Flame ionization detection for the determination of the chemical composition distribution of non-UV absorbing copolymers

Citation for published version (APA):

van Doremaele, G. H. J., Kurja, J., Claessens, H. A., & German, A. L. (1991). Flame ionization detection for the determination of the chemical composition distribution of non-UV absorbing copolymers. *Chromatographia*, 31(9-10), 493-499. <https://doi.org/10.1007/BF02262395>

DOI:

[10.1007/BF02262395](https://doi.org/10.1007/BF02262395)

Document status and date:

Published: 01/01/1991

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Flame Ionization Detection for the Determination of the Chemical Composition Distribution of Non-UV Absorbing Copolymers

G. H. J. van Doremaele¹ / J. Kurja¹ / H. A. Claessens^{*2} / A. L. German¹

¹Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Eindhoven University of Technology, P.O.Box 513, 6500 MB Eindhoven, The Netherlands.

²Laboratory of Instrumental Analysis, Department of Chemistry, Eindhoven University of Technology, P.O.Box 513, 5600 MB Eindhoven, The Netherlands.

Key Words

Column liquid chromatography
Flame ionization detection
Poly(styrene-co-methyl acrylate)
Poly(methyl acrylate-co-*n*-butyl acrylate)
Chemical composition distribution

Summary

This investigation is focused on the development of HPLC with subsequent flame ionization detection as a tool to determine the chemical composition distribution of non- or poorly UV absorbing copolymers. Experiments were carried out with poly(styrene-co-methyl acrylate) and poly(methyl acrylate-co-*n*-butyl acrylate) copolymers. HPLC combined with FID provided useful qualitative information. Quantitative information could be obtained after calibration.

Introduction

It is generally recognized that the chemical composition distribution (CCD) of a specific copolymer is one of the important factors determining its final product properties. Many investigations have been devoted to developing methods for the accurate determination of the CCD. Nowadays, in principal, quantitative information can be provided by gradient thin layer chromatography (TLC) in combination with Flame Ionization Detection (TLC/FID) [1]. This technique has been investigated for e.g. poly(styrene-co-acrylonitrile) and several styrene-methacrylate copolymers [2–7]. More recently the most widely investigated method for the determination of CCDs is gradient High-Performance Liquid Chromatography (HPLC) [8–11]. In the separation of copolymers with gradient elution, precipitation and/or adsorption-desorption mechanisms play a dominant role. A sufficient difference in polarity of both the different monomeric units of a specific copolymer is a prerequisite for a successful separation. The main advan-

tages of HPLC compared to TLC are the improved separation efficiency and reproducibility.

Gradient HPLC is in many cases performed in combination with a UV detector, which is suitable for many compounds. However, this is a limitation in some cases, for instance in poly(co-methacrylate) and poly(styrene-co-methacrylate), the methacrylate monomeric units can hardly be detected, because the extinction coefficient of the ester groups is too low. In the case of poly(styrene-co-methacrylate) the detection is generally carried out with UV detection at 254–260 nm. This results in serious detection problems in the methacrylate-rich copolymers. In order to overcome this problem, alternative detection methods have been studied. One possibility is to use an evaporative light-scattering mass detector [12–15]. The eluent together with the (co)polymer is evaporated in air and the polymer particles so formed are subsequently detected by light scattering. These detectors are not straightforward, since the particle size distribution (PSD) produced by the nebulizer depends on the (co)polymer composition and eluent composition and the PSD strongly influences the detector response.

Another possibility is to use a moving belt flame ionization detector [16–18]. Here, the column effluent is sprayed onto a transport device, for example a moving quartz fibre, placed around a wheel, rotating in a heated housing. Subsequently, the solvent is evaporated by heating. The non-volatile solutes, i.e. (co)polymers, retained on the fibre can be detected by an FID. Compared to UV-detectors, FID detectors are more sensitive and suitable for the detection of copolymers which contain few or even non UV chromophores like, for instance, the methacrylate-rich copolymers. This paper describes an investigation of the feasibility of using HPLC combined with FID detection (LC/FID) to determine the CCD of poly(styrene-co-methyl acrylate) and poly(methyl acrylate-co-*n*-butyl acrylate).

Batch emulsion copolymers of styrene and methyl acrylate are known to often exhibit a bimodal CCD with one peak representing real copolymer molecules and another peak representing polymethyl acrylate [7, 19], which cannot be detected by means of a UV detector. This bimodality is caused by a strong composition drift during the emulsion copolymerization process.

Experimental

HPLC Equipment and Solvents

Gradient elution was performed with a system controller (Model 720) and two HPLC pumps (Model 510, Millipore-Waters Corp., Milford, MA, USA). A Waters Intelligent Sample Processor (Wisp) (Model 710) was used to inject 1–100 μL samples. A Waters Multi-wavelength Detector, Model 490, (operating at 260 and/or 235 nm) and a TRACOR model 945 LC/FID moving braid flame ionization detector were installed in series to monitor the eluent from the column.

HPLC solvents. Methanol (HPLC-grade) was obtained from Aldrich Chemicals (Brussels, Belgium). Dichloromethane (DCM) and n-heptane were from Merck (Darmstadt, FRG). n-Heptane was distilled before use. All solvents were filtered prior to use through a 0.45 μm filter. HPLC-grade water was prepared in-house. Subsequently, this was on-line purified by a precolumn, containing a DOWEX cation exchanger and an ODS packing material, (1 : 1), in order to remove organic impurities and alkali metals from the water. This prohibited a significant decrease or, in the case of 100 % water, even negative signals due to alkali metal interferences [17].

HPLC conditions for the copolymer analysis. All (co)-polymer samples were dissolved in THF prior to analysis. In the case of the separation of poly(styrene-co-methyl acrylate) a linear gradient of 18 minutes was applied ranging from a mixture of 90 % heptane, 9 % dichloromethane and 1 % methanol as the non-solvent to 100 % (DCM 10 % methanol) as the solvent (System I). The eluent flow rate was 0.5 mL/min using a normal phase Chromsep 5 μm silica cartridge column, 100 $\times$ 3.0 mm (Chrompack, Middelburg, The Netherlands) at room temperature. In the case of the separation of poly(methyl acrylate-co-n-butyl acrylate) copolymers a linear gradient of 13 minutes was applied ranging from a mixture of 80 % n-hexane, 18 % DCM and 2 % methanol as the non-solvent to 15 % n-hexane and 85 % (DCM + 10 % methanol) as the solvent (System II).

Polystyrene samples were isocratically eluted on a 5 μm Lichrospher C 18 column, 100 $\times$ 4 mm (Knauer, Berlin, FRG), at a flow rate of 0.6 mL/min; the eluents were THF and DCM with different percentages of MeOH.

The Tracor LC/FID detector was equipped with a continuous quartz braid to transport the column effluent, which is sprayed on by a suitable applicator. Subsequently the braid is passed through a solvent removal zone and into the analytical and cleaning flames. Several stainless steel and home-made silica applicators of i.d. 50 μm were used. The hydrogen and air flows were 130 and 400 mL/min, respectively, for the FID. The cleaning flame was fed by H_2 and O_2 flows of 600 and 300 mL/min, respectively. Small variations of the flows hardly affected the detector response. Base line correction (background subtraction) was always applied and the electronic filter was in the high position. Due to the heating of the two flames, an external vent was installed in order to maintain the FID housing block temperature at the desired setting. In this study, it turned out that the installation of the proper applicator with respect to the material and

internal diameter was very important. Also a sufficiently large eluent flow rate must be maintained in order to obtain a 100 % application of the eluate on the transporting silica braid.

Preparation of Copolymers

Chemicals. Styrene (S), methyl acrylate (MA) and butyl acrylate (BA) (Merck) were distilled under nitrogen at reduced pressure, and subsequently stored at 277 K under nitrogen. The initiator potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) (Merck p.a.), the chain-transfer agent n-dodecylmercaptan (NDM) (Fluka for synthesis), the emulsifier sodium dodecylsulphate (SDS) (Fluka purity $\approx$ 99 %), and the solvent toluene (Merck p.a.), were used as received. The water was distilled twice and stored under nitrogen. The initiator α , α' -azobis(isobutyronitrile) (AIBN) (Fluka p.a.) was recrystallized once from methanol.

Preparation of standard solution copolymers. The reference copolymers were synthesized by low-conversion solution copolymerization in toluene at 335 K for the poly(styrene-co-methyl acrylate) and at 323 K for the poly(methyl acrylate-co-n-butyl acrylate) copolymers. The total monomer concentration was 3 mol/L. The AIBN concentration was 8 mmol/L. Conversion and monomer feed ratio were measured by means of gas chromatography using toluene as the internal standard. Conversion was always kept below 10 mol% in order to prevent serious composition drift that would result in the formation of inhomogeneous copolymers. The solution copolymers were isolated and purified by pouring out the reaction mixture into a 15 fold excess of cold (273 K) hexane. The final products were dried at 328 K in a vacuum oven for at least 6 h at 10^{-1} Torr and finally for 8 h at 10^{-5} Torr. The average copolymer chemical composition was determined by means of ^1H NMR.

In Table I the chemical composition determined by ^1H NMR and the molecular mass determined by GPC of the standard low conversion solution (homogeneous in chemical composition) copolymers and of the emulsion copolymers are given. Polystyrene standards were used for the calibration of the GPC.

Preparation of emulsion copolymers. The emulsion copolymers were prepared under nitrogen in a 1.3 L stainless steel reactor thermostated at 323 K in the case of styrene – methyl acrylate and at 308 K in the case of methyl acrylate – butyl acrylate. SDS was used as emulsifier, $\text{K}_2\text{S}_2\text{O}_8$ as initiator and NDM as chain transfer agent. The amounts of the different chemicals used are given in Table II. Latices were purified by removing SDS and unreacted $\text{K}_2\text{S}_2\text{O}_8$, monomers and NDM by means of dialysis.

Results and Discussion

In earlier investigations it was shown that poly(styrene-co-methyl acrylate) copolymers can be separated according to their chemical composition on both reversed phase and normal phase columns [4, 11]. From this work it was concluded that normal phase columns gave a slightly better resolution in the styrene rich range, whereas for reversed

Table I List of reference copolymers, prepared by solution polymerisation, compositions and weight average molecular weights.

poly(styrene-co-methyl acrylate) copolymers	
mol% styrene	molecular weight (kg/mol)
100	43
83	190
76	66
57	74
46	75
29	58
12	110
0	111
poly(methyl acrylate-co- <i>n</i> -butyl acrylate) copolymers	
mol% butyl acrylate	molecular weight (kg/mol)
100	256
90	594
77	557
70	589
52	464
42	432
21	339
9	389
0	111

Table II The amounts of chemicals used for the preparation of the emulsion copolymers PSMA and PMABA.

	PSMA (g)	PMABA (g)
water	600.2	723.5
styrene	34.50	—
methyl acrylate	85.50	14.59
butyl acrylate	—	21.55
NDM	2.01	0.40
NLS	2.01	2.00
K ₂ S ₂ O ₈	0.20	0.20

phase columns a slightly better performance in the methyl acrylate rich range was observed. In this study it was found that the separation of methacrylate rich copolymers on reversed phase columns with mixtures of THF, MeOH and water as the eluent resulted in a severe decrease of the FID response.

In order to calculate the response of the FID, constant amounts of a standard solution of polystyrene were repeatedly injected under isocratic conditions using THF as the eluent. The variation in the resulting peak areas was less than 4 % with a response of circa 3.8×10^{-5} coulomb/g carbon, which is in satisfying agreement with the literature values for the moving wire FID [17]. However, it has to be noticed that this response is about three orders of magnitude lower than the value of about 10^{-2} coulomb/g carbon normally observed for C and H-containing compounds in gas-chromatography with FID. The response and reproducibility were shown to be independent of the block (i.e. FID housing) temperature in the range of 80–200 °C.

Under the same experimental conditions at a block temperature of 80 °C and using a silica applicator of 50 µm i.d., the

addition of polar solvents (H₂O or methanol) to the isocratic elution system resulted in a large decrease in the FID response. As an example, the addition of 5 % v/v of MeOH to the DCM eluent resulted in a 35 % decrease of the original response. A similar signal decrease was observed for polyacrylic acid samples eluted on the Lichrospher column with methanol as the eluent, containing different amounts of water.

From these experiments it can be concluded that the addition of polar solvents like water and methanol decreases the response of the FID for the (co)polymer samples. Therefore, to obtain reliable results the amounts of these solvents in the eluent should be kept constant and as low as possible. Since, water and methanol are very often used in reversed-phase chromatography this limits the applicability of the technique in combination with FID.

Poly(styrene-co-methyl acrylate), PSMA Copolymers

A number of PSMA copolymer samples were analyzed under the experimental conditions given under system I in the experimental section, with a normal phase column. The composition and concentrations of the reference (co)polymers are given in Table III (1A and 1B).

In Figure 1 two typical chromatograms are given representing a separation of 3 copolymers and both the homopolymers of methyl acrylate and styrene. In Figure 1a the chromatogram obtained at 260 nm UV detection exhibits a response decrease with decreasing styrene content, whereas the chromatogram obtained with FID detection, given in Figure 1b, shows all (co)polymer peaks including the almost non-UV-absorbing PMA peak. Also from these data the calibration curve of the retention time versus the chemical composition of the copolymers was plotted (Figure 2).

In Figure 3 the FID response as peak areas coulomb is given as a function of the injected copolymer mass. From this

Table III Composition of the standard test solutions of the reference copolymers.

no. 1 poly(styrene-co-methyl acrylate) copolymers			
1A		1B	
% styrene	concentration (g/L)	% styrene	concentration (g/L)
100	0.2	100	0.22
83	0.18	76	0.16
57	0.18	46	0.16
29	0.19	12	0.16
0	0.18	0	0.25
no. 2 poly(methyl acrylate-co- <i>n</i> -butyl acrylate) copolymers			
2A		2B	
% butyl acrylate	concentration (g/L)	% butyl acrylate	concentration (g/L)
100	2.1	90	1.4
77	1.8	70	1.9
52	1.7	42	2.0
21	1.7	9	2.9
0	2.2	—	—

Figure 1
HPLC chromatograms of a mixture of 5 reference PSMA (co)polymers with various compositions. 75 μ l injected of solution 1A in Table III; column: Chromosphere Si; eluent A: n-heptane; eluent B: DCM + 10 % methanol; Gradient 10 % $\rightarrow$ 100 % B, 18 min; flow = 0.6 mL/min; Temperature ambient.
UV = 260 nm; FID, block temp. = 120 $^{\circ}$ C, att. = 20. The copolymer compositions, as mol% styrene are indicated in the figure.

Figure 2
Retention time as a function of the fraction of styrene in a PSMA copolymer. Conditions: 75 μ l injected of solutions 1A and 1B in Table III; column: Chromosphere Si; eluent A: n-heptane; eluent B: DCM + 10 % methanol; Gradient 10 % $\rightarrow$ 100 % B, 18 min; flow = 0.6 mL/min; Temperature ambient.

Figure 3
FID response in coulomb as a function of the injected mass of various styrene - methyl acrylate copolymers. Conditions: different injection volumes of solutions 1A and 1B in Table III; column: Chromosphere Si; eluent A: n-heptane; eluent B: DCM + 10 % methanol; Gradient 10 % $\rightarrow$ 100 % B, 18 min; flow = 0.6 mL/min; Temperature ambient. Block temp. = 120 $^{\circ}$ C, att. = 20.
(+) = PS; Δ = 83 % S; O = 76 % S; ∇ = 57 % S; $\diamond$ = 92 % S; $\square$ = 29 % S; $\blacksquare$ = 12 % S, $\blacktriangledown$ = PMA.

Figure 4
FID response in coulomb/g PSMA (co)polymer as a function of the copolymer chemical composition given in mol% styrene. Conditions: different injection volumes of solutions 1A and 1B in Table III, column: Chromosphere Si; eluent A: n-heptane; eluent B: DCM + 10 % methanol; Gradient: 10 % $\rightarrow$ 100 % B, 18 min; flow = 0.6 mL/min; Temperature ambient. Block temp. = 120 $^{\circ}$ C, att. = 20.
 Δ = 5 μ l; + = 10 μ l; o = 30 μ l.

figure it can be concluded that below circa 0.07 mg the response of a specific component is linearly dependent on the injected mass. Furthermore the absolute response of the FID depends on the copolymer composition. The observation in gas chromatography that the response of the FID depends on the carbon content of a specific component and also on its chemical structure is confirmed to be valid for the larger molecules involved in this study.

Figure 4 represents the response of some PSMA copolymers as a function of the styrene content. The plot of the relative response as a function of percentage styrene exhibits a maximum at approximately 85 % styrene. This complicates

the accurate calculation of the CCD from an HPLC/FID chromatogram.

It can be concluded that for accurate quantitative measurements it is necessary for both UV- and flame ionisation detection modes to be carefully calibrated. However, the detection of non- and low UV-absorbing copolymer samples requires a detector whose operating principle is not based upon UV-absorption, e.g. a transport mechanism in combination with an FID (present case) or an evaporative light-scattering detector.

As an example of this in Figure 5 the UV (260 nm) and the FID chromatograms of a bimodal emulsion copolymer are given. In contrast to the UV chromatogram, which does not reveal the polymethyl acrylate peak, the FID chromatogram shows the expected bimodality.

Figure 5

HPLC chromatogram of a high conversion (96 wt%) emulsion copolymer of styrene and methyl acrylate of an average chemical composition of 25 % styrene. Column: Chromosphere Si; eluent A: n-heptane, eluent B: DCM + 10 % methanol; gradient 10% → 100 %, B, 18 min, 0.6 ml/min; temperature: ambient. 60 μ L injected of a copolymer solution in THF (20 mg/10 mL).

260 nm, UV detection; moving wire FID, block temp. = 120 °C, att. = 50.

Poly(methyl acrylate-co-n-butyl acrylate), PMABA Copolymers

A number of PMABA samples were analyzed under the experimental conditions given under system II in the experimental section. The composition and concentrations of the reference (co)polymers are given in Table III, 2A and 2B.

In Figure 6 the separation of a mixture of 3 methyl acrylate-butyl acrylate copolymers and the two homopolymers, is given using UV detection at 235 nm and the FID. Relatively strong FID responses, compared to the UV signals, were observed. Moreover, the FID response is not influenced by the gradient eluent composition, facilitating quantitative calculations.

The reference (co)polymers were prepared by means of low-conversion solution (co)polymerization with AIBN as the initiator. Therefore, the copolymers formed contain C $\equiv$ N end groups, which can be detected at 235 nm. This

Figure 6

HPLC chromatogram of a mixture of 5 reference (co)polymers of methyl acrylate and butyl acrylate with various compositions. 20 μ L injected of solution 2A in Table III; column: Chromosphere Si; eluent A: n-heptane; eluent B: DCM + 10 % methanol; Gradient 20 % → 85 % B, 13 min; Temperature ambient. UV detection 235 nm; FID, 50 μ m i.d. silica applicator, block temp. = 120 °C, Att. = 50.

Figure 7

Retention time as a function of the fraction of butyl acrylate units in the copolymer. Conditions: 20 μ l injected of solutions 2A and 2B in Table III; column: Chromosphere Si; eluent A: n-heptane; eluent B: DCM + 10 % methanol; Gradient 20 % $\rightarrow$ 85 % B, 13 min; Temperature ambient.

Figure 8

FID response in coulomb as a function the injected mass of various methyl acrylate-co-n-butyl acrylate (co)polymers. + = PB, Δ = 90 % BA, $\circ$ = 77 % BA, $\times$ = 70 % BA, $\blacktriangle$ = 52 % BA, $\bullet$ = 42 % BA, ∇ = 21 % BA, $\diamond$ = 9 % BA, $\square$ = PMA.

Conditions: different injection volumes of solutions 2A and 2B in Table III; column: Chromosphere Si; eluent A: n-heptane; eluent B: DCM + 10 % methanol; Gradient 20 % $\rightarrow$ 85 % B, 13 min; Temperature ambient. FID, 50 μ m i.d. silica applicator, block temp. = 120 $^{\circ}$ C.

results in unwanted molecular weight dependence of the signal. In contrast to the solution copolymers, the emulsion copolymers, which are generally prepared with persulphate initiators, do not exhibit any significant UV absorption.

Various separations of the PMABA copolymer samples were performed at different injection volumes. From the chromatograms obtained the FID response of all polymer peaks and the retention data were determined.

In Figure 7 the retention time of the copolymers as a function of % butyl acrylate is given. Figure 8 shows the copolymer FID response in coulombs as a function of injected mass of the individual (co)polymers.

Figure 9

FID response in coulomb/g PMABA polymer as a function of the copolymer chemical composition given in mol% butyl acrylate at several injection volumes: + = 5 μ l, Δ = 20 μ l, $\circ$ = 40 μ l, ∇ = 100 μ l, $\square$ = 200 μ l.

Conditions: different injection volumes of solutions 2A and 2B in Table III; column: Chromosphere Si; eluent A: n-heptane; eluent B: DCM + 10 % methanol; Gradient 20 % $\rightarrow$ 85 % B, 13 min; Temperature ambient. FID, 50 μ m i.d. silica applicator, block temp. = 120 $^{\circ}$ C.

From this it can be concluded that the response as a function of the injected mass of the copolymer is nearly linear up to 0.1 mg. Moreover, it is clear that the response also depends on the chemical composition of a specific copolymer; a similar behaviour to that observed for PSMA copolymers. The FID response in coulombs/g as a function of the % butyl acrylate at different injected masses of the copolymers is shown in Figure 9. This plot exhibits a similar behaviour to that observed for the poly(styrene-co-methyl acrylate) copolymers: a maximum in the response in this plot also appeared. The highest response was determined at an injection volume of 20 μ L of solution 2.

In Figure 10 a typical chromatogram, recorded under optimal conditions, is shown of poly(methyl acrylate-co-n-butyl acrylate) copolymer prepared in emulsion. The chromatogram obtained with 235 nm UV detection does not reveal the copolymer, since no AIBN but $K_2S_2O_8$ initiator has been used for the emulsion copolymer preparation. The FID detector, however, detects both these types of copolymers. Assuming a FID response independent on chemical composition and a linear dependence of the response on (co)polymer mass, a chemical composition distribution (CCD) has been calculated. In Figure 11 the experimentally determined CCD is compared with a model calculation of the CCD. The model CCD has been calculated using the simulation program "SIEMCO" (Simulation Emulsion Copolymerization). This model takes into account the effect of composition drift on the copolymer composition (conversion heterogeneity) as well as the instantaneous (= statistical) heterogeneity [7, 20]. The average chemical composition of the emulsion copolymer is 55 % butyl acrylate. The CCD predicted by the model and the experimentally determined CCD reveal the occurrence of composition drift during preparation, as indicated by the asymmetrical shape of the peaks.

Figure 10

HPLC chromatogram of a high conversion (92 wt%) emulsion copolymer of methyl acrylate and *n*-butyl acrylate having an average chemical composition of 55 mol% *n*-butyl acrylate, prepared at an initial monomer ratio of $(MA/BA)_0 = 1$ (mol/mol) and an initial monomer to water ratio of 0.05 g/g. M_w of the sample (determined by SEC) 800000 g/mol. Column: Chromosphere Si; eluent A: *n*-heptane; eluent B: DCM + 10 % methanol; gradient 10 % $\rightarrow$ 100 %, B, 18 min, 0.6 ml/min; temperature: ambient. 25 μ L injected of a copolymer solution in THF (22 mg/10 mL). 235 nm UV detection; moving wire FID, 50 μ m i.d. silica applicator, att. 50, block temp. = 250 °C.

Figure 11

CCD of the emulsion copolymer of Figure 10. Dashed line: model calculation plot on the basis of $M_w = 800000$ g/mol; full line: experimentally determined plot by means of HPLC/FID.

Conclusions

UV detection in the HPLC separation of some types and composition ranges of copolymers has its limitations due to the lack of sufficiently strong UV chromophores and/or the concentration of those substances. In these cases the detection of the substances by a moving wire FID is an attractive alternative as has been shown in this study.

The FID response is decreased by cosolvents like water and methanol in the eluent. The FID response depends on the chemical composition of a specific copolymer, which is also the case for UV-detection. For accurate quantitative measurements careful calibration is therefore necessary for both FID and UV-detection. For some specific (co)polymers the FID response is superior to the response of the UV detector.

Acknowledgement

The authors thank Ir. R. Sparidans for carrying out some preliminary experiments with the moving wire FID, Ir. R. Mommers for preparing the PMABA copolymers, Mr. W. Kingma for the SEC analyses and Mrs. D. Tjallema for the accurate handling of the manuscript.

References

- [1] F. B. Padley, *J. Chromatogr.*, **39**, 37 (1969).
- [2] S. Teramachi, A. Hasegawa, N. Uchiyama, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 71 (1984).
- [3] J. C. J. F. Tacx, J. L. Ammerdorffer, A. L. German, *Polymer*, **29**, 2087 (1988).
- [4] S. Teramachi, A. Hasegawa, Y. Shima, M. Akatsuka, M. Nakajima, *Macromolecules*, **12**, 992 (1979).
- [5] S. Teramachi, A. Hasegawa, S. Yoshida, *Macromolecules*, **16**, 542 (1983).
- [6] H. Inagaki, H. Matsuda, F. Kamiyama, *Macromolecules*, **1**, 520 (1968).
- [7] G. H. J. van Doremaele, A. M. van Herk, A. L. German, *Makromol. Chem., Macromol. Symp.*, **35**, 36 (1990).
- [8] G. Glöckner, "Analysis of Compositional and Structural Heterogeneities of Polymers by Non-Exclusion Chromatography", *Advances in Polym. Sci.*, Springer-Verlag, Berlin, **79**, 159 (1988).
- [9] S. Mori, *Anal. Chem.*, **60**, 1125 (1988).
- [10] S. Mori, *J. Chromatogr.*, **507**, 473 (1990).
- [11] R. W. Sparidans, H. A. Claessens, G. H. J. van Doremaele, A. M. van Herk, *J. Chromatogr.*, **508**, 319 (1990).
- [12] J. L. Robinson, R. Macrae, *J. Chromatogr.*, **303**, 386 (1984).
- [13] J. L. Robinson, M. Tsimidou, R. Macrae, *J. Chromatogr.*, **324**, 35 (1985).
- [14] L. E. Oppenheimer, T. H. Mourey, *J. Chromatogr.*, **323**, 297 (1985).
- [15] M. Righezza, G. Guiochon, *J. Liq. Chrom.*, **22**, 2709 (1988).
- [16] K. Aitzetmüller, *J. Chrom. Sci.*, **13**, 454 (1975).
- [17] J. B. Dixon, *Chimia*, **38**, 83 (1984).
- [18] R. L. Veazey, *JAOCS*, **63**, 1043 (1986).
- [19] G. H. J. van Doremaele, Ph.D. Thesis, "Model Prediction, Experimental Determination, and Control of Emulsion Copolymer Microstructure", Eindhoven, University of Technology, The Netherlands, 1990.
- [20] W. H. Stockmayer, *J. Chem. Phys.*, **13**, 199 (1945).

Received: Jan 7, 1991
Revised manuscript
received: Feb 27, 1991
Accepted: Mai 5, 1991
B