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On-line coupling of high temperature GPC and ^{1}H NMR for the analysis of polymers

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Abstract

The on-line coupling of gel permeation chromatography (GPC) and ^{1}H NMR operating at temperatures up to 130 °C is presented. A NMR flow probe with a cell volume of 120 μL and a stop-flow valve are developed for on-flow and stop-flow NMR measurements at high temperatures. To maintain high and constant temperatures through the whole probe, the flow probe contains two separate heating circuits. A modified stop-flow valve is developed as a control device for enabling on-flow and stop-flow experiments at high temperature conditions. Heated transfer lines connect the flow probe with the high temperature GPC system. Due to their semicrystalline nature, polyolefins can be studied by liquid chromatography only at temperatures above 100 °C. The novel high temperature GPC–NMR system is used for the separation of complex polyolefins regarding their molar mass and for the analysis of different chemical structures. Blends of polyethylene, poly(methyl methacrylate), and ethylene-methyl methacrylate copolymers are separated according to the molar masses of the components. The compositions of the components are directly studied by on-line NMR. Moreover, the chemical composition distribution of an ethylene-methyl methacrylate copolymer sample is analysed. Differences between results of on-flow and stop-flow measurements are discussed.

Keywords: High temperature GPC–NMR; Flow probe; On-flow; Stop-flow measurements; Polyethylene

1. Introduction

The on-line coupling of high performance liquid chromatography (HPLC) and proton NMR is well established for the analysis of complex mixtures of organic compounds [1]. Coupled HPLC–NMR measurements are frequently conducted at ambient temperature with mobile phases comprising deuterated solvents, such as D_2O/acetonitrile or D_2O/methanol. For the analysis of synthetic polymers this coupling has been used only in a few cases where single mobile phases and ambient temperature conditions could be applied. Hatada et al. used GPC–NMR for the analysis of polymethacrylates [2–4]. He studied isotactic poly(methyl methacrylate) (PMMA) with different molar masses [5] to analyse the endgroups and the number-average molar mass as well as the chemical composition distribution (CCD) of (methyl methacrylate)-co-(butyl methacrylate) copolymers [6]. These polymers were studied at slow flow rates in fully deuterated solvents. Blends of isotactic and syndiotactic PMMA were also studied regarding the stereocomplexation in non-deuterated solvents [7].

Albert and Händel also reported about GPC–NMR measurements of polymers. In particular, they studied the chemical composition of poly(styrene-co-butyl acrylate) copolymers [1].

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Further studies on coupled HPLC–NMR have shown the power of liquid adsorption chromatography (LAC) for the analysis of polymers regarding the chemical composition [8–13]. It was shown that polyethylene oxides can be analysed with regard to functionality type distribution by identifying the different end groups [8]. In particular, liquid chromatography at the critical point of adsorption coupled to NMR allows the full assignment of the chemical structure and the degree of polymerisation of all oligomer species [10,11]. The critical point of adsorption was also used for the analysis of tacticity of poly(ethyl methacrylate)s by HPLC–NMR [12]. In further studies on copolymers, gradient HPLC–NMR was used for the analysis of the CCD of random poly(styrene-co-ethyl acrylate) copolymers [13]. The same copolymer system was also studied by GPC–NMR [14].

One major drawback of all previous experimental setups is the fact that measurements could only be conducted at ambient or slightly elevated temperatures. This is a major limitation, as very many polymers are not soluble at ambient temperature and in standard NMR solvents. Polyethylene, polypropylene, and polyolefin copolymers, for example, are semicrystalline polymers that dissolve in special solvents only at temperatures above 100 °C. Accordingly, all liquid chromatographic measurements, including GPC, must be conducted at such high temperatures. Typical mobile phases for high temperature GPC of polyolefins are 1,2,4-trichlorobenzene (TCB) and *o*-dichlorobenzene (ODCB). Other alternatives would be decalin and tetrachlorethylene.

In this contribution, we will present for the first time an on-line GPC–NMR setup that can be used at high operating temperatures, in particular useful for polyolefin analysis. Olefin homopolymers and copolymers as well as polyolefin blends will be separated with regard to molar mass by high temperature GPC, and analysed with regard to chemical composition by on-flow and stop-flow ^{1}H NMR.

2. Experimental

2.1. Samples

Two samples of polyethylene (PE) with number average molar masses of $M_n = 1.100$ g/mol ($M_w/M_n = 1.11$), and $M_n = 60.000$ g/mol ($M_w/M_n = 1.52$), respectively, one sample of poly(methyl methacrylate) (PMMA) with $M_n = 263.000$ g/mol ($M_w/M_n = 1.06$), and one sample of poly[(ethylene)-co-(methyl methacrylate)] (E-MMA) with $M_n = 10.600$ g/mol ($M_w/M_n = 2.34$) were studied. PE and PMMA were produced by PSS, Mainz, Germany. The E-MMA copolymer was prepared by the group of H. Höcker [15] at RWTH Aachen, Germany. The monomer composition measured by ^{1}H NMR was 87.6:12.4 mol% (E/MMA). Two polymer blends were prepared:

- blend A—PE (1.100 g/mol) + PMMA + E-MMA
- blend B—PE (60.000 g/mol) + PMMA + E-MMA.

The blend components were mixed in ratios of 1:1:1 (2 mg/mL for each component) in both cases.

2.2. GPC

A high temperature chromatograph Waters 150C (Waters, Milford, USA) operating at temperatures up to 150 °C was used. The pump of the Waters system was bypassed using an Agilent G1311A quarternary pump (Agilent, Waldbronn, Germany). Two sets of GPC columns were used: (1) SDV 10^7, 10^6, 10^5, 10^3, 100 Å, all of 10 μm average particle size, and column sizes of 300×8 mm I.D. (Polymer Standards Service GmbH, Mainz, Germany); (2) Styragel HT-2, HT-3, HT-4, HT-5, HT-6, all of 10 μm average particle size, and column sizes of 300×8 mm I.D. (Waters Inc., Eschborn, Germany). Operating temperature was 130 °C. 1,2,4-Trichlorobenzene (Synthesis or HPLC grade, Merck, Darmstadt, Germany) was used as the mobile phase.

The GPC–NMR system (except chromatograph Waters 150 C) was controlled by the Hystar software (Bruker BioSpin GmbH, Rheinstetten, Germany). The sample concentration was 2 mg/mL for each polymer component of the mixtures A and B. Concentrations of 3 mg/mL were used for the injection of the copolymer. The separation of the copolymer was performed with both the column set of Waters and a single column HT-4 (Waters). The injection volume was 300 μL of the sample solution for all measurements.

2.3. NMR

The NMR experiments were executed on a 400 MHz spectrometer AVANCE (Bruker BioSpin GmbH, Rheinstetten, Germany). The measurements were performed with a high temperature flow probe containing a 120 μL flow cell. The probe was an inverse detection probe equipped with a shielded pulsed field-gradient coil. The gradient strength was 53 G cm^{-1}. The 90 degree ^{1}H pulse was 6.7 μs. WET solvent suppression [16] was applied to 1,2,4-trichlorobenzene. Three frequencies were suppressed.

3. Results and discussion

The goal of the present development was the on-line coupling of high temperature GPC and ^{1}H NMR operating at temperatures up to 150 °C. To realize this setup, a new high temperature NMR flow probe was developed that allows flow experiments in the given temperature range. In addition to the flow probe, a novel interface was required which could be coupled to the NMR and GPC systems and enables for on-flow and stop-flow experiments at high temperature conditions.

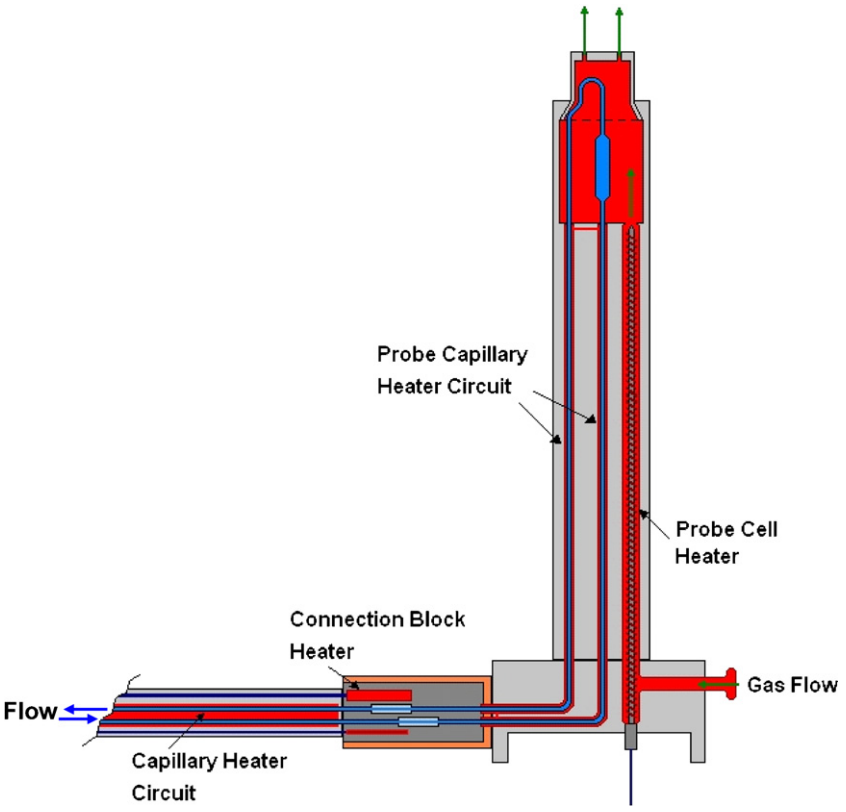
3.1. High temperature flow probe

A new high temperature NMR flow probe was designed which can operate at temperatures up to at least 130 °C. The probe has a flow cell with an NMR active volume of 120 μL. The outer diameter of the flow cell is 4 mm. It is a dual inverse $^{1}H/^{13}C$ probe with pulse field gradients. The design of the probe is shown in Scheme 1. It indicates the parts of the probe which are controlled by temperature. One important focus of the development was the temperature stability along the capillaries and the flow cell. Whereas standard flow probes possess a single heating circuit for the flow cell, this probe was designed with two different heating circuits since both the flow cell and the capillaries have to be heated. The first circuit heats the incoming and outgoing capillaries. They are placed in the same heating coil leading from the probe body up to the flow cell. The flow cell is heated separately by the second circuit. Both temperatures are controlled by the same variable temperature unit of the spectrometer. The two capillaries of the flow probe are connected to a heated transfer line. The connection of both the capillaries and the transfer line is embedded in a heated stainless steel block which is attached to the probe. The temperature of the flow cell and both capillaries can be regulated within an accuracy of ±0.1 °C.

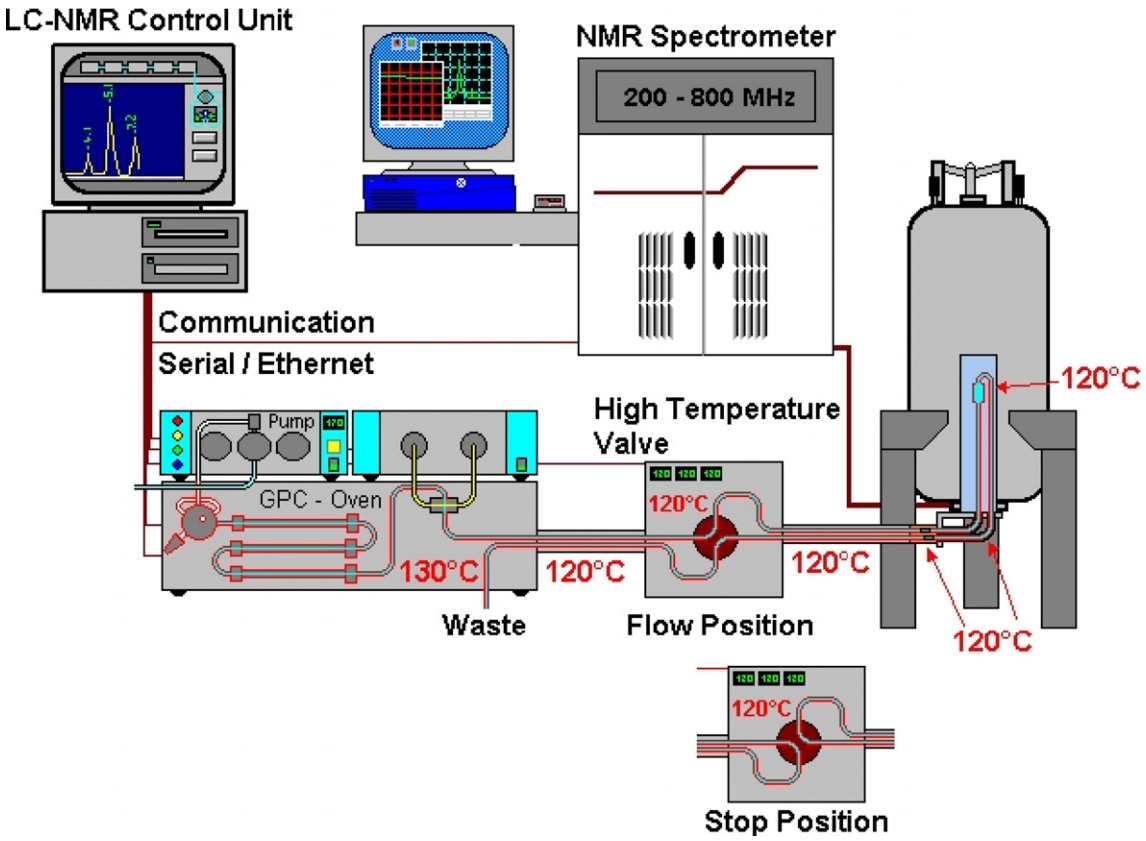
3.2. High temperature stop-flow valve

The stop-flow valve was developed as an interface for the GPC and the NMR. It physically connects the GPC with the flow probe. The valve is a two position device and guides the flow either from the GPC to the NMR or directly to the waste. The latter case corresponds to the stop-flow position (see Scheme 2). In this case, the flow probe is part of a closed circle. Since the stop-flow valve is fully controlled by the Hystar software, the flow can be stopped at any time. The pressure is then released to the waste line. Pumping can be resumed by guiding the flow either through the flow cell or into the waste. This setup allows on-flow experiments, automatic stop-flow experiments, and time-slicing.

Specific attention was paid to temperature control. The stop-flow valve consists of a heated two-position valve and two heated transfer lines. Both parts can be heated up to 150 °C. The stainless steel cylinder of the valve together with the ends of the stainless steel capillaries are placed within a heated block. Both the incoming and the outgoing transfer lines are heated in one control loop. The outgoing capillaries return to the GPC instrument to avoid any crystallization of the polymers before entering the waste container. Therefore, both capillaries are placed in the same heating circuit. Furthermore, the transfer line of the



Scheme 1. High temperature flow probe operating at temperatures up to 130 °C. The scheme is indicating the two separated heating circuits and the connection to the heated transfer lines.

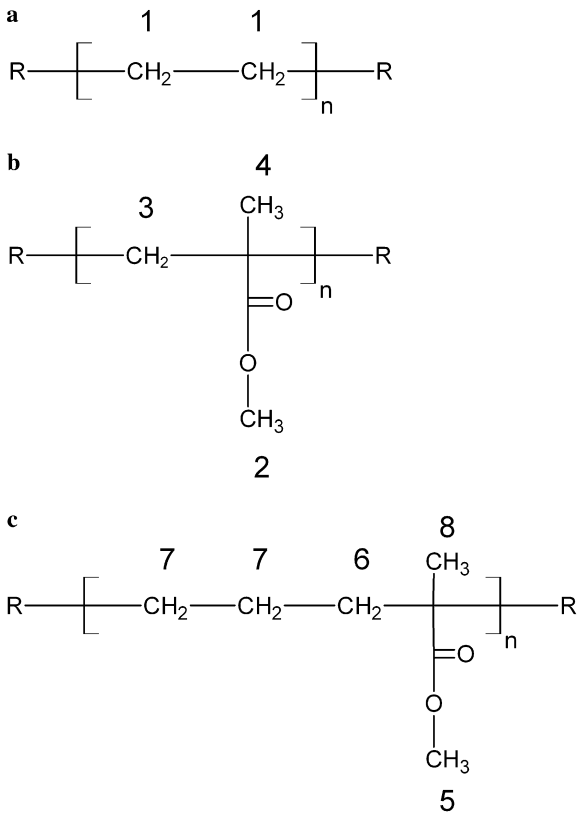


Scheme 2. Experimental setup of the high temperature GPC–NMR (GPC: 130 °C; LC probe, stop-flow valve and transfer lines: 120 °C).

stop-flow valve connected to the flow probe is also combined with a heating line which is controlling the temperature of the heating block attached to the probe. The temperatures of these lines can be regulated with an accuracy of ±1 °C. To summarize, five different circuits are responsible for controlling the temperature of the stop-flow valve including transfer lines as well as the flow probe. This setup is expected to maintain the higher temperature through the whole flow system (Scheme 2).

3.3. High temperature GPC–NMR coupling

As indicated in Scheme 2, the high temperature GPC system is combined with the NMR instrument via the stop-flow valve. The transfer line of the stop-flow valve attached to the GPC is connected to the columns. The columns are placed in the heated column compartment of the GPC at temperatures up to 150 °C. These temperatures are required to enable for good solubility of the polymers. The operating temperature of the studied polymers was 130 °C. To improve the flow stability of the GPC system, an external Agilent quaternary pump was attached the GPC–NMR system. It is bypassing the internal GPC pump and can be fully controlled by the Hystar software. The external HPLC pump can be used due to the fact that the solvent delivery system can operate at ambient conditions. The solvent is heated as soon as it enters the heated GPC system.



Scheme 3. Structures of the polymers. (a) PE, (b) PMMA, (c) E-MMA copolymer.

The GPC system contains an autosampler and an injector. Both devices are kept at a temperature of 130 °C. In this case, the polymer sample solution is at operating temperature before the injection. This is important to ensure homogeneously dissolved samples.

As is shown in Scheme 2 the flow is guided as follows. After injection, the sample is transferred to the columns. The columns will separate the sample with respect to molecular size. The largest macromolecules will elute first followed by molecules of lower sizes. In the case of an on-flow experiment, the separated components will flow through the transfer lines to the NMR flow probe passing the stop-flow valve and entering the flow cell. During the NMR measurements, the flow returns back to the heated GPC system, again passing the stop-flow valve. Finally, it is leaving the GPC to the waste container via a tubing of a larger diameter.

3.4. Polymer applications

To evaluate the capabilities of the novel high temperature GPC–NMR system, two polymer blends comprising PE and PMMA homopolymers and an E-MMA copolymer were prepared and analysed, see blends A and B in the experimental part. The molar masses of PE were $M_n = 1.100$ g/mol and $M_n = 60.000$ g/mol, accordingly, for blends A and B. To dissolve the blended components in TCB, a temperature of 130 °C was required. The same temperature was used as the operating temperature for the whole GPC system. The NMR accessory was kept at a temperature of 120 or 130 °C, respectively.

On-flow and stop-flow experiments of both blends and the copolymer were carried out. All experiments were performed with 1,2,4-trichlorobenzene as the mobile phase. WET suppression was applied to the intrinsic solvent signals, i.e., three aromatic proton signals were suppressed. No lock solvent was added. The GPC column sets were chosen to cover a wide range of molar masses (100–1.000.000 g/mol).

Figs. 1 and 2 show the on-flow runs of the two blends. Two data sets were generated for each run. Fig. 1a shows the raw data including the impurities of the solvent. Fig. 1b corresponds to the corrected plot by subtracting signals, which correspond to impurities of the solvent. The signals of these impurities were found in "TCB for synthesis", in redestilled TCB, as well as in the most expensive "TCB for HPLC". In all cases the sample concentration was 2 mg/mL, the injection volume was 300 μL.

The separation of blend A is shown in Fig. 1. As can be seen in Fig. 1a, due to impurities in the TCB there are residual solvent signals appearing at about 1.18, 1.28, 2.15 and 2.3 ppm. These signals partially overlap other signals that are due to the polymer components. To enhance the sensitivity of the polymer signals, the residual solvent signals are subtracted resulting in a corrected contour diagram as given in Fig. 1b. Clearly, the corrected plot gives much better information on the composition of the sample components. In the present chromatographic system, the elution of the blend components is in the order of decreasing molar mass. Accordingly, the highest molar mass PMMA elutes first, followed by the E-MMA copolymer. The very low molar mass PE elutes last. This elution order can be clearly seen in the GPC–NMR contour plot given in Fig. 1b. The spectra of the early eluting fractions show signals for PMMA but not for ethylene. In contrast, the late eluting fractions exhibit signals for ethylene but not for MMA and can be assigned to PE. Between the two homopolymers, the elution of the copolymer can be measured by detecting signals for both MMA and ethylene. Fig. 1b also shows the vertical projections taken from the sum of the NMR signals. It can be used as the chromatogram which also indicates three separated peaks.

The separation and analysis of blend B is presented in Fig. 2. This blend contains PE with a higher molar mass and, accordingly, the elution order of the blend components is different. PMMA elutes first, followed by PE and the copolymer. In this case, the interpretation of the contour plot is not straightforward. This is due to the fact that the elution curves of the blend components overlap significantly. Accordingly, the early eluting fraction of PMMA exhibits a signal for PE and vice versa, the PE homopolymer exhibits signals for PMMA. The insufficient separation of the blend components can be caused by different effects. First of all, the resolution of the column set must be adequate. Due to a certain axial dispersion of the columns resolution may decrease. A much more important parameter, however, is the chemical composition distribution of the blend components. Same elution volumes mean same hydrodynamic volumes but not necessarily same molar masses. For chemically different species, at the same elution volume molecules of different molar masses and chemical compositions may co-elute. Finally, the large volume of the NMR detector cell must be taken into account. Due to non-laminar flow and diffusion effects a significant band broadening may take place that causes partial overlap of the component elution peaks. Therefore, a better assignment of the signals can be given from the tallest peaks of each separated region, which is described later.

Figs. 3 and 4 show different traces of the on-flow experiments taken at the peak maximum of the corresponding compound. These traces clearly indicate the different components of the blends. Three spectra are displayed for each mixture. Fig. 3 shows the traces of mixture A. The signals of the PMMA (a) correspond to syndiotactic species of this homopolymer. The second trace (b) contains the copolymer. It is a block copolymer where MMA is mainly isotactic. The tacticity of the corresponding PMMA homopolymers was already reported by Hatada et al. [4]. The third trace contains only the PE component. It even shows the CH_3 endgroup at 0.86 ppm. The signal-to-noise ratio of the CH_3 group is not sufficient enough for a precise molar mass calculation. Anyway, a rough estimation of M_n (~2700) at the peak maximum could be done. This value is higher than the GPC determination.

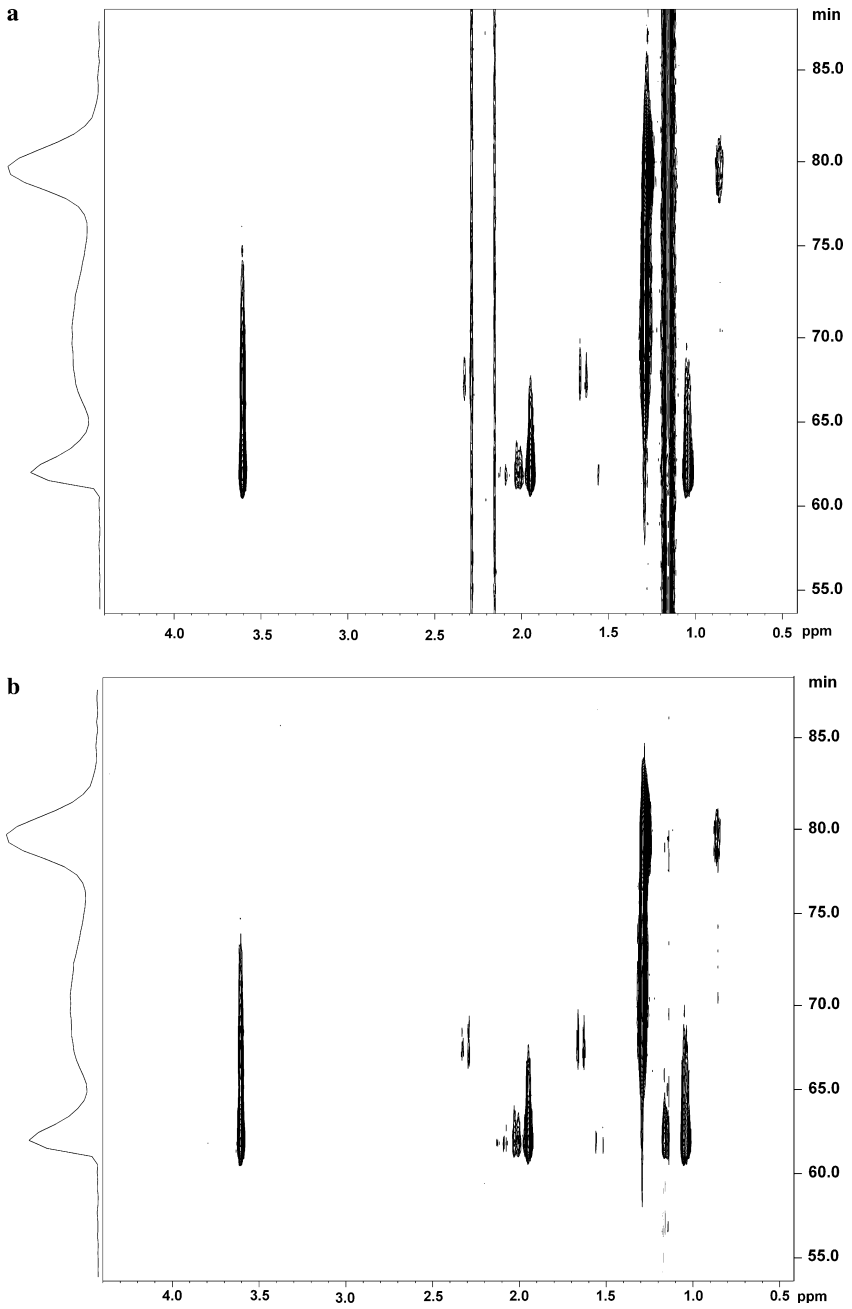


Fig. 1. (a) GPC–NMR (400 MHz) on-flow run of mixture A at 130 °C in 1,2,4-trichlorobenzene. (flow rate 0.5 mL/min, concentration 2 mg/mL of each polymer, 300 μL injection volume, 5 Waters columns, 24 scans per FID, 1.24 s repetition delay). Projection is generated by adding the vertical traces. (b) Corrected on-flow run of (a) by subtraction of signals corresponding to the impurities of 1,2,4-trichlorobenzene. Projection is generated by adding the vertical traces.

The traces of the first and second eluting peaks (RT = 44.2 min, RT = 46.1 min) of mixture B (Fig. 4) show an overlap of PMMA and PE due to the smaller differences of molar masses at these retention times. In this case, the first eluting peak at 44.2 min representing PMMA already contains PE (indicated by the signal at 1.291 ppm). The second trace shows a maximum of PE. However, it also clearly shows signals of PMMA. Due to the different intensities, the NMR signals could be unambiguously assigned to the polymer components. The third trace represents the copolymer only.

It should be noted that the signal-to-noise ratio is sufficient for even a quantitative analysis of the monomer compositions of the copolymer. However, we should firstly assign the full structure of the copolymer sample. It was assumed that different structural units give similar chemical shifts and, therefore, overlapping peaks of the copolymer are obtained. Thus, an HSQC (Fig. 5) was measured off-line as well. This experiment confirms that the signal of the α-CH_3 group of the MMA totally overlaps with the signal of the CH_2 groups of the ethylene units. Therefore, the ethylene content was calculated from the difference of the

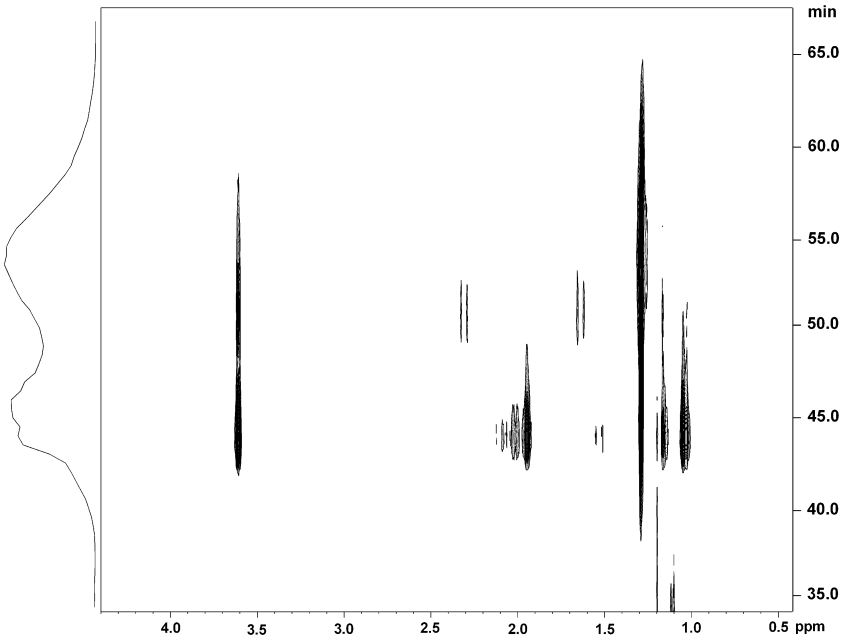


Fig. 2. GPC–NMR (400 MHz) on-flow run of mixture B at 120 °C in 1,2,4-trichlorobenzene (flow rate 0.5 mL/min, concentration 2 mg/mL of each polymer, 300 μL injection volume, 5 PSS columns, 24 scans per FID, 1.24 s repetition delay) corrected by subtraction of the impurities of 1,2,4-trichlorobenzene. Projection is generated by adding the vertical traces.

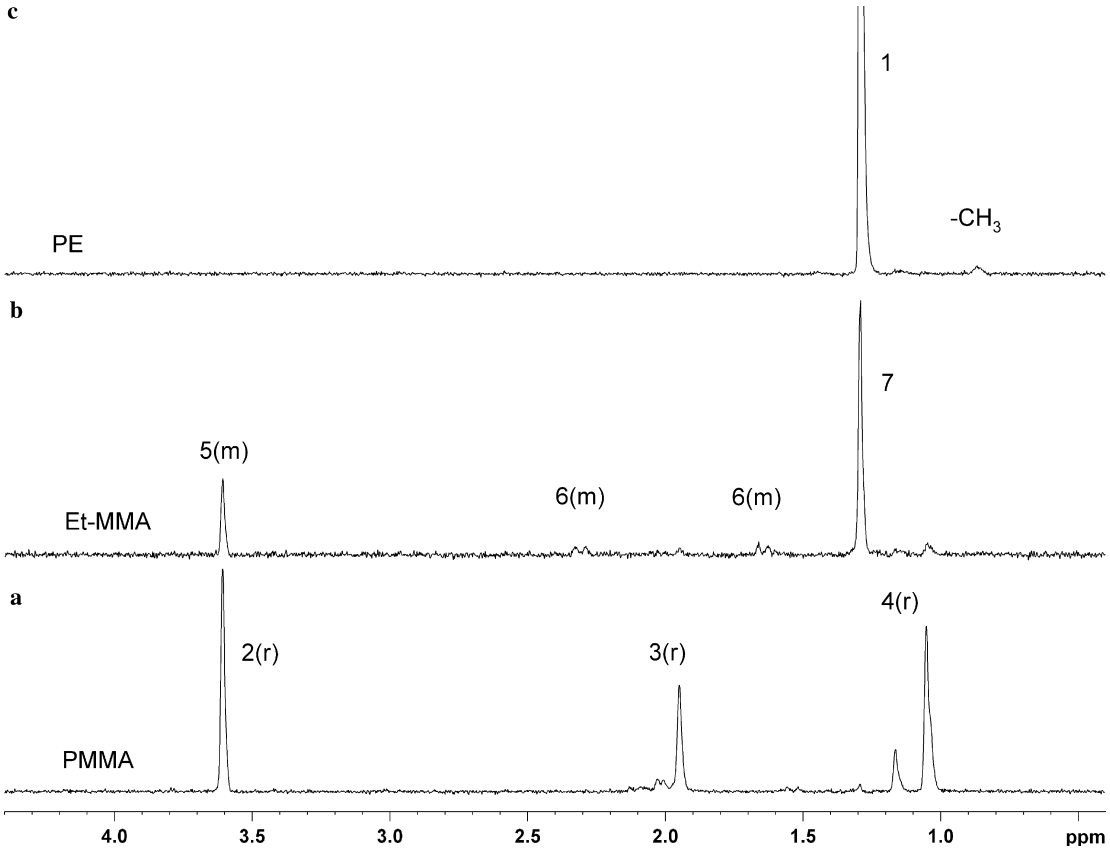


Fig. 3. ^{1}H traces of the on-flow run of Fig. 1b (labels according to Scheme 3) (a) PMMA (RT = 60.5 min); (b) E-MMA copolymer (RT = 66.0 min); (c) PE 1.100 g/mol (RT = 79.4 min).

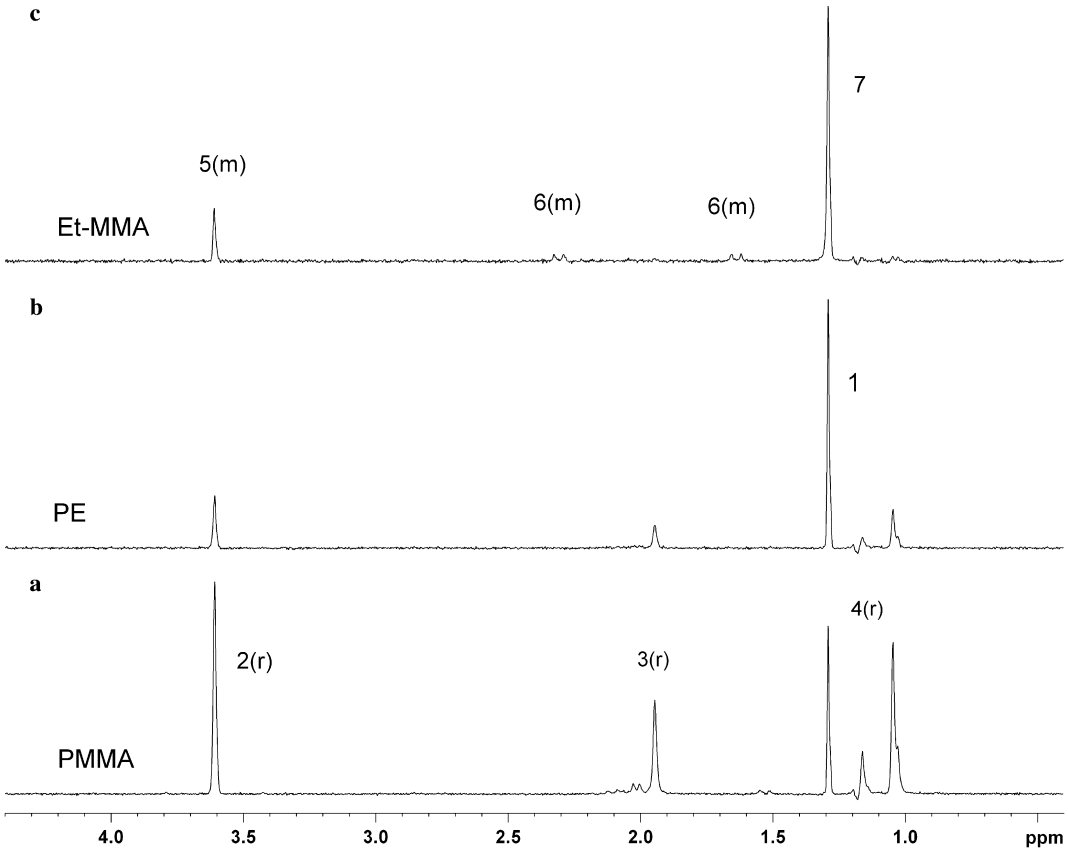


Fig. 4. ^{1}H traces of the on-flow run of Fig. 2 (labels according to Scheme 3) (a) PMMA (RT = 44.2 min); (b) PE 60.000 g/mol (RT = 46.1 min); (c) E-MMA copolymer (RT = 50.6 min).

sum of signals 7 + 8 m + 8r and the methoxy group 5(m, r) of MMA. While the signals indicated by (r) are belonging to the syndiotactic part of MMA, the signals of (m) are assigned to the isotactic MMA. Moreover, the sample contains also branched parts. In this case, the CH_3 group at 0.86 ppm (Fig. 5) could be assigned to a side chain of ethylene by including HMBC data. The branching point (presence of –CH–) is already indicated in the HSQC.

In a second set of experiments, the chemical composition distribution of the E-MMA copolymer was investigated by using on-flow and stop-flow experiments. To achieve an excellent separation the first measurement was done by using column set 1 (Waters). This separation is presented as an on-flow run in Fig. 6. In this case, 24 scans per FID were recorded. In order to compare on-flow and stop-flow experiments single column separations of the copolymer were performed by using the HT-4 column. The on-flow run was carried out by using only 8 scans per FID to accommodate the chromatographic separation, see Fig. 7. The stop-flow run was set up as a time-slicing experiment with a slicing time of 60 s, see Fig. 8. Both experiments are presented as stacked plots in Figs. 7 and Fig. 8. Because of using only one column the retention times are much shorter than for 5 columns. However, the separation is sufficient for a determination of the chemical composition as a function of elution time. NMR is one of the best detectors which will deliver the composition of the copolymer at any retention time without further calibrations.

The distributions of the different structural moieties corresponding to MMA and ethylene can be seen and correlated with the corresponding molar masses. The quantification of the chemical composition based on the on-flow data for 5 columns is presented in Fig. 9. This figure also represents the NMR projections of two separate signals (1.29 and 3.61 ppm) taken from the on-flow run. These projections correspond to the chromatograms of the individual monomer units. Whereas the dashed line represents only MMA, the solid line contains the sum of the ethylene CH_2 and the α-CH_3 group of the MMA. These intensity lines already indicate that MMA elutes at shorter elution times. Ethylene, however, has a much higher intensity and elutes also at longer elution times where no MMA is detected anymore. The data points of Fig. 9 represent the real composition of the monomer units. The figure shows that the MMA monomer units are mainly distributed at higher molar masses. A maximum of MMA (46.2 mol%) could be observed at RT = 63.5 min. On the other hand, the chemical composition distribution starts with a higher ethylene content at the very beginning of the elution curve (corresponding to high molar masses). This region contains

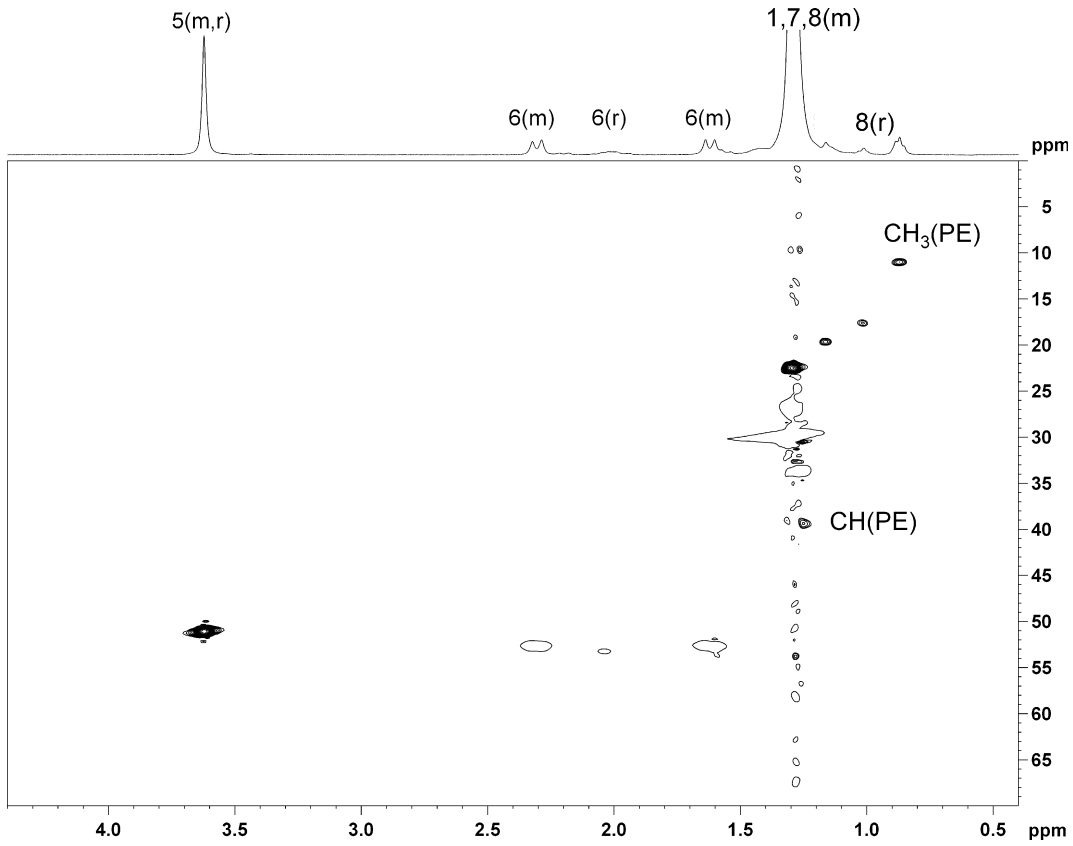


Fig. 5. Off-line ^{1}H–^{13}C gradient HSQC of poly[(ethylene)-co-(methyl methacrylate)] at 100 °C in 1,2,4-trichlorobenzene (no lock solvent added), 8 scans per increment, 256 increments, 1k × 1k FT; Empty cross peaks correspond to CH_2, filled cross peaks are CH or CH_3 (labels according to Scheme 3).

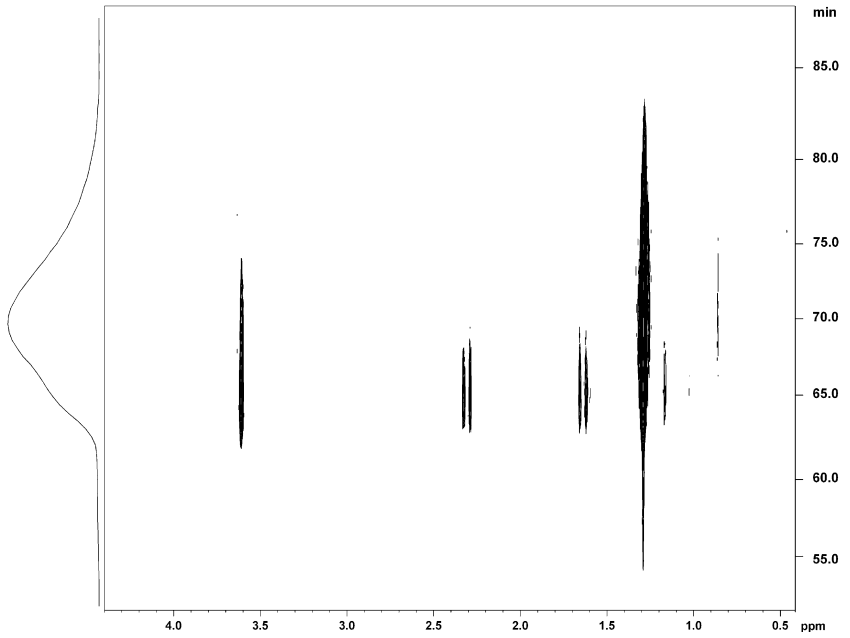


Fig. 6. GPC–NMR (400 MHz) on-flow run of poly[(ethylene)-co-(methyl methacrylate)] at 120 °C in 1,2,4-trichlorobenzene (flow rate 0.5 mL/min, concentration 3 mg/mL, 300 μL injection volume, 5 Waters columns, 24 scans per FID, 1.24 s repetition delay) corrected by subtraction of the impurities of 1,2,4-trichlorobenzene. Projection is generated by adding the vertical traces.

very small amounts of sample as indicated by the projections. The composition then passes a minimum of ethylene (RT = 63.5 min) and finally results into almost pure ethylene (low molar masses). Therefore, it can be concluded that the sample is very heterogeneous. It might be that it even contains PE.

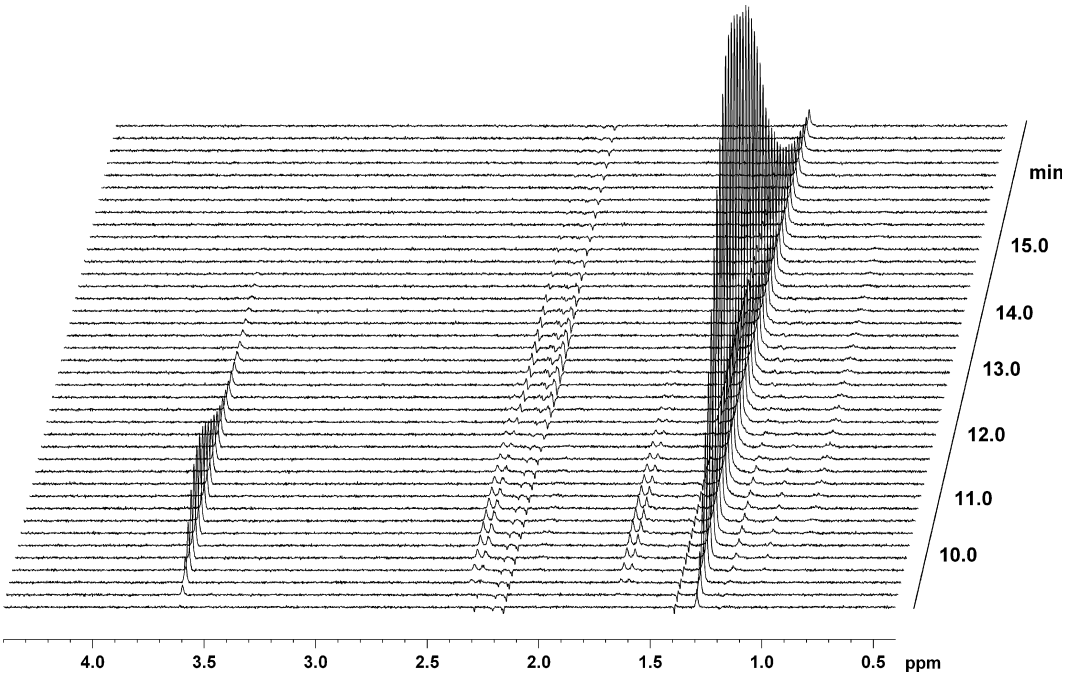


Fig. 7. GPC–NMR (400 MHz) on-flow run of poly[(ethylene)-co-(methyl methacrylate)] at 120 °C in 1,2,4-trichlorobenzene (flow rate 0.5 mL/min, concentration 3 mg/mL, 300 μL injection volume, 1 Waters HT-4 column, 8 scans per FID, 1.24 s repetition delay) corrected by subtraction of the impurities of 1,2,4-trichlorobenzene.

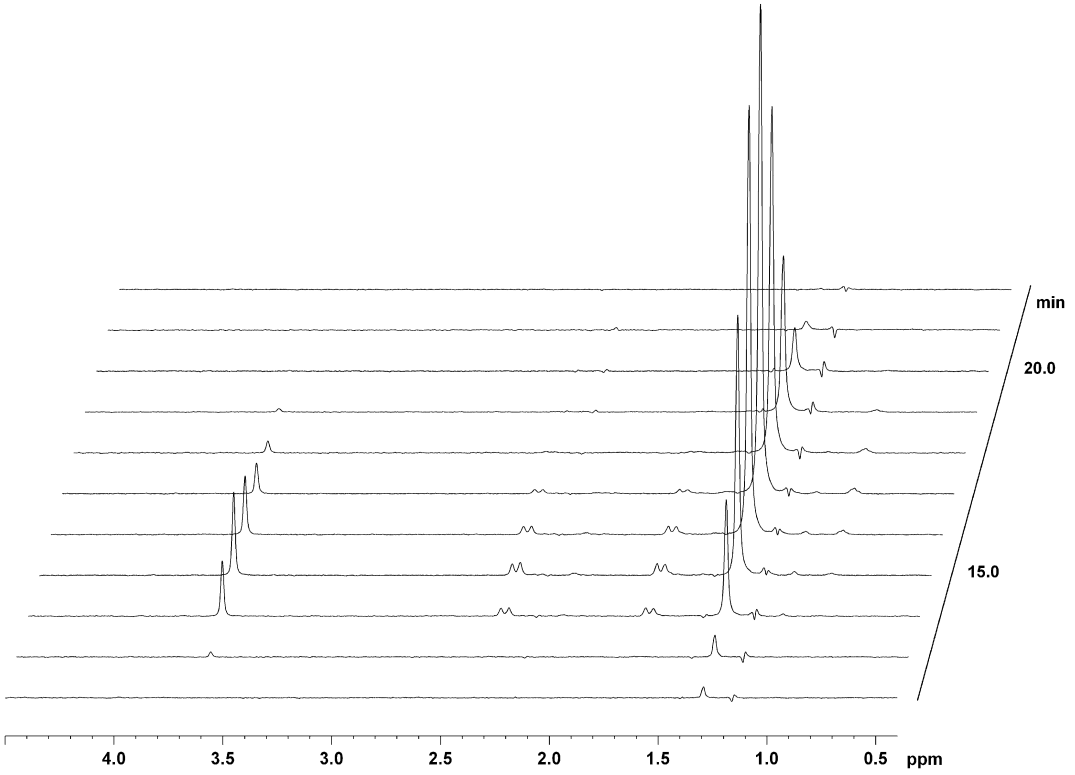


Fig. 8. GPC–NMR (400 MHz) stop-flow run with time slicing (60 s slice time) of poly[(ethylene)-co-(methyl methacrylate)] at 120 °C in 1,2,4-trichlorobenzene (flow rate 0.5 mL/min, concentration 3 mg/mL, 300 μL injection volume, 1 Waters HT-4 column, 16 scans per FID, 8s repetition delay, 1,2,4-trichlorobenzene).

Fig. 10 shows the quantification of the chemical composition based on Figs. 7 and 8. The empty points represent the on-flow data whereas the filled data belong to the stop-flow experiments. Again, the NMR projections are also included in this figure. The on-flow data reflect a similar curve as the one using 5 columns. The

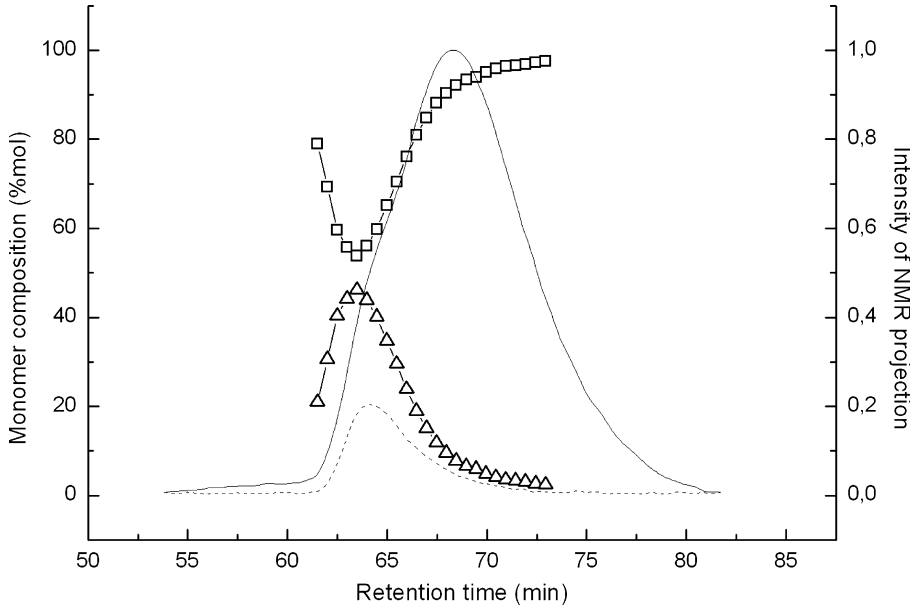


Fig. 9. Monomer composition of poly[(ethylene)-co-(methyl methacrylate)] vs. retention time calculated from Fig. 6 for 5 columns (□ = mol% ethylene, Δ = mol% MMA) solid line, NMR projection of the signal at 1.29 ppm; dashed line, NMR projection of the methoxy group (both taken from Fig. 6).

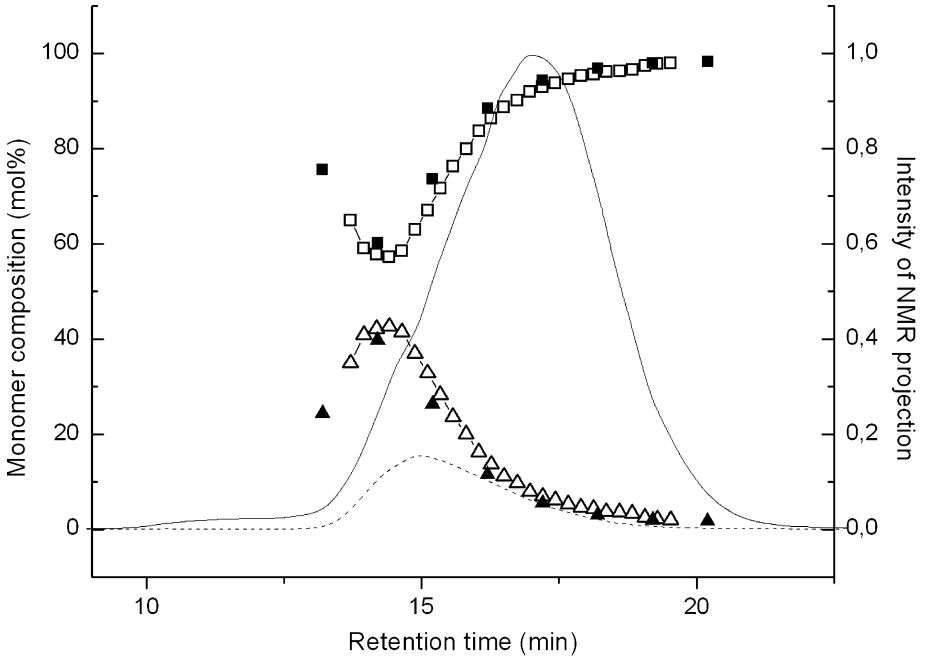


Fig. 10. Monomer composition of poly[(ethylene)-co-(methyl methacrylate)] vs. retention time calculated from Fig. 7 (on-flow) for 1 column (□, mol% ethylene; Δ, mol% MMA) and Fig. 8 (stop-flow) for 1 column (■, mol% ethylene; ▲, mol% MMA) solid line, NMR projection of the signal at 1.29 ppm, dashed line, NMR projection of the methoxy group (both taken from Fig. 8).

separation, however, does not have the same performance indicated by the lower MMA content (37.7 mol% at RT = 10.1 min) of the maximum compared to Fig. 9. It also should be noticed that the stop-flow data are in good agreement with the on-flow experiment. According to Fig. 10, the stop-flow data are matching the chemical composition of MMA and ethylene of the on-flow run for the same retention times. This behaviour is very important, especially for cases of lower concentration of the polymer where on-flow data will not deliver sufficient sensitivity. In this case, stop-flow data should represent the determination of the chemical composition. Therefore, the composition was also determined by using shorter slicing times to prove the reliability of the data. Fig. 11 shows the comparison of the chemical composition as the function of the elu-

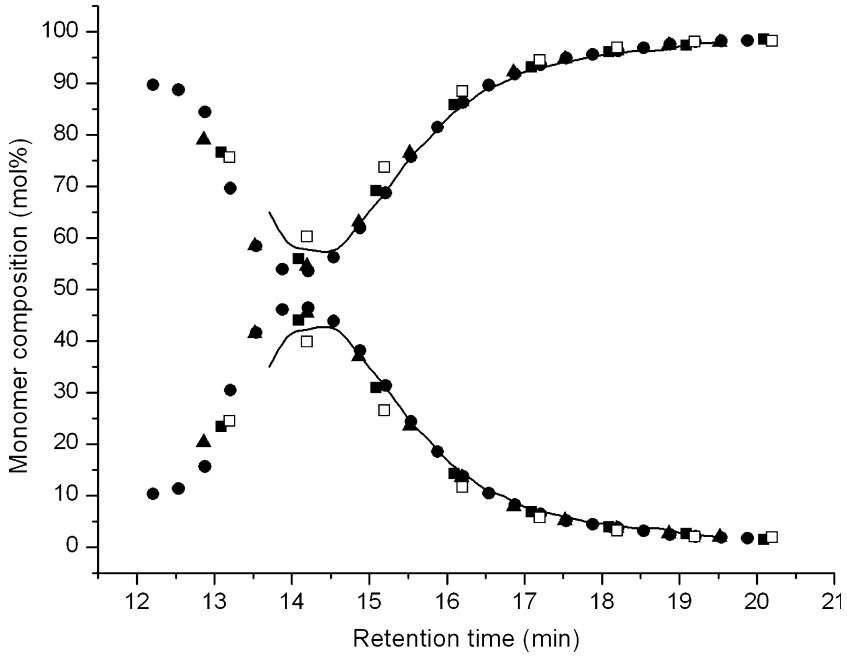


Fig. 11. Monomer composition of poly[(ethylene)-co-(methyl methacrylate)] vs. retention time for stop-flow at different slicing times for 1 column (□, slicing time of 60 s (recycle delay 7 s); ■, slicing time of 60 s (recycle delay 1.1 s); ▲, slicing time of 40 s, ●, slicing time of 20 s); solid line, on-flow data taken from Fig. 10.

tion time measured with slicing times of 20, 40, and 60 s in comparison with the on-flow data. This figure contains stop-flow data which were recorded with conditions of the on-flow experiment as well as longer relaxation delays to evaluate the position of the retention times of the on-flow and stop-flow experiments. It turns out that both the stop-flow and on-flow data are in good agreement. As a consequence the chromatogram was not affected by several stops. In this case, stop-flow experiments can also be used for determining the chemical composition. To prove this point further all traces of the on-flow and stop-flow runs containing polymer signals were co-added. In this case, the total composition should be obtained. It was found that the sum of all traces yielded 87.9:12.1 mol% and 87.7:12.3 mol% (E/MMA) for on-flow runs by using 1 and 5 columns, respectively. These ratios are in very good agreement with the bulk measurement (87.6:12.4 mol%). In case of the stop-flow experiments, similarly good values of the total composition were determined (86.9:13.1, 86.3:13.7, 86.8:13.2 mol%) for the slicing times 20, 40, and 60 s, respectively.

It is also evident from Figs. 9–11 that MMA is mainly distributed at lower retention times corresponding to higher molar masses. Ethylene, however, is mainly eluting at lower molar masses. This behaviour is in agreement with recently published GPC–FTIR data [17]. Moreover, it can be concluded that the sample is a heterogeneous copolymer with MMA-rich units at higher molar masses and ethylene-rich units at lower molar masses. The high intensity of ethylene units at higher retention times proposes PE of lower molar masses.

4. Conclusion

Finally it can be concluded that the new setup of the high temperature GPC–NMR opens new possibilities for the analysis of homopolymers, copolymers, and polymer blends. Especially, polyolefins can now be analysed with the new accessory. This very powerful tool can be the basis for a number of different applications of flow NMR at high temperatures. It is especially useful for the analysis of polymers which are soluble at higher temperatures.

We have demonstrated that it is possible to analyse blends of homopolymers and copolymers by using on-line GPC–NMR at temperatures up to 130 °C. It is capable to separate polymers with respect to differences of molar masses. In particular, copolymers consisting of ethylene and methyl methacrylate could be investigated regarding their chemical composition. The NMR used as the detector allows the direct quantification of the monomer composition at different elution volumes for both on-flow and stop-flow experiments.

It will be part of forthcoming papers to show further applications of the high temperature GPC–NMR. In particular other polyolefins will be investigated. Moreover, it will be dealt with the possibilities of studying branches.

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