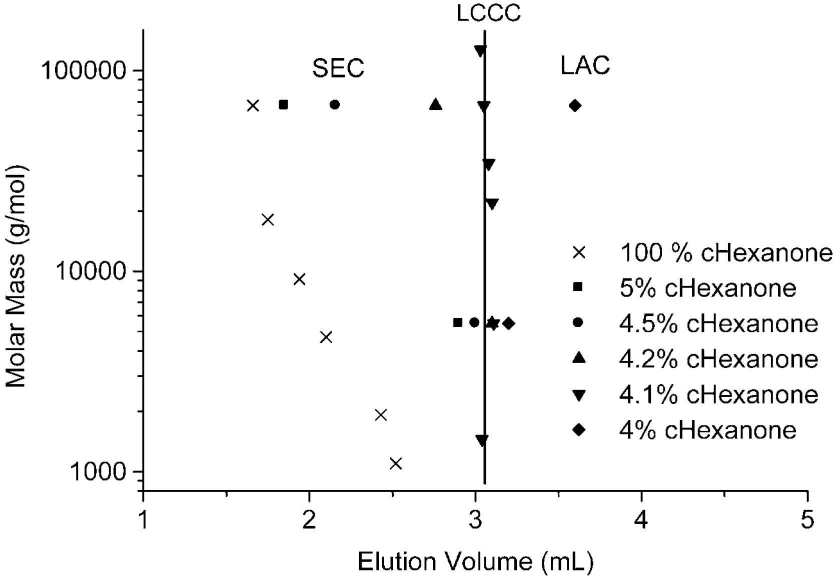

Figure 1. Dependence of the elution volumes of PS standards on the composition of the mobile phase; mobile phase: decalin-cyclohexanone, stationary phase: LiChrosorb 100, temperature: 140°C, detector: ELSD, flow rate: 1 mL/min.

Figure 1 illustrates the elution behavior of PS standards in mixtures of decalin and cyclohexanone at different compositions. With 5–100% by volume cyclohexanone in the mobile phase the entropic interactions in the chromatographic system are predominant and, accordingly, PS elutes in the SEC mode. The adsorptive interactions dominate above 96% decalin in the mobile phase. A mobile phase composition of decalin-cyclohexanone of 95.9:4.1% by volume corresponds to the critical point of adsorption for PS. Under these conditions PS standards with different molar masses elute at almost constant elution volume.

As the transition between the SEC and LAC modes takes place quite suddenly, i.e., with a change of the mobile phase composition of only 0.2% by volume, the system is very sensitive to any changes of the sample solvent and mobile phase composition. Thus, care must be taken to keep the sample vials tight to prevent any preferential solvent evaporation.

The critical conditions for PS are perfectly suitable for the selective separation polyethylene-polystyrene blends according to chemical composition. Due to the fact that PS elutes almost at one elution volume irrespective of molar mass and PE elutes in the SEC mode, there is a complete separation of the elution zones of both homopolymers, and even blends of polyethylene and polystyrene with similar molar masses can be separated perfectly; see Figure 2.

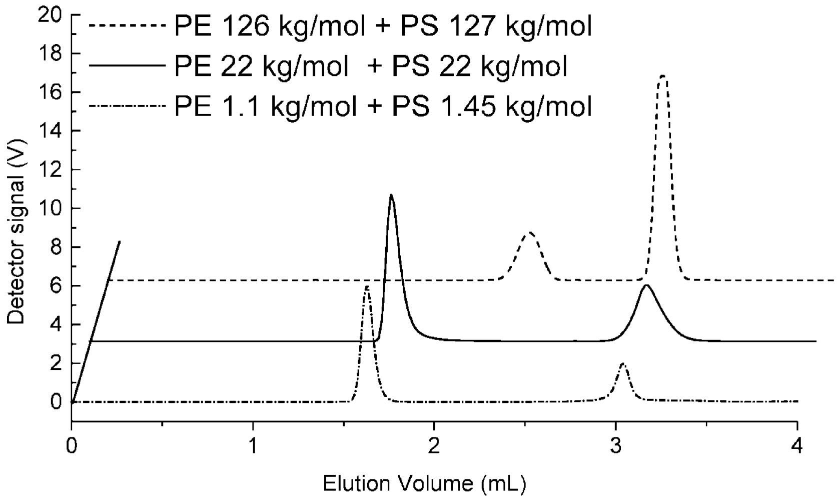

Figure 2. Chromatograms of polyethylene-polystyrene blends at critical conditions. Samples: PE + PS: 126 kg/mol + 127 kg/mol (dashed line), 22 kg/mol + 22 kg/mol (solid line), 1.1 kg/mol + 1.45 kg/mol (dot-dashed line). For experimental conditions, see Figure 1.

The present chromatographic system was used to analyze reaction products of the synthesis of ethylene-styrene block copolymers. Due to the very specific preparation procedure of the block copolymers it was expected that the reaction products contain certain fractions of precursor homopolymers. The LCCC separation of a crude reaction product is shown in Figure 3. Two peaks at elution volumes of 1.7 mL and 2.9 mL are detected, with the first peak exhibiting the highest peak intensity. The first peak appears at an elution volume that corresponds to the SEC elution range of both PE and PS. The peak can be assigned to the ethylene-styrene block copolymer fraction. In addition, this peak could contain PE homopolymer. The second peak appears at the critical elution volume of PS and can be assigned, therefore, to PS homopolymer.

The crude product was purified by Soxhlet extraction using tert.-butylmethylether in an attempt to remove the homopolymer. When the extracted sample was injected, no peak at around 2.9 mL was detected, meaning that the PS homopolymer was completely removed from the sample.

The molar mass of the PE block of the block copolymer could not be calculated from a calibration curve for PE under critical conditions for PS, as has been done previously for other applications. Unfortunately, all ethylene-styrene block copolymers at our disposal had relatively high molar masses (>150 kg/mol) and thus they were sterically excluded from

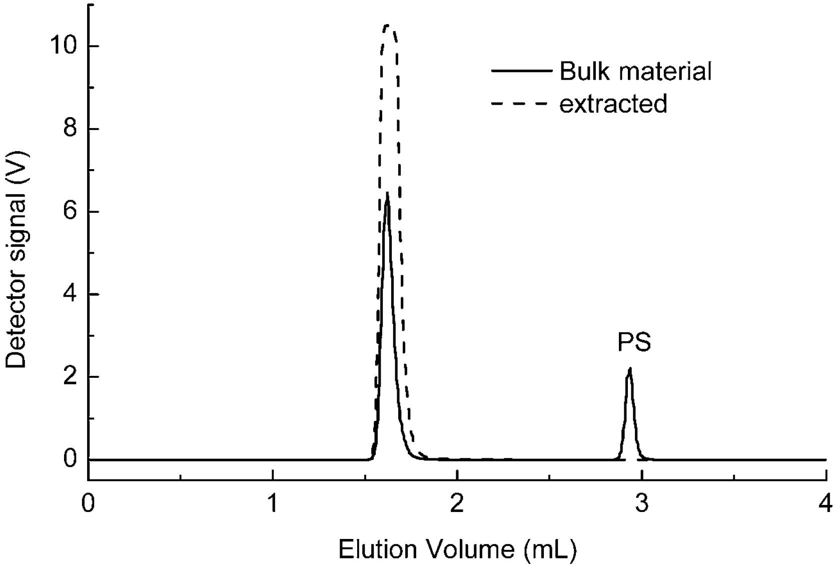

Figure 3. Chromatograms of a crude block copolymer sample (solid line) and the extracted sample (dashed line). For experimental conditions, see Figure 1.

the present column packing. The LiChrosorb stationary phase under investigation had an average pore size of 100 Å and, accordingly, an exclusion limit of roughly 30 kg/mol for polyethylene. Unfortunately, the column packing material LiChrosorb was not commercially available with bigger pore sizes.

As mentioned before, of all tested silica gel columns, only the LiChrosorb column retained PS from decalin at high temperatures. In any case, with this chromatographic system the amount of PS homopolymer in the experimental samples may be estimated and the efficiency of the Soxhlet extraction of PS from the crude samples may be controlled.

CONCLUSION

The first system for LCCC of polystyrene at a temperature of 140°C was identified. Both components of the mobile phase are good solvents for PS and PE, eliminating problems with solubility of the polymer samples in the mixed mobile phase. The described chromatographic system separates blends of PE and PS as well as blends of PS with corresponding copolymers. Ethylene-styrene block copolymers can be analyzed with regard to the presence of PS homopolymer. The stationary phase can also be applied for the separation of styrene-ethylene or styrene-propylene random copolymers using solvent gradients of decalin and cyclohexanone. This topic will be the subject of a forthcoming publication.

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