CHARACTERIZATION OF DI- AND TRIBLOCK COPOLYMERS USING COUPLED CHROMATOGRAPHIC METHODS

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Introduction
Block copolymers represent a class of functional polymers and materials for a multitude of applications. Novel synthesis strategies by means of ionic or radical polymerization allow for the synthesis of new "tailor-made" block copolymers. Thus it is possible to combine the properties of incompatible but well-known monomers. Especially the ability of these polymers to modify interfacial properties and to enhance the compatibility of polymer blends make this polymer type attractive for many applications.

Block copolymer synthesis by sequential monomer addition has to be controlled effectively, including the determination of unreacted precursor content, the characterization of the molar mass distribution (MMD) and of the chemical heterogeneity. These parameters influence the properties and application possibilities of the resulting polymers.

In the last decade a considerable progress in the development of synthesis strategies for preparing blockcopolymers of various architecture, solubility and functionality was reached. The main advantage of living polymerization techniques is the synthesis of polymers of narrow MMD with predetermined degrees of polymerization of both blocks, where the degree of polymerization depends only on the molar ratio of the monomers A and B to initiator.

In this contribution we wish to demonstrate that the combination of two different chromatographic techniques is a very useful method to obtain detailed information on the composition of di- and triblock copolymers. In the first dimension, separation according to chemical composition is performed by Liquid Adsorption Chromatography at Critical Conditions (LACCC) followed by the injection of fractions into SEC which provides information on the total MMD. Furthermore, it is emphasized that the complete characterization of a diblock copolymer by reversal of separation phase system in the LACCC is possible without the application of two-dimensional technique. It is shown that the MMD of the blocks can even be determined without knowing the MMD of the precursor polymers.

Experimental
Synthesis. The polymers were synthesized by living anionic polymerization using a novel initiator system reported recently. Ethyl α-lithionobutyrate was used as an initiator in the presence of a 2:1 complex of AlEt3 and NBu3Br in toluene at −20 °C. In one set of experiments, MMA was polymerized first, a sample was taken as precursor and then tert-butyl methacrylate was introduced for the second block. In order to obtain different block lengths for the second block, samples were taken at different conversions. In a second experiment, the order of monomers was reversed. For the ABA triblock copolymers, the procedure was analogous, with the monomer for the third block added to the living AB precursor.

Characterization. The block copolymers were characterized by two-dimensional chromatography. The first dimension (LACCC) was connected with the second dimension (SEC) by a dual-loop automatic injection system. The measurements were conducted on a Hewlett Packard HP1090 HPLC system. An Evaporative Light Scattering Detector (ELSD, SEDEX 45, ERC) operating at 45 °C with gas flow of 2.2 l/min was used for mass detection. The LACCC flow rate was 0.5 ml/min (for 2D chromatography 0.01 ml/min); 25 µl of ca. 2 wt.% polymer solutions were injected. Column temperature was 45°C.

Reversed Phase System: Two Nucleosil RP18 columns (250 x 4 mm i. d.); 30 Å pore diameter, 5 µm average particle size, and 1000 Å pore diameter, 7 µm average particle size. Eluent THF:acetonitrile (49.5:51.5 by weight).

Normal Phase System: Two Nucleosil Silicagel columns with 5 µm average particle size: 100 Å pore diameter, 150 x 4 mm i. d. and 300 Å pore diameter, 250 x 4 mm i. d. Eluent THF:n-hexane (81.5:18.5 by weight).

The SEC experiments were performed on an HP1090 HPLC system, including a Mistral column oven (SunChrom). For detection the SEDEX 45 ELSD and additionally a variable wavelength UV detector was used. Two linear columns (300 x 8 mm i. d.) filled with PS SDVgel of 5 µm average particle size and THF as mobile phase were used. Injection amount was 100 µl of a 1 wt.% polymer solution. The PSS 2D software was used for collecting and evaluating the raw data.

Results and Discussion
Diblock copolymers. In Fig. 1 the SEC-chromatograms of three PtBMA-b-PMMA copolymers (1-3) and the PtBMA precursor are shown. The small side peaks of samples 2 and 3 are due to residual precursor. If only PtBMA standards are used in SEC the result in molar masses of copolymers can only be apparent. Furthermore, no information can be obtained on the existence of unreacted precursor in sample 1.

![Figure 1. SEC chromatograms of PtBMA-b-PMMA (precursor PtBMA, M_w = 73000 g/mol) with different block length of PMMA.](image1)

![Figure 2. LACCC chromatograms of PtBMA-b-PMMA (precursor PtBMA, M_w = 73000 g/mol) with different block length of PMMA at critical conditions of PtBMA (RP system).](image2)

![Figure 3. LACCC chromatograms of PtBMA-b-PMMA with different block length of PtBMA and the PMMA precursor (M_w=31000 g/mol) at critical conditions of PtBMA (RP system).](image3)
Fig. 4 shows the two-dimensional plot of sample 1. Integration leads to the amount of unreacted precursor. After SEC-calibration the molar mass of precursor and of the whole block copolymer (apparent) is accessible (abscissa). Retention time at the ordinate leads to the PMMA block length.

Conclusions

It is demonstrated, that Liquid Chromatography at Critical Conditions of Adsorption (LACCC) in two-dimensional connection with Size Exclusion Chromatography (SEC) is an exclusive method for the complete characterization of diblock copolymers. Homopolymers (e.g., precursors) can be characterized qualitatively and quantitatively beside block copolymers. This is indispensable for controlling the synthesis. Block lengths were estimated up to a technically interesting ratio of 1:15. The characterization of each block was realized in both cases in size exclusion mode, on the one hand in a normal phase system, on the other hand in a reversed phase system. This separation phase reversal is the base for characterization of both blocks of a diblock copolymer without the two-dimensional technique. Molar mass and polydispersity of blocks were determined via calibration with homopolymers. The results agree quite well with the values measured by two-dimensional chromatography. The LACCC method allows the complete characterization of a diblock copolymer even without any knowledge about the precursor. Furthermore it is shown that the described techniques are applicable to the characterization of triblock copolymers.

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