CHARACTERIZATION OF DI- AND TRIBLOCK COPOLYMERS USING COUPLED CHROMATOGRPHIC 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-[1,2] 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[3]. 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[4,5]. Ethyl α-lithioisobutyrate was used as an initiator in the presence of a 2:1 complex of AlEt$_3$ and NBu$_4$Br 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[6]. 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 0.01ml/min); 25µl 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.): 300 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 HP1050 HPLC system, including a Mistral column oven (SunChrom). For detection the SEDEX 45 ELSD and additionally a variable wave length UV detector was used. Two linear columns (300 x 8 mm i. d.) filled with PSS 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.
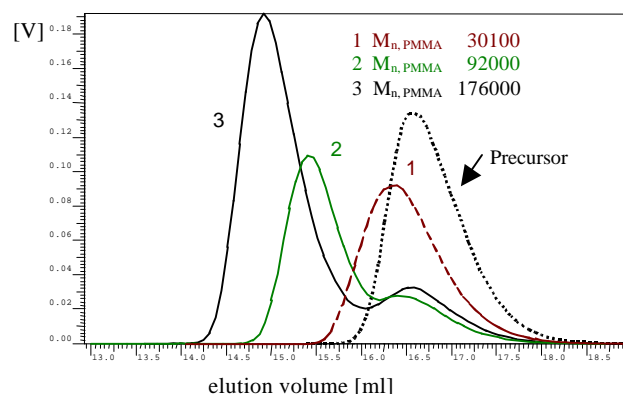

Figure 1. SEC chromatograms of PtBMA-*b*-PMMA (precursor PtBMA, M$_n$ = 73000 g/mol) with different block length of PMMA

The first system which chosen for LACCC was the the reversed phase (RP) system. Under critical conditions of the PtBMA precursor different molar masses of PtBMA elute at the same retention time and PMMA elutes in SEC mode. Separation of block copolymers occurs according to the molar mass of the PMMA block (Fig.2). It is clearly seen that sample 1 contains unreacted precursor too, which now can be determined quantitativly.
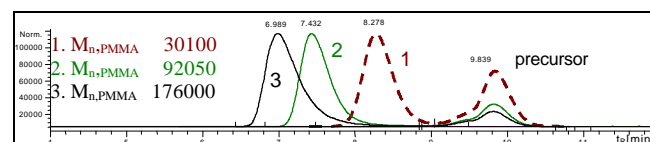

Figure 2. LACCC chromatograms of PtBMA-*b*-PMMA (precursor PtBMA, M$_n$ = 73000 g/mol) with different block length of PMMA at critical conditions of PtBMA (RP system).

The definitive proof that elution takes place according to the block length of the non-critical eluting block is to be seen in Fig.3. Under critical conditions of PtBMA block copolymers with different molar masses of PtBMA and the same block length of PMMA elute at the same time.
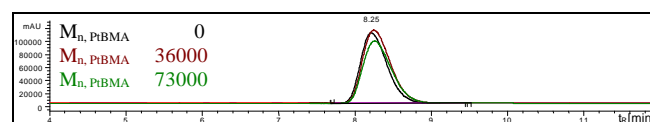

Figure 3. LACCC chromatograms of PMMA-*b*-PtBMA with different block length of PtBMA and the PMMA precursor (M$_n$ =31000 g/mol) at critical conditions of PtBMA (RP system).

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.
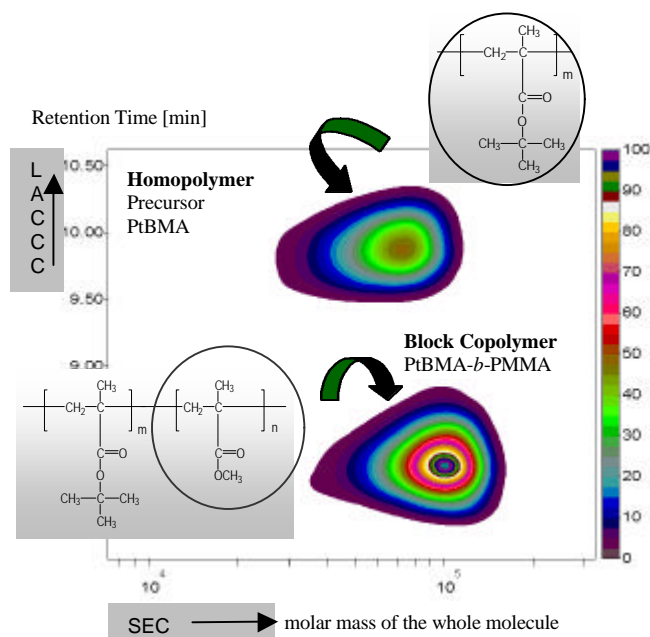

Figure 4. 2D Contour plot of PtBMA and PtBMA-*b*-PMMA at critical conditions of PtBMA

The results obtained by different methods and compared in Table 1 show a very good agreement. In the same way as described above it is possible to determine the PtBMA block under critical conditions of PMMA in the normal phase system.

Table 1. Comparison of Molar Masses from Different Methods

Copolymer	$M_{n,PMMA}$ (LACCC)	$M_{n,PMMA}$ (from $M_{n,block}$ - $M_{n,PtBMA}$)	$M_{n,Block}$ (SEC, 2D)
1 PtBMA-*b*-PMMA	30200	29600	102600
2 PtBMA-*b*-PMMA	113300	108100	181100
3 PtBMA-*b*-PMMA	174900	167500	240500

Triblock copolymers. In Fig. 5 the LACCC of di- and triblock copolymers at critical conditions of PtBMA (Fig. 5a) is shown. Under these conditions homopolymer and diblock copolymer of the same PMMA block length elute at the same retention time.

Triblock copolymers with PMMA as outer block elute at a retention time characteristic for the sum of the molar mass of both outer blocks (Fig. 5b).

For the first time it is shown that even the center block of the triblock copolymer can be characterized in this system at critical conditions of the outer blocks. A calibration with homopolymers is the only requirement. The proof is given by the chromatograms in Fig. 5c were the diblock and the triblock copolymers of the same PMMA block length elute at exactly the same retention time.
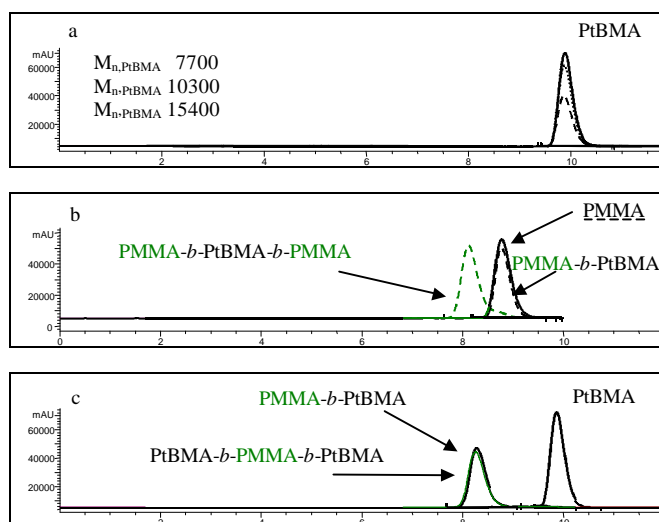

Figure 5. LACCC chromatograms at critical conditions of PtBMA (RP system). a) PtBMA of different molar masses; b) PMMA-*b*-PtBMA and PMMA-*b*-PtBMA-*b*-PMMA (precursor PMMA); c) PtBMA-*b*-PMMA and PtBMA-*b*-PMMA-*b*-PtBMA (precursor PtBMA)

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.

References

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