



## Determination of chemical composition and molar mass distribution of random styrene-ethyl acrylate copolymers by high-throughput liquid chromatography

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**Abstract:** Synthesis and characterization of random copolymers by spectroscopic and chromatographic techniques are normally slow and expensive because most measurements are conducted consecutively and no high-throughput techniques are used. In the present work parallel synthesis and high-throughput analytical techniques for random styrene-ethyl acrylate copolymers were developed. With combinatorial methods, high-throughput instruments and a better design of experiments, the molar mass and chemical composition analyses were carried out simultaneously with time savings of more than 90% as compared to conventional set-ups. The chemical heterogeneity of high-conversion styrene-ethyl acrylate copolymers was determined successfully by fast gradient HPLC. Determination of the average composition was carried out via selective UV detection in size exclusion chromatography. The results were verified by  $^1\text{H}$  NMR and calculations based on the copolymerisation parameters. Differential scanning calorimetry and optical microscopy techniques were used for determination of the phase separation behaviour of the copolymers and correlated with the chemical heterogeneity.

### Introduction

Experimental techniques of combinatorial chemistry [1,2] are frequently applied in the pharmaceutical industry and have become more and more popular in materials research for the discovery of novel polymeric materials. Parallel and high-throughput methods are applied to synthesize large compositional libraries with minimum amounts of material in order to save time and costs [3].

The preparation of large numbers of target compounds is only the first step in a combinatorial set-up. As important as the fast synthesis is the fast analysis of the prepared sample sets. This, however, is much more complicated for polymers as compared to drug molecules or other low molar mass species. Synthetic polymers are highly complex materials that very frequently exhibit chemical or functional heterogeneities in addition to the molar mass distribution. In order to evaluate a new material properly, the different distributions have to be determined quantitatively [1].

The different modes of interaction chromatography (HPLC) [4] and size exclusion chromatography (SEC) [5] are typical techniques for the analysis of complex polymers. HPLC can separate polymer samples according to chemical composition, while SEC is the preferred technique to analyse the molecular size distribution. Using

conventional equipment, an HPLC or SEC experiment takes not less than 20 min [6,13]. However, these techniques can be developed to get maximal information in a minimal amount of time and costs using high-throughput experimental approaches.

It has been shown previously that data obtained by high-throughput experimental approaches may deviate from those obtained by conventional techniques. It was found, however, that the comparison between different samples is as good as with conventional measurements. Therefore, the faster and less expensive high-throughput techniques can be used for a first materials screening.

In this work, high-throughput HPLC and SEC using short chromatographic columns and optimised flow rates were used to analyse random copolymers of styrene and ethyl acrylate (SEA). Using the fast HPLC procedure, time savings of almost 90% in comparison with conventional techniques were achieved. Time savings in fast SEC were even higher than 90%. For the present applications, refractive index (RI) and evaporative light scattering (ELS) detection were used. The chemical composition of the SEA copolymers was determined by SEC with dual RI-UV detection.

## Results and discussion

### *Copolymer synthesis*

Six low-conversion and nine high-conversion styrene-ethyl acrylate (SEA) copolymers were synthesized in parallel by free radical polymerization in a Polymer Laboratories PL-SP 260 high temperature sample preparation instrument. The monomers, the initiator and the solvents were placed into 15 screw-neck vials of 4 mL. The vials were heated to 70°C and agitated. The polymerisation times were 1 h and 20 h, respectively, for the low- and high-conversion copolymers. After polymerization the polymer solutions were precipitated in methanol and dried in vacuum. Monomer, initiator and solvent amounts are summarized in Tab. 1.

### *Molar mass analysis of the copolymers by fast SEC*

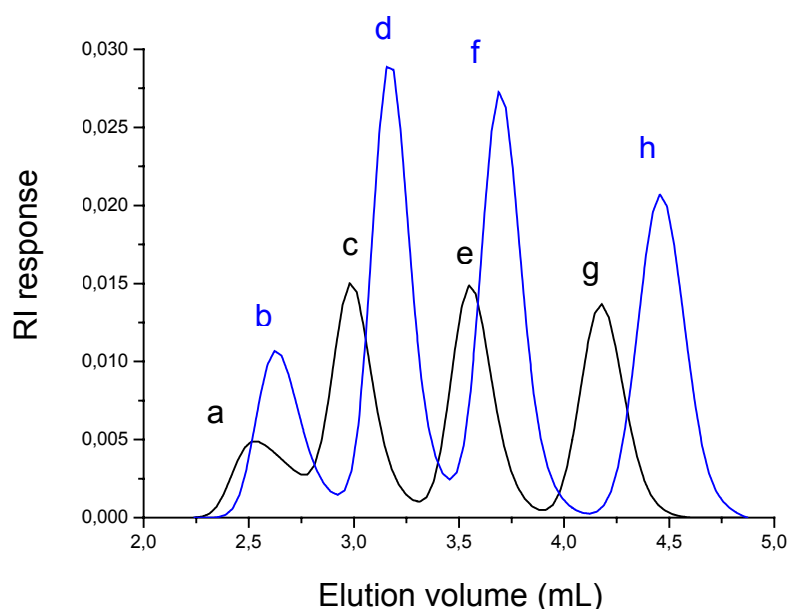
As described in previous publications [3,7], analysis time for SEC experiments can be reduced significantly by using stationary phases that are specifically dedicated to high-throughput experimentation. Such stationary phases have been developed by companies such as Polymer Standards Service GmbH, Mainz, Germany, and Polymer Laboratories, Church Stretton, UK, within the last couple of years. In this work, a PL Rapide M linear column was used for the SEC measurements, covering a large molar mass range of  $2 \cdot 10^2$  to  $2 \cdot 10^6$  g/mol. The size of the column was 15 x 0.75 cm I.D.; the average particle size of the packing material was 5  $\mu$ m.

The calibration of the present SEC system was conducted with an elution volume of 13 mL using two mixtures of polystyrene calibration standards with molar masses of 376 to 1 040 000 g/mol. Using a flow rate of 2 mL/min, the calibration took 6.5 min. As can be seen in Fig. 1, the efficiency of the column was sufficient to obtain baseline resolution of the calibration standards.

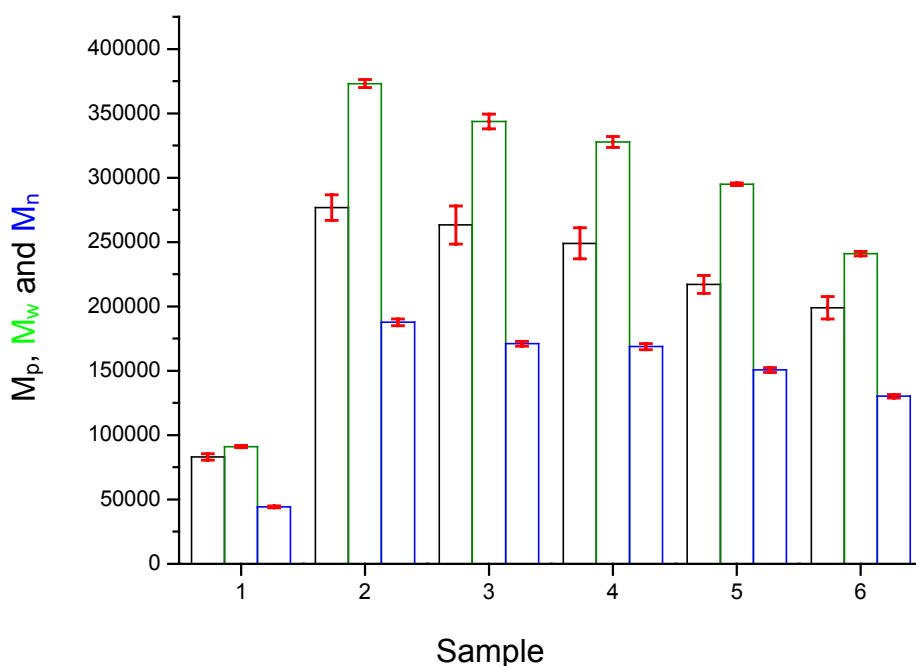
The reproducibility of this high-speed system was checked by measuring the low-conversion SEA copolymer samples. The copolymers were analysed five times and the standard deviation for each sample was determined. In all cases the standard deviation of  $M_w$  was less than 2%. Average values of  $M_p$  (peak molecular weight),  $M_w$  and  $M_n$  together with the error bars are presented in Fig. 2.

**Tab. 1.** Monomer ratios, solvents and initiator concentrations of the reaction mixtures and styrene (S) contents of the copolymers as determined by  $^1\text{H}$  NMR. BPO: Benzoyl peroxide, AIBN: azoisobutyronitrile, low-conversion copolymers: samples 1 - 6, *high-conversion copolymers: samples 7 - 15*

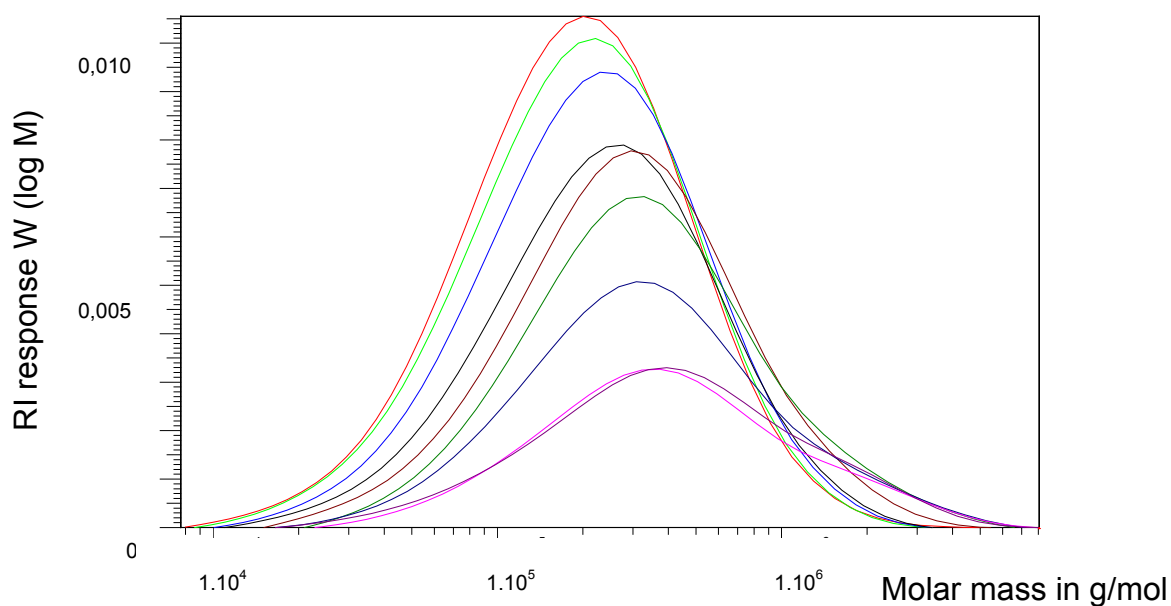
Sample	S in mol-%/g	EA in mol-%/g	BPO in mg	AIBN in mg	Toluene in $\mu\text{L}$	S in polymer in mol-%
1	0/0	100/1.84	0	6	200	0
2	20/0.37	80/1.47	6	0	0	40
3	40/0.73	60/1.1	6	0	0	54
4	60/1.10	40/0.73	6	0	0	66
5	80/1.46	20/0.36	6	0	0	78
6	100/1.81	0/0	6	0	0	100
7	10/0.18	90/1.65	0	6	300	-
8	20/0.37	80/1.47	6	0	200	-
9	30/0.55	70/1.28	6	0	100	-
10	40/0.73	60/1.1	6	0	0	-
11	50/0.92	50/0.91	6	0	0	-
12	60/1.10	40/0.73	6	0	0	-
13	70/1.28	30/0.54	6	0	0	-
14	80/1.46	20/0.36	6	0	0	-
15	90/1.63	10/0.18	6	0	0	-



**Fig. 1.** Calibration of the SEC system with two mixtures of PS calibration standards; stationary phase: PL Rapide M linear; mobile phase: tetrahydrofuran (THF); refractive index (RI) detector; calibration standards: PS 1040 (a), 659 (b), 128 (c), 67.5 (d), 18.1 (e), 8.4 (f), 1.6 (g), 0.38 kg/mol (h)



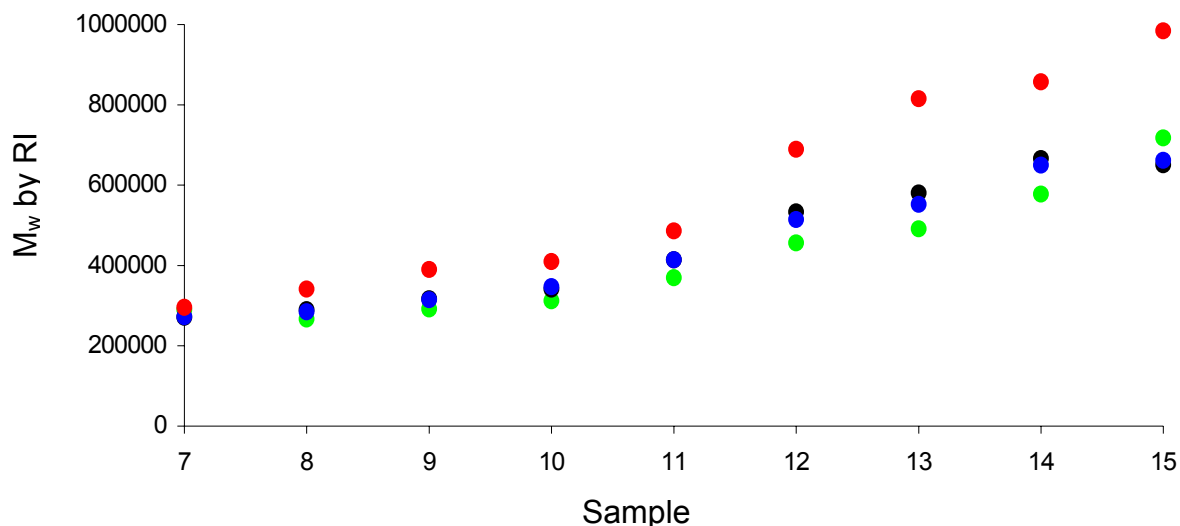
**Fig. 2.** SEC analyses of the low-conversion SEA samples with error bars for  $M_p$  (peak molecular weight),  $M_w$  and  $M_n$ ; stationary phase: PL Rapide M linear; mobile phase: THF; RI detector; flow rate: 2 mL/min



**Fig. 3.** Molar mass distributions of high-conversion SEA copolymers; experimental conditions see Fig. 2; samples: 7 (violet), 8 (pink), 9 (dark blue), 10 (dark green), 11 (brown), 12 (black), 13 (blue), 14 (green), 15 (red)

The high-conversion SEA copolymers exhibiting broad chemical composition distributions were also analyzed by fast SEC (Fig. 3). Similar to the low-conversion samples, higher molar masses and polydispersities were observed with increasing contents of ethyl acrylate in the copolymers. This tendency was also observed for other styrene-acrylate copolymers.

In order to find the maximum flow rate at which the SEC experiments can be conducted, the copolymers were measured at flow rates of 1 mL/min (standard instrument), 1, 2, and 3 mL/min (high-throughput instrument). A comparison of the molar masses that were determined at the different flow rates is given in Fig. 4.



**Fig. 4.** Molar masses of high-conversion SEA measured on high-throughput set-up at different flow rates, 1 mL/min (black), 2 mL/min (blue), 3 mL/min (red), as compared to a standard experiment on a conventional SEC instrument at 1 mL/min (green)

For the standard instrument the following column set was used: three PSS SDV 5  $\mu\text{m}$  columns,  $10^3+10^5+10^6$   $\text{\AA}$  with column sizes of 30x0.8 cm, while for the high-throughput experiments a PL Rapide M column of size 15x0.75 cm was used. Assuming that the conventional instrument gives the most reliable results, a maximum deviation of 40% for the measurements at 3 mL/min with the high-throughput instrument was observed. Such large deviation is not acceptable and, therefore, the flow rate for the following SEC experiments was fixed at 2 mL/min. Using these conditions, the maximum deviation from the standard results was less than 13%.

A comparison of the time requirements for a standard SEC experiment and a high-throughput SEC experiment is presented in Fig. 5. While a standard experiment took about 27 min per sample, with the high-throughput experimental set-up all nine high-conversion SEA copolymers could be analysed within just 17 min. This corresponds to time savings of more than 90% per sample. According to Fig. 1 one run takes 2.5 min and, accordingly, nine samples would take 22.5 min. This is true for very large ranges of molar masses, but in the present case the molar mass ranges are lower. Thus, it was possible to overlay the injections and by this way to save time.

#### *Fast compositional analysis of SEA copolymers by UV absorption measurements*

For the analysis of the bulk chemical composition of the copolymers or the chemical composition as a function of molar mass the SEC system can be coupled to a UV detector in addition to the conventional RI detector. The UV absorption at 254 nm is caused only by the styrene units in the copolymers. The ethyl acrylate units are optically transparent at this wavelength and do not cause a detector response. This was repeatedly checked with poly(ethyl acrylate) samples of different molar masses.

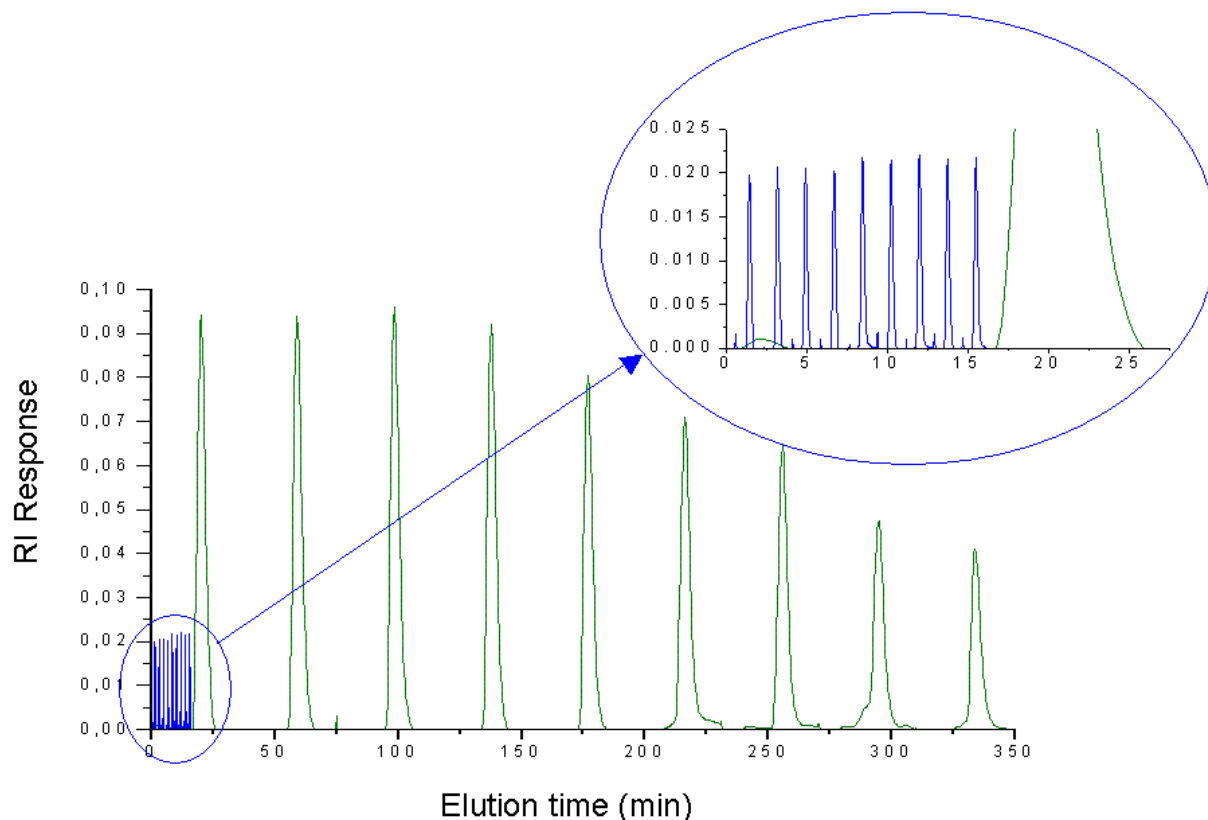


Fig. 5. Comparison of the time requirements for standard (green) and high-throughput SEC measurements (blue)

The calibration of the UV detector coupled to the SEC system was conducted with polystyrene. As can be seen in Fig. 6, a linear calibration function of absorbance vs. injected amount of polystyrene is obtained. This calibration function was used subsequently to calculate the styrene contents of the copolymers from the UV absorbance at 254 nm. If the exact injected amount of copolymer is known, the mass ratio styrene-to-ethyl acrylate in the copolymer can be calculated.

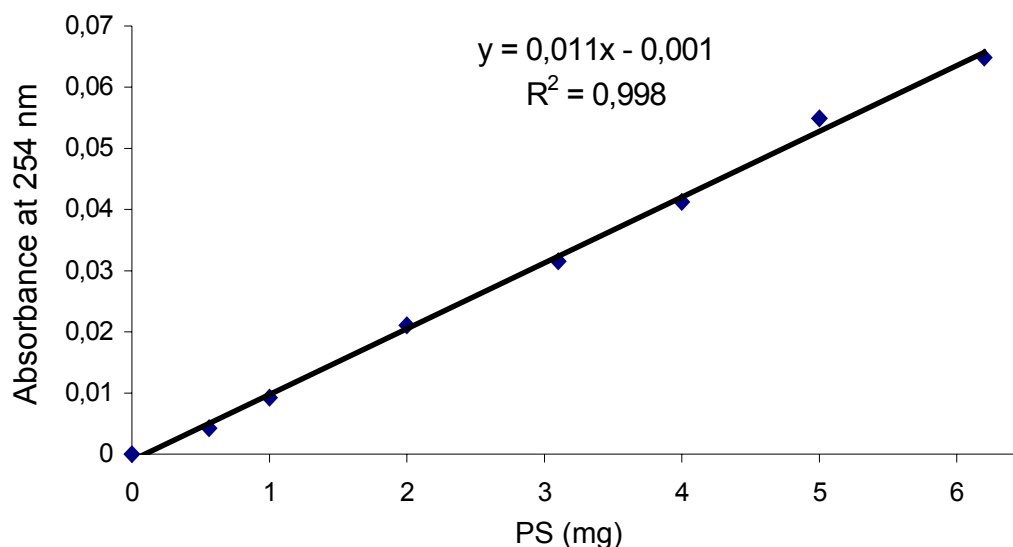


Fig. 6. UV detector calibration based on polystyrene

Using UV detector calibration, the low-conversion SEA copolymers were analysed with regard to the chemical composition, repeating the measurements five times. The results of the analyses are presented in Fig. 7 as a copolymerisation diagram. The average copolymer compositions are compared to theoretical copolymer compositions and to compositions that were determined by  $^1\text{H}$  NMR. The latter measurements were conducted in deuterated chloroform. Calculations of the chemical compositions were based on the signals of the aromatic protons for styrene and the O-CH<sub>2</sub> protons for ethyl acrylate [8,9]. As can be seen in Fig. 7, both methods show a very good agreement with the theory with maximum deviations of less than 3%. The results obtained from UV analysis are even closer to theory than the NMR data.

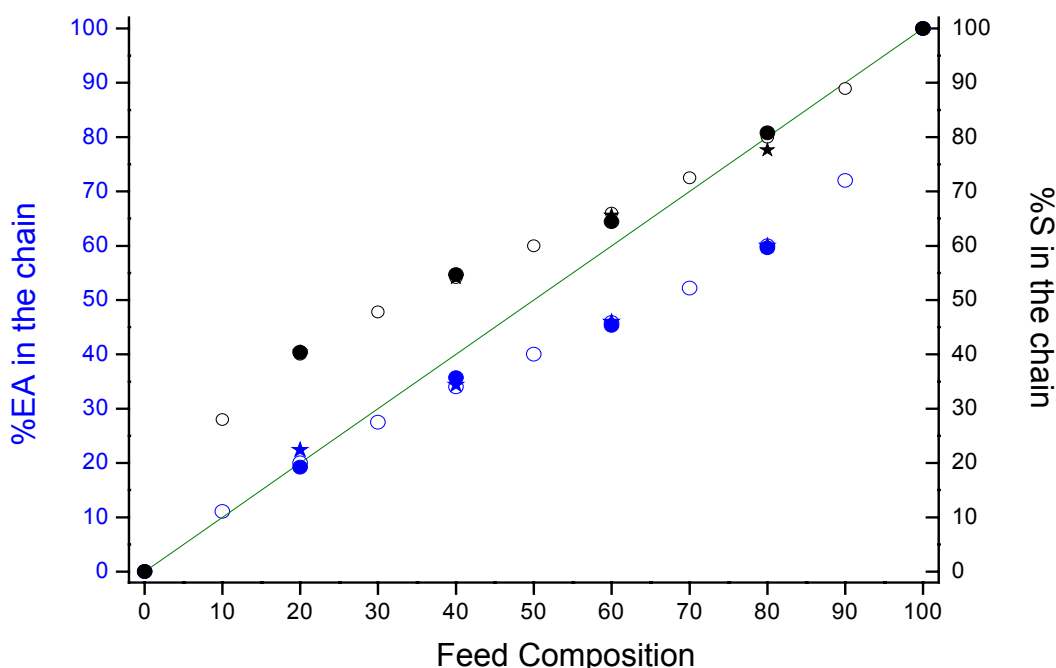


Fig. 7. Copolymerisation diagram for SEA: theoretical copolymer compositions (open circles) compared to UV data (filled circles) and  $^1\text{H}$  NMR results (filled stars); the green line is the azeotrope

These results indicate that the bulk chemical composition of the copolymers can be analysed very efficiently using the UV detector attached to the SEC instrument. Accordingly, within the SEC experiments the bulk composition comes as additional information without additional time requirements.

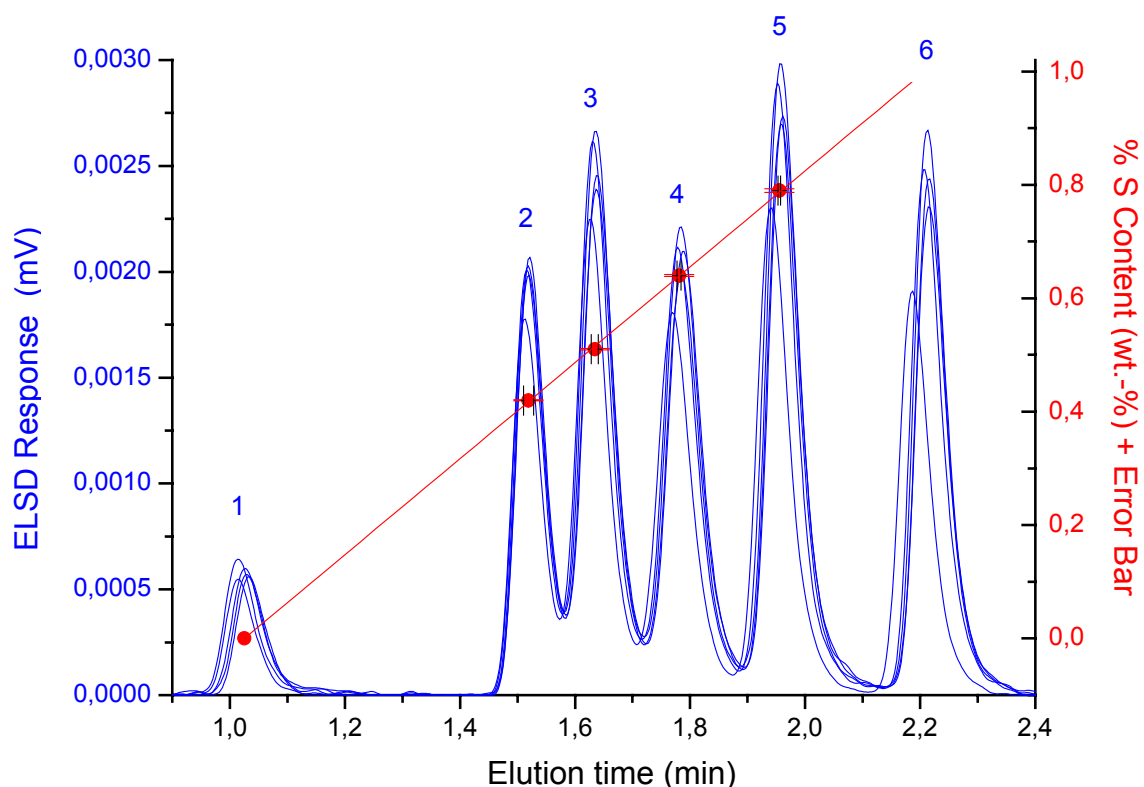
#### *Chemical heterogeneity of high-conversion SEA copolymers*

As is indicated in the copolymerisation diagram, styrene and ethyl acrylate show different reactivities in the copolymerisation. In agreement with ref. [8], the copolymerization parameters are 0.8 for styrene and 0.2 for ethyl acrylate. Due to the higher reactivity of styrene this monomer is preferentially polymerised in the early stages of the copolymerisation. Accordingly, at low conversions the styrene content in the copolymers is higher than the azeotropic composition. In the later stages of the copolymerisation, the major part of styrene is consumed and higher amounts of ethyl acrylate are incorporated into the polymer chains. As a result, at higher conversion the polymer chains contain higher amounts of ethyl acrylate [8,10].

This difference in the monomer reactivities leads to a significant chemical heterogeneity of high-conversion copolymers. For the quantitative analysis of this chemical heterogeneity, gradient HPLC can be used as has been shown previously [3,10]. To fit the requirements of the high-throughput screening, a very short HPLC column was used at high flow rate.

**Tab. 2.** Optimized gradient for the HPLC separation of SEA copolymers; mobile phase: THF-ACN (acetonitrile)

Time in min	%THF
0	0
0.01	15
0.5	20
0.8	36
1.0	40
1.1	45
1.6	58
1.7	100
2.0	100
2.1	0



**Fig. 8.** Overlay of five HPLC separations of SEA copolymers. The average styrene contents and the standard deviation bars are given. Stationary phase: Luna C18 100 Å; mobile phase: THF-ACN gradient (Tab. 2); numbers represent the samples



Aiming at the separation of the copolymers with regard to the styrene content, a reversed phase system was used with a RP-18 stationary phase (Luna of Phenomenex) and a mobile phase of THF-acetonitrile (ACN). The size of the column was 3x0.46cm I.D. to ensure short analyses times. With the gradient described in Tab. 2 and a flow rate of 2 mL/min one gradient HPLC separation could be accomplished within 2.5 min.

Using the low-conversion SEA copolymers that have a low chemical heterogeneity a calibration for the dependence of elution time vs. styrene content in the copolymer could be established. As can be seen in Fig. 8 a linear calibration line is obtained. The peak resolution and the reproducibility of the measurements is excellent making it possible to carry out a reproducibility test with five measurements in only 13 min.

The reproducibility of the separations was analysed by comparing the peak maxima. With regard to the compositional analysis the reproducibility is almost perfect, with a maximal relative standard deviation of 0.9%.

Under the same experimental conditions, the high-conversion SEA copolymers were analysed (Fig. 9). The peaks are broader as compared to the low-conversion SEA samples indicating a higher chemical heterogeneity. As could be expected, the copolymers with high styrene contents exhibit rather narrow and monomodal chemical composition distributions, see samples 13 - 15. On the contrary, the copolymers with low styrene contents exhibit bimodal and quite broad chemical composition distributions, see samples 7 - 9.

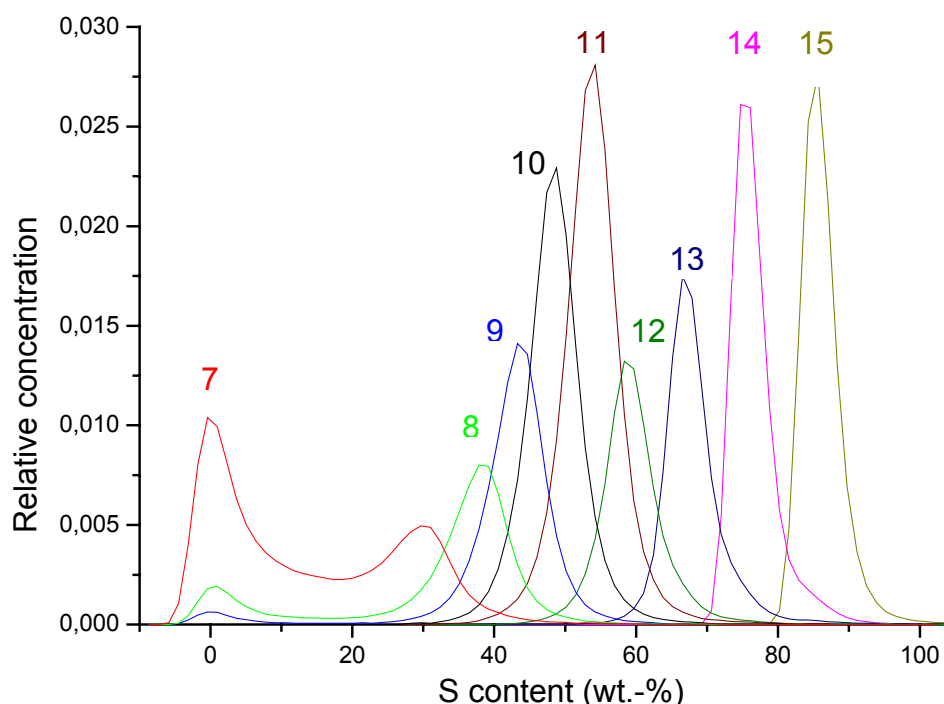


Fig. 9. Chemical composition distributions of high-conversion SEA copolymers; the sample numbers are given as labels

#### *Phase separation behaviour of high-conversion SEA copolymers*

It has been found previously that high-conversion random copolymers can exhibit *in situ* phase separation [8,10]. The formation of different phases is due to the fact that, when going to high-conversion polymerisation, macromolecules are formed that have

distinctively different chemical compositions. As is shown in Fig. 9, sample 7 (feed composition styrene-ethyl acrylate 10:90) exhibits a bimodal chemical composition distribution with a large amount of poly(ethyl acrylate) homopolymer combined with copolymer species having a styrene content of up to 40 wt.-%. Due to the large polarity differences between styrene and ethyl acrylate, the different polymer species are immiscible and show *in situ* phase separation when casted from polymer solution.

For the establishment of the relation between CCD and phase separation it was interesting to monitor the *in situ* phase separation. In previous work [8], the influence of conversion on copolymer composition and, thus, on phase separation was analysed by measuring the glass transition by differential scanning calorimetry (DSC). The glass transition temperature,  $T_g$ , is an important property, which determines the application range of the polymeric system. The occurrence of two or more transition temperatures is an evidence of phase separation. Two transitions can be detected when the phase size is at least 20 nm, the  $T_g$  difference of the homopolymers is not less than 30 K, and the concentration of the minority phase is more than 15% [11].

DSC measurements can be conducted in a relatively fast and efficient way. Using autosamplers and high heating and cooling rates, the thermal behaviour can be analysed in a relatively short period of time. The recent development of high-performance DSC (Hyper DSC) by Mathot et al. allows obtaining melting curves in a few seconds [12].

In the present work measurements on a conventional instrument were optimized through a screening of different temperature ramps and sample amounts to get sufficient sensitivity as compared to previous reports [8]. The experimental results of the DSC measurements for the high-conversion copolymers are summarized in Fig. 10 and Tab. 3. Using a heating rate of 7.5 K/min, in a temperature range of -50 to 110°C glass transitions were measured in the second heating run. Significantly different DSC behaviours were obtained for different copolymers. The optimum sample amount was 10 mg.

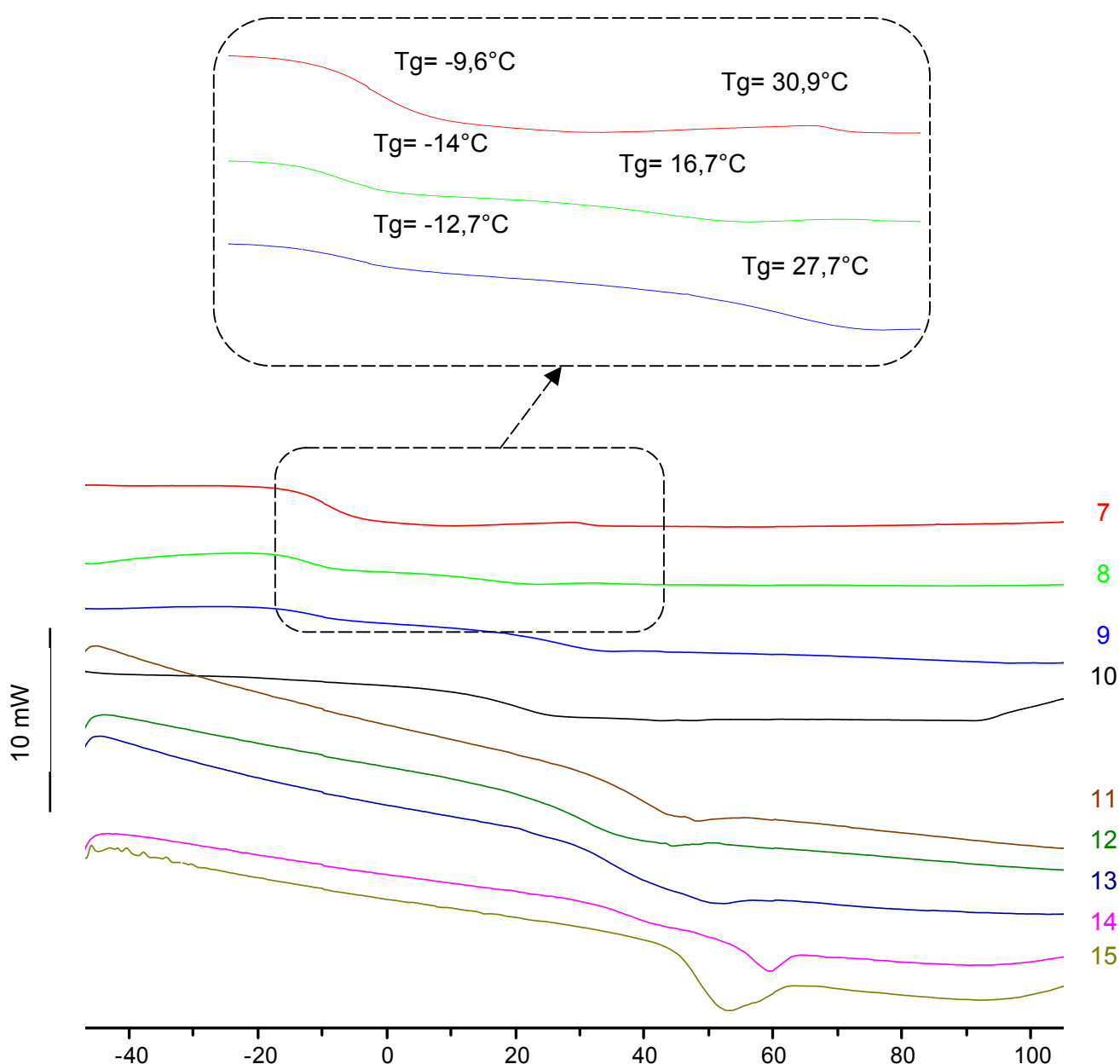
**Tab. 3.** Glass transition temperatures observed for the copolymers

Samples	$T_g$ in °C
7	-9.6 and 30.9
8	-14.0 and 16.7
9	-12.7 and 27.7
10	21.0
11	42.0
12	30.6
13	34.1
14	36.4
15	48.7

For samples 7 - 9, two glass transitions were observed, while for the other samples only one glass transition could be detected. The glass transition temperatures increased with increasing styrene contents in the copolymers. The two glass transitions for the copolymers with high ethyl acrylate contents clearly indicate the

presence of different domains in the samples, at least one domain that is rather rubbery-like with a glass transition  $< 0^{\circ}\text{C}$  and at least one domain that is rather thermoplastic. Each sample was measured five times with reproducible results. Comparison with a temperature ramp of 50 K/min and a sample amount of 1 mg showed poorer reproducibility and sensitivity as compared to the slow heating rate. Further studies on the application of higher heating rates and lower sample amounts (Hyper DSC) are underway.

Another most frequently used option to evaluate phase separation is microscopy. Typically, expensive and time-consuming techniques like ultramicrotome-TEM are used. Compared to TEM, optical microscopy is a quick, easy and cheap technique, which can determine the phase separation behaviour of samples provided that the domains are sufficiently large.

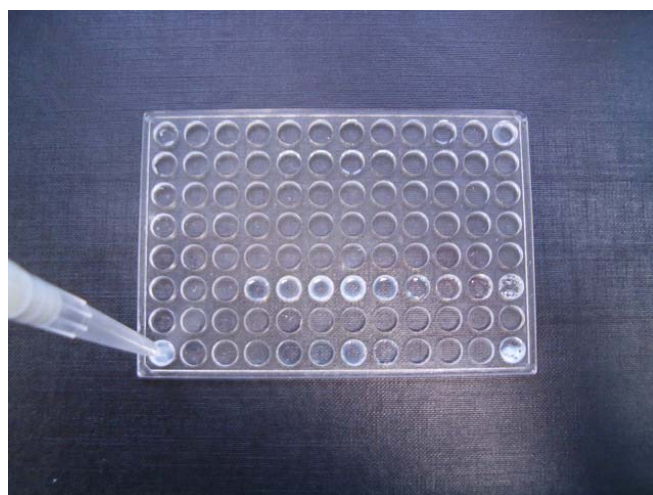


**Fig. 10.** DSC traces of high-conversion SEA copolymers; heating rate 7.5 K/min; temperature range  $-50$  to  $110^{\circ}\text{C}$ ; the numbers indicate the samples

With an easy and fast sample preparation, solutions of the polymers under investigation can be deposited in microtiter plates (Fig. 11). After evaporating the solvent, the phase morphology can be analysed directly. Due to limited magnification of the used experimental set-up the lowest domain size that can be resolved is about 0.24  $\mu\text{m}$ . Lower domain sizes have to be analysed by more sophisticated microscopic techniques.

It is clear that the described microscopic method can be used only for first and very preliminary information. The optical microscopy data alone cannot be used to evaluate the phase separation behaviour of the present copolymers. Combining these data, however, with the results of HPLC and DSC, a clear picture on phase separation can be obtained.

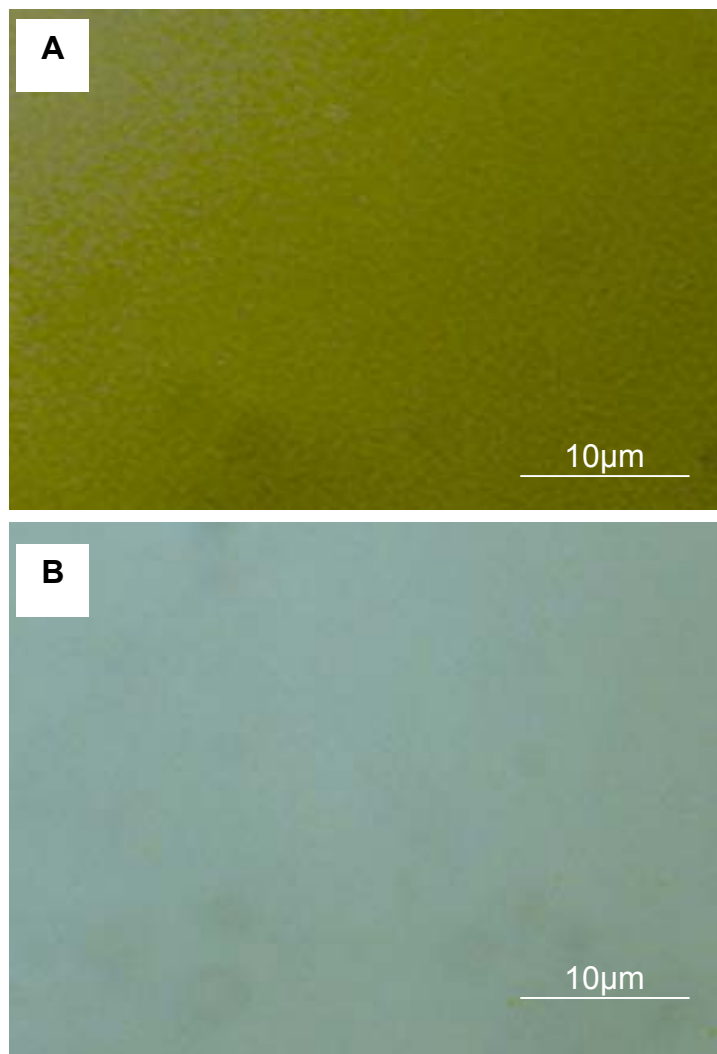
Optical micrographs of samples 9 and 14 are shown in Fig. 12. Clearly, phase separation can be observed in sample 9 with domain sizes ranging from 0.5 to 1  $\mu\text{m}$ . Sample 14 does not show different domains indicating that, if any, phase separation occurs to a much lower extent. This is in perfect agreement with the HPLC and DSC results for these samples.



**Fig. 11.** Deposition of sample solutions in a microtiter plate for microscopic investigations

## Conclusion

Random styrene-ethyl acrylate copolymers of different compositions and molar masses were prepared efficiently and reproducibly by parallel synthesis set-ups. The chemical compositions and the molar masses of the copolymers were analysed by fast spectroscopic and chromatographic techniques. It was shown that the reproducibility of the analytical approach is sufficiently good for high-throughput applications. Molar masses by high-throughput SEC and chemical composition by spectroscopy deviate not more than 15% and 1%, respectively, from the conventional techniques. The reproducibility of the gradient HPLC system and the calculated compositions are very good. With these high-throughput techniques we are able to describe reproducibly the chemical heterogeneity and the molar mass distribution with time savings of 90% or more. Using fast methods of DSC and light microscopy, the phase separation behaviour of the copolymers was studied. The results of these techniques are in very good agreement with the gradient HPLC data.



**Fig. 12.** Optical micrographs of samples 9 (A) and 14 (B) obtained by light microscopy in the transmission mode

## **Experimental part**

### *Copolymers*

Fifteen styrene-ethyl acrylate copolymers were synthesised in parallel in a Polymer Laboratories PL-SP 260 high temperature sample preparation instrument. Freshly distilled destabilized styrene and ethyl acrylate, recrystallised initiators and distilled solvents were used. The compositions of the reaction mixtures are given in Tab. 1. High temperature screw-neck vials of 4 mL volume were used. The reaction mixtures were agitated at a temperature of 70°C. The polymerisation time for the low-conversion copolymers was 1 h and for the high-conversion samples 20 h. The selection of initiators and the use and amount of solvents were optimised in preparatory experiments to avoid cross-linking. After polymerisation the copolymers were precipitated in methanol and dried in vacuum at 40°C.

### *Chromatographic system*

An Agilent 1100 Series HPLC modular system (Agilent Technologies GmbH, Böblingen, Germany) comprising a quaternary pump, an auto-sampler and a column

oven was used. For data collection and processing the software package 'WinGPC-Software' (Polymer Standards Service, Mainz, Germany) was used.

Just one sample preparation was necessary for each SEC and HPLC technique. For SEC 3 mg of the copolymer were dissolved in 1 mL THF, for HPLC 1 mg of the copolymer was dissolved in 1 mL THF-ACN 50:50. All copolymers were filtered through a 0.45  $\mu\text{m}$  filter before analysis. The injection volume was 10  $\mu\text{L}$  for all copolymers.

### *Columns and mobile phases*

A high speed linear PL Rapide M Column from Polymer Laboratories Ltd, UK, was used for the SEC measurements. The dimensions of the column were 15x0.75 cm I.D., the average particle size was 5  $\mu\text{m}$ . The flow rate was 2 mL/min; the mobile phase was THF.

For the HPLC measurements a high-throughput Luna reversed phase column (C18) of Phenomenex was used with a solvent gradient of acetonitrile and tetrahydrofuran, see Tab. 2. The column size was 3x0.46 cm I.D., the particle size was 3  $\mu\text{m}$ , and the pore size was 100  $\text{\AA}$ . A flow rate of 2 mL/min was used and the column temperature was 35°C.

### *Detectors*

Agilent 1100 Series refractive index detector; temperature: 35°C.

Agilent 1100 Series variable wavelength detector.

Polymer laboratories evaporative light scattering detector ELS 1000; gas flow: 1 mL/min; nebulizer temperature: 40°C; evaporation temperature: 80°C.

### *DSC*

DSC measurements were conducted using a Mettler Toledo STAR<sup>e</sup>-System DSC822<sup>e</sup> (Module of Mettler-Toledo GmbH, 400 W). The weight of the samples was 10 mg for each measurement. During the measurements N<sub>2</sub> gas was purged at constant flow rate. The samples were heated a first time from -50 to 110°C using a heating rate of 7.5 K/min. After cooling to -50°C using a cooling rate of 7.5 K/min the samples were heated a second time using the same heating conditions. The glass transitions were measured in the second heating run.

### *NMR*

NMR measurements were executed on a 400 MHz Bruker AVANCE spectrometer equipped with a 5 mm broadband probe. <sup>1</sup>H Measurements were conducted using a 30° pulse, 3.9 s acquisition time (32k data, 8278 Hz spectral width), 10 s relaxation delay, 512 scans, respectively. The polymers were dissolved in CDCl<sub>3</sub>. The concentration was 16.6 mg/mL.

### *Optical microscopy*

Highly concentrated THF solutions were dosed in a microtiter plate with holes of 96  $\mu\text{L}$ . The solvent was evaporated at ambient conditions. The same probe preparation

was carried out five times for each sample with the same results. The microscopic measurements were conducted with an Orthoplan optical instrument from Leitz, Germany.

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