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Characterization of poly(methyl methacrylate)-*graft*-poly(styrene)s using various chromatographic techniques

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ABSTRACT

Two graft copolymer samples of identical average composition were synthesized by grafting living polystyrene anions onto a broadly distributed PMMA backbone. Size exclusion chromatography (SEC) with only RI-detection, SEC with viscometry and light scattering detection, SEC with UV and RI dual detection, gradient chromatography and 2-dimensional chromatography were applied to compare the information that can be obtained by the different techniques. While only limited information was retrieved by conventional SEC or SEC with molar mass sensitive detection, SEC with UV and RI revealed different chemical heterogeneity of the samples. Using gradient chromatography and 2-dimensional chromatography it was possible to identify non-grafted side chains and unreacted parent PMMA besides the actual graft copolymer molecules. While in one sample a heavily grafted product was formed besides non-grafted PMMA, the second sample did not contain ungrafted PMMA but a graft product of lower grafting density. The different product distributions were explained by the different synthetic procedures.
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1. Introduction

Graft copolymers form an interesting class of copolymers. They can often be used as alternative to block copolymers. However, their synthesis is much simpler. Furthermore, comonomers that cannot be polymerized by sequential monomer addition can be combined in an elegant way by grafting techniques. Graft copolymers have been applied in a variety of applications, e.g. as polymer blend compatibilizers [1–3] for impact modification [4], in targeted drug delivery [5], or thermoplastic elastomers [6]. The characterization of graft copolymers is quite complex because copolymers are heterogeneous with respect to different parameters. Besides being heterogeneous in molar mass, graft products may contain non-reacted side chains and ungrafted backbone molecules besides the truly grafted structures [7–10]. In addition, the actual graft copolymer can also be heterogeneous with respect to composition and molar mass [11]. Heterogeneities in polymers can be addressed using different chromatographic techniques, with size exclusion chromatography (SEC) being the most common one. Since graft copolymers are branched, additional information can be obtained from SEC using structure sensitive detection devices, e.g viscosity or light scattering detectors [12–14]. The variation in chemical composition along the SEC elution axis can be followed by application of several concentration detectors having different responses to the comonomers [15]. However, SEC separates by size, making interpretation of data difficult, if coelution of chemically different species occurs. Separation by chemical composition can be realized using methods of interaction chromatography, e.g. gradient chromatography or chromatography at critical conditions [16–19]. While SEC separates according to molecular size, rendering coelution of chemically or topologically different molecules, gradient chromatography separates high molar mass polymers nearly independent of molar mass according to chemical composition, rendering coelution of macromolecules differing in molar mass [20]. Two-dimensional chromatography allows separations according to two different structural parameters, e.g. composition and molecular size and therefore allows gaining additional information as compared to one-dimensional separations [19,21–24].

The present paper uses different chromatographic separation techniques for the characterization of two poly(methyl methacrylate)-*graft*-poly(styrene) copolymers. It will be shown how the process conditions affect the complex distribution of the final product.

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2. Material and methods

2.1. Graft copolymer synthesis

Graft copolymers were synthesized by reacting living polystyrene anions with a broadly distributed PMMA (M_w = 66000 g/mol, M_n = 27500 g/mol by SEC vs. PMMA calibration, batch number mmb040996, PSS, Mainz, Germany) in solution. For this purpose, 50 g of the broadly distributed PMMA were dissolved in 500 mL tetrahydrofuran (THF, A.+E. Fischer-Chemie Wiesbaden, Germany). To remove potential impurities in the polymer or solvent, 2 mL *n*-butyllithium (Sigma-Aldrich, Steinheim, Germany) were added at room temperature. Protic impurities will be destroyed by the butyllithium, while excess butyllithium will react with the ester groups of the PMMA forming a small amount of ketone groups. The PMMA solution was divided equally into two ampoules under inert conditions for further use.

The living polystyrene solution was prepared by dissolving 60 g styrene (Sigma-Aldrich, Steinheim, Germany) in 300 mL cyclohexane (Scharlab S.L., Sentmental, Spain). *s*-Butyllithium (Sigma-Aldrich, Steinheim, Germany) was added dropwise until a pale yellow color was observed, indicating formation of living polystyryl anions after removing protic impurities. Afterwards 20 mmol *s*-butyllitium in cyclohexane were added to obtain the desired molar mass of 3000 g/mol. The polymerization was performed at 35 °C for 1 h. The living polystyrene solution was split into two identical aliquots under inert conditions.

For the synthesis of sample 1 the PMMA solution was slowly added to the living polystyrene solution which was cooled in an ice bath. For the preparation of sample 2 the PMMA solution was cooled in an ice bath and the living polystyrene solution was added slowly.

2.2. SEC

SEC experiments were conducted on a PSS SECcurity SEC system (PSS, Mainz, Germany) composed of isocratic pump, autosampler, PSS SECcurity RI-detector, PSS DVD 1260 viscosity detector, PSS SLD 7000 multi angle light scattering and PSS SECcurity UV-detector operated at 254 nm. For data acquisition and evaluation PSS WINGPC UniChrom software was applied. SEC separations were done at a flow rate of 1 mL/min on a 5 μ PSS SDV column set composed of guard column (50 x 8 mm) and three 300 x 8 mm PSS SDV columns of 10^3, 10^5, 10^6 Å pore size. Injection volumes and sample concentrations were adjusted to the respective experiments (viscometry, light scattering or UV/RI analysis). Conventional and universal calibration curves were established using a ReadyCal-Kit Poly(styrene) (PSS, Mainz, Germany). Individual PSS polystyrene and PMMA standards (PSS, Mainz, Germany) were used for determination of detector response factors in copolymer evaluation.

2.3. Gradient chromatography

Gradient chromatography was performed using a PSS SECcurity system equipped with a low pressure gradient pump, an autosampler, column thermostat, a variable wavelength UV-detector operated at 254 nm and a PSS SECcurity 1400 evaporative light scattering detector (ELSD). Flow rate was 1 mL/min. Data were acquired and evaluated using PSS WINGPC UniChrom Software. A Macherey & Nagel (Düren, Germany) 5 μ 300 Å Nucleosil column (250 x 4.6 mm) was applied at a column temperature of 35 °C. The samples were dissolved at a concentration of 1 mg/mL in chloroform. The injection volume was 10 μL. Samples were injected every 22 min. A binary gradient of chloroform and tetrahydrofuran (THF) was applied. Eluents A and B were pure chloroform and a mixture of 30% THF in chloroform, respectively. The applied gradient is summarized in Table 1.

Table 1
Applied gradient in gradient chromatography.

Time/min.	%A	%B
0	95	5
10–12	0	100
13	100	0
14	95	5

Table 2
Details for gradient applied in first dimension of two-dimensional separations.

Time/min.	%A	%B	Flow rate/mL/min
0	95	5	0.05
200–240	0	100	0.05
260	100	0	0.05
280	95	5	0.05
281	95	5	1
289	95	5	1
290	95	5	0.05

2.4. Two-dimensional separations

For the two-dimensional separations the detector of the gradient system was replaced by a transfer valve equipped with two loops of 150 μL. Care was taken to assure identical loop sizes. The transfer valve allows for identical either co- or countercurrent filling/emptying of both loops, depending on configuration. The fact that both loops are filled/emptied in identical directions eliminates questions arising from non-identical filling/emptying of both sample loops, occurring with other transfer valves. The cocurrent configuration was employed in the preset investigation. For the second dimension separation an isocratic PSS SECcurity pump was applied using THF as eluent at a flow rate of 1.6 mL/min. Following the transfer valve a single 5 μ PSS linear M column (300 x8 mm) was installed. Detection was performed using the above mentioned ELS detector. For the first dimension gradient separation the flow rate was reduced to 0.05 mL/min. The gradient times in Table 1 were adjusted accordingly. To increase sample throughput, the flow rate was increased for flushing and equilibration. Gradient details are given in Table 2. Sample transfer between both separation dimensions was achieved by valve actuation every 2.5 min, resulting in 125 μL transfer volumes. Valve control, data acquisition and evaluation were performed using PSS WINGPC UniChrom Software.

3. Results and discussion

Among the different chromatographic techniques for polymer characterization SEC with RI detection is the most commonly applied one. The RI-chromatograms of the two graft products (Fig. 1) show similar peaks and shapes. Both chromatograms show a narrow peak at approximately 31.5 mL, which corresponds to non-grafted poly(styrene) as was confirmed by comparing with the chromatogram of the polystyrene precursor (not shown). Another narrow peak is observed at 30.4 mL, which corresponds to approximately twice the molar mass of the original poly(styrene). This peak might stem from relatively short PMMA backbones, with only two polystyrene sidechains attached. At a molar mass for the grafts of M_P = 3000 g/mol and an average polystyrene fraction of 55% (see below) a backbone molar mass of 5500 g/mol mass is required in average to attach two side chain. Therefore only a low fraction of the PMMA backbone molecules can thus contribute to such lowly grafted molecules. For sample 1 the broad peak eluting below 29.5 mL is clearly shifted to lower elution volume (higher molar

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