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Two-dimensional chromatography of complex polymers Part 1. Analysis of a graft copolymer by two-dimensional chromatography with on-line FTIR detection

J. Adrian, E. Esser, G. Hellmann, H. Pasch*

German Plastics Institute, Schlossgartenstraße 6, 64289 Darmstadt, Germany

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Abstract

The grafting of butyl acrylate onto poly(styrene-*block*-butadiene) is investigated by two-dimensional (2D) liquid chromatography. Separating the graft backbone and the graft product by liquid chromatography at the critical point of adsorption in the first dimension and size exclusion chromatography in the second dimension, detailed information in the coordinates chemical composition and molar mass are obtained. It is shown that the grafting reaction results in the formation of a complex product due to the fact that in addition to grafting the graft backbone undergoes partial degradation. Combining 2D chromatography and FTIR spectroscopy in a quasi on-line setup, all components of the graft product can be identified. Via selective detection, the chemical composition drift of the different fractions can be determined.

Keywords: Complex polymer; Poly(styrene-*block*-butadiene); FTIR spectroscopy

1. Introduction

Graft copolymers are effective compatibilizers for polymer blends. They can be prepared by radical grafting of a polymerizable monomer A onto a reactive polymer backbone B. As a result of the grafting reaction, a complex product is obtained comprising the graft copolymer AB, residual ungrafted polymer backbone B and homopolymer poly-A. Accordingly, the reaction product is distributed in molar mass (MMD) and chemical composition (CCD).

To evaluate the two-dimensional (2D) composition and molar mass distribution of such copolymers, classical [1] and chromatographic cross-fractionation [2–5] can be used. The classical approach is based upon the dependence of copolymer solubility on composition and chain length. A solvent/nonsolvent combination fractionating solely by molar mass would be appropriate for the evaluation of MMD, another one separating with respect to chemical composition would be suited for determining CCD. However, in reality precipitation fractionation yields fractions, which vary both in chemical composition and molar mass. Even high-resolution fractionation would not improve the result.

By the use of different modes of liquid chromatography it is possible to separate polymers selectively with respect to hydrodynamic volume (molar mass), chemical composition or functionality. Using these techniques and combining them with each other or with a selective detector, 2D information on different aspects of molecular heterogeneity can be obtained. An excellent overview on different techniques and applications involving the combination of size exclusion chromatography (SEC) and gradient high performance liquid chromatography (HPLC) was published by Glöckner in Ref. [6]. In most cases SEC was used as the first separation step, followed by HPLC [7,8]. Investigation of this kind demonstrated the efficiency of gradient HPLC for separation by chemical composition. Graft copolymers of methyl methacrylate onto EPDM rubber were analyzed by Augenstein and Stickler [9], whereas, Mori reported on the fractionation of block copolymers of styrene and vinyl acetate [10].

The major disadvantage of all early investigations on chromatographic cross-fractionation was related to the fact that both separation modes were combined to each other off-line or in a stop-flow mode. In the first separation step fractions were collected, isolated, and then subjected to the second separation step. This procedure, of course, is

* Corresponding author. Tel.: +49-6151-163407; fax: +49-6151-29-2855.

E-mail address: hpasch@dki.tu-darmstadt.de (H. Pasch)

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time-consuming and the reliability of the results at least to a certain extent depends on the skills of the operator. A fully automated 2D chromatographic system was developed by Kilz et al. [11–13]. It consists of two chromatographs; one which separates by chemical composition or functionality and a SEC instrument for subsequent separation by size. Via a storage loop system, fractions from the first separation step are automatically transferred into the second separation system.

An application of 2D gradient HPLC-SEC was published by Kilz et al. describing the analysis of styrene–butadiene star polymers [12]. The analysis of ethoxylated fatty alcohols and ethylene oxide–propylene oxide block copolymers by 2D chromatography was discussed by Trathnigg et al. [14]. They combined liquid adsorption chromatography (LAC) and SEC and were able to determine CCD and MMD of the polyethers. The combination of liquid chromatography at the critical point of adsorption (LC–CC) and SEC for the analysis of functional homopolymers and block copolymers was demonstrated by Adrian et al. [15], while polyalkylene oxides have been analyzed by Murphy et al. [16,17]. The analysis of methacryloyl-terminated polyethylene oxides by LC–CC vs. SEC was described by Krüger et al. [18]. A technical C_{13},C_{15}-alkoxy-terminated PEO was analyzed by Pasch and Trathnigg using LC–CC vs. SEC [19]. The analysis of aliphatic polyesters with respect to functionality type distribution (FTD) and MMD was demonstrated by Much et al. [12,18].

The present paper describes the analysis of a graft copolymer by 2D chromatography. In order to be selective towards chemical composition, LC–CC is used in the first dimension. In the second dimension, SEC provides information on molar mass distribution. Different from all other applications so far, a quasi on-line infrared detection device is used giving detailed information on the different chromatographic fractions.

2. Experimental part

2.1. Chromatographic system

A modular chromatographic system comprising two chromatographs connected via one eight-port injection valve and two storage loops was used. The chromatograph for the first separation step (chromatograph 1) comprised a Rheodyne six-port injection valve with a 50 μl injection loop and an isocratic ISCO 100 DX syringe pump. One electrically driven eight-port injection valve (Valco EHC8W) was used to connect the two chromatographs. In addition, they were connected to two storage loops of a volume of 100 μl each. The chromatograph for the second separation step (chromatograph 2) comprised a Waters model 510 pump. The operation of the coupled injection valves was controlled by the software, which was used for data collection and processing. In the present case the software package "PSS-2D-GPC-Software" of Polymer Standards Service, Mainz, Germany, was used. Molar mass calibration is based on polystyrene.

2.2. Columns

Chromatograph 1: Knauer Si 300 + 1000 *Å*, 10 μm average particle size. Column size was 250 × 4 mm I.D. Chromatograph 2: PL Mixed D, 5 μm average particle size and column size of 300 mm × 7.5 mm I.D.

2.3. Mobile phase

Chromatograph 1: THF-cyclohexane 15.5:84.5 (v/v), Chromatograph 2: THF, all solvents were of the HPLC grade.

2.4. Detectors

Waters 486 tunable UV detector at 254 nm and evaporative light scattering detector (ELSD) model ELSD 500 of Altech both after chromatograph 2.

2.5. FTIR interface

LC Transform® Model 400 of Lab Connections.

2.6. Samples

The crude graft copolymer was a laboratory sample of German Plastics Institute. It was prepared by radical grafting of butyl acrylate onto a styrene–butadiene diblock copolymer in solution of toluene. The block copolymer was a technical product of BASF AG, Ludwigshafen, prepared by anionic polymerization. The average molar mass was about 108,000 g/mol with sizes of the blocks of 38,000 (PB) and 70,000 g/mol (PS). The butyl acrylate contained a small amount of maleic anhydride (2 wt% of total butyl acrylate) for introducing carboxy groups. The grafting initiator was dibenzoyl peroxide, *n*-dodecyl mercaptane was used as a chain transfer agent. The chain transfer agent was used for adjusting the chain lengths of the polybutyl acrylate grafts. The reaction mixture was continuously purged with nitrogen. After the reaction the solvent was evaporated from the crude product.

The chromatographic behavior of polystyrene, polybutadiene and polybutyl acrylate was investigated using narrow disperse calibration standards of Polymer Standards Service GmbH, Mainz, Germany.

3. Results and discussion

The graft copolymer under investigation was prepared by the radical grafting of butylacrylate and a small amount of maleic anhydride onto poly(styrene-*block*-butadiene) using dibenzoyl peroxide as the grafting initiator. Due to the fact that in addition to the grafting reaction homopolymerization of the acrylate takes place, a complex reaction product is

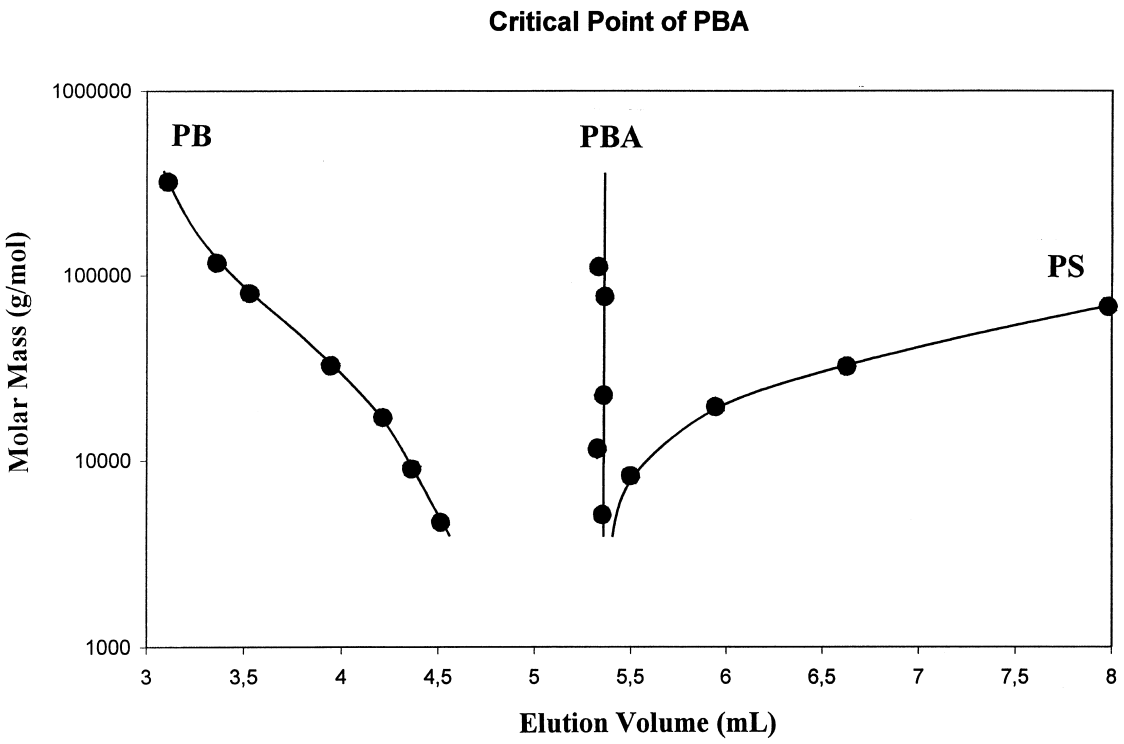

Fig. 1. Representation of the behavior of PS and PB at the critical point for PBA; stationary phase: Knauer Si-300 + 1000 Å, eluent: THF:cyclohexane 15.5:84.5% by volume.

obtained, consisting of the graft copolymer poly(styrene-*block*-butadiene-*graft*-butyl acrylate), ungrafted poly(styrene-*block*-butadiene) and polybutyl acrylate (PBA). The grafting takes place at the double bonds of the polybutadiene block, while the polystyrene block not containing reactive double bonds remains unchanged.

For the quantitative determination of the amount of PBA homopolymer, it must be separated from the graft copolymer and the ungrafted backbone polymer. This can be achieved by liquid chromatography at the critical point of adsorption (LC–CC) [19–22]. At the critical point of adsorption of PBA, this part of the complex mixture behaves chromatographically invisible and separation is accomplished solely with respect to the styrene and butadiene containing fractions. The critical conditions of adsorption for PBA can be established on silica gel as the stationary phase and THF–cyclohexane as the eluent. The critical point corresponds to an eluent composition of THF–cyclohexane 15.5:84.5% by volume. Under these chromatographic conditions polybutadiene (PB) elutes in the SEC mode, while polystyrene (PS) is separated in the adsorption mode, see representation in Fig. 1. The chromatographic behavior of PS, PB and PBA is investigated using narrow disperse calibration standards.

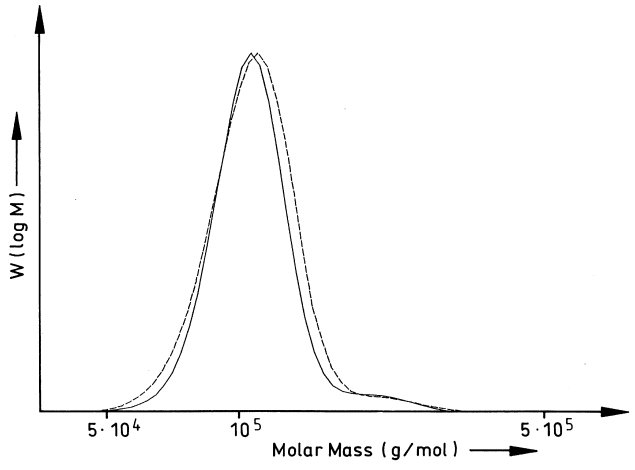

Fig. 2. Molar mass distributions of the PS–PB block copolymer; stationary phase: PL Mixed D + Mixed E, eluent: THF, detection: (—) UV 254 nm, (- - -) ELSD.

The complexity of the graft product results partially from the fact that the graft backbone is a complex polymer itself. Therefore, in the first set of experiments the styrene–butadiene block copolymer was analyzed by SEC, LC–CC and 2D chromatography. From the manufacturer it was known that the block copolymer was prepared by anionic polymerization, the average molar mass was about 108,000 g/mol and the sizes of the blocks were about 38,000 g/mol and 70,000 g/mol for the PB and the PS blocks, respectively. Under the conditions of the present experiment the molar mass distribution given in Fig. 2 is obtained. As has to be expected, the polydispersity is very low (1.06), the average molar masses are 111,000 and 105,000 g/mol for M_w and M_n, respectively (PS calibration). As can be seen in Fig. 2, in addition to the main copolymer peak a second peak is

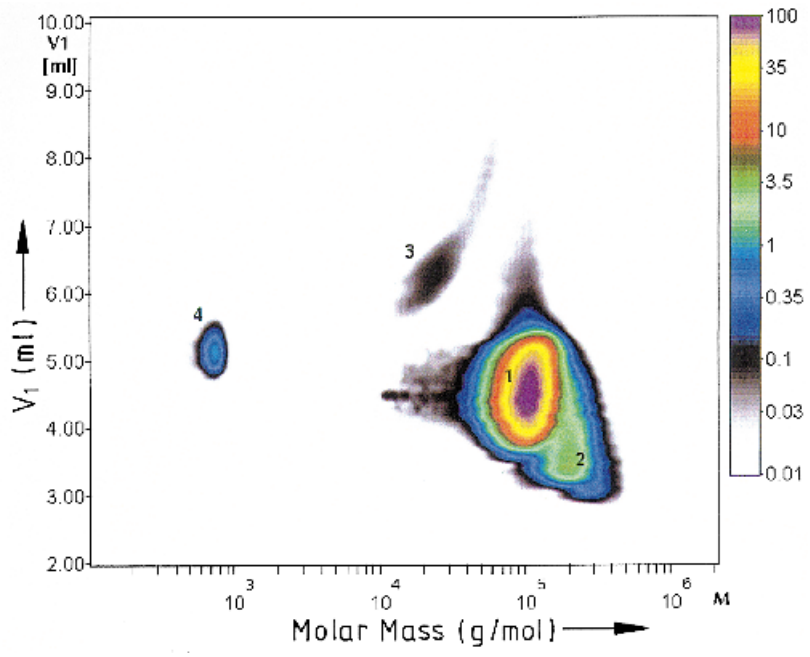

Fig. 3. Contour plot of the 2D separation of the PS–PB diblock copolymer, first-dimension: LC–CC (PBA), second-dimension: SEC, detection: ELSD.

obtained at the high molar mass end of the distribution curve. The molar mass of this copolymer fraction is exactly double the molar mass of the main fraction, indicating that coupling of two block copolymer molecules to a "dimer" took place. This is not unexpected due to the reactivity of the double bonds of the PB block, and the possible influence of residual oxygen and carbon dioxide.

A much more detailed insight into the chemical heterogeneity of the block copolymer can be obtained by a 2D chromatographic experiment, where in the first dimension a separation according to chemical composition is conducted, while in the second dimension SEC separation is carried out. In view of the forthcoming experiments the chromatographic conditions of the first dimension correspond to the critical conditions for PBA. As was shown in Fig. 1, under these conditions PB and PS behave differently. With respect to the block copolymer this means, that styrene rich fractions are longer retained on the stationary phase than butadiene rich fractions. Since the polydispersity is very low, it can be assumed that separation in the first dimension is mainly directed by the styrene/butadiene ratio.

The results of the 2D separation of the diblock copolymer are presented as a contour diagram in Fig. 3. The ordinate represents the separation in the first dimension, while the abscissa indicates the SEC separation of the fractions. The molar mass calibration was carried out using PS calibration standards. The generation of a contour diagram from the individual SEC chromatograms of the fractions is discussed in Refs. [14,19]. The contour plot indicates four fractions which are different in chemical composition and/or molar mass. Fraction 1 unambiguously can be assigned to the block copolymer exhibiting a narrow molar mass distribution with an average of about 100,000 g/mol and a certain distribution in chemical composition, which is indicated by the broadness of peak 1 in the ordinate direction. Fraction 2 corresponds to a molar mass of about 200,000 g/mol and a gradually higher butadiene content compared to fraction 1. Obviously, this fraction belongs to "dimer" block copolymer molecules, which have been detected in the SEC experiment, see Fig. 2.

In addition to these expected fractions, fraction 4 is obtained at an elution volume corresponding to the dead volume of the column in the first dimension. This fraction has a very low molar mass and does not indicate a molar mass distribution or chemical composition distribution (narrow elution ranges in both dimensions). It can be assumed that this fraction belongs to a stabilizer added to the block copolymer to increase the storage stability. Finally, the contour plot reveals the presence of a fraction 3, which has a molar mass between 20,000 and 70,000 g/mol. This fraction cannot be detected by LC–CC or SEC alone because in both cases it is partially overlapped by the strong block copolymer peak. In the contour plot, however, it can readily be detected although the concentration is very low (<0.2 area%). Fraction 3 elutes in the LAC mode in the first dimension. i.e. after the dead volume of the column. Another indication for the LAC elution mode is the fact that elution volume in the first dimension increases with increasing molar mass. In agreement with the chromatographic behavior of the different components of the block copolymer, fraction 3 can be assigned to a small amount of polystyrene present in the block copolymer. Polystyrene is frequently encountered as a by-product in technical

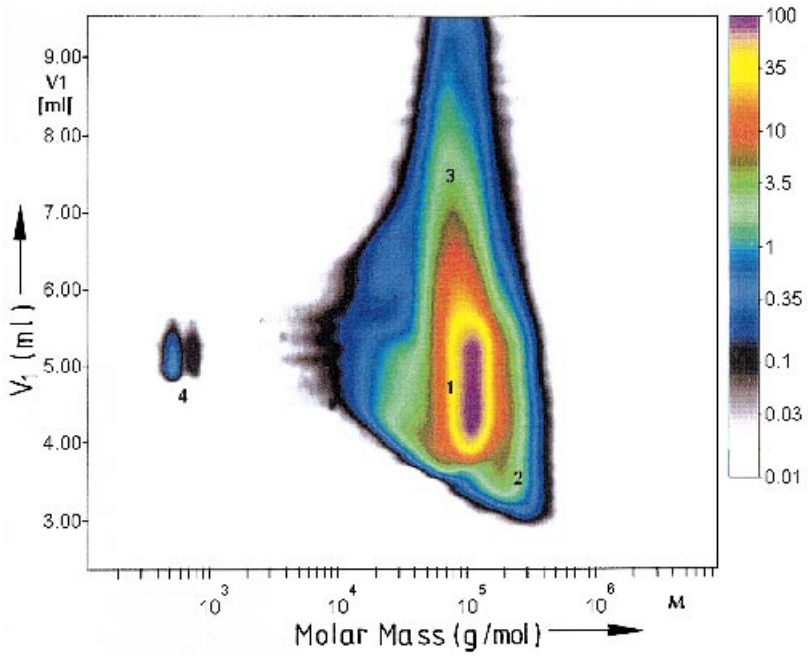

Fig. 4. Contour plot of the 2D separation of the PS–PB diblock copolymer after treatment with dibenzoyl peroxide for 16 h; first dimension; LC–CC (PBA), second dimension: SEC, detection: ELSD.

PS–PB block copolymers due to a certain amount of chain termination after the first step of the living polymerization.

Styrene–butadiene copolymers exhibit a high reactivity of the butadiene double bonds and in the presence of peroxides branching, cross-linking or chain scission can be encountered. For a better understanding of the grafting process with butyl acrylate it is, therefore, necessary to investigate the behavior of the graft backbone under the conditions of the grafting reaction in the absence of butyl acrylate. In the following experiment the diblock copolymer was dissolved in toluene and treated with dibenzoyl peroxide for 16 h at 80°C. The resulting product was analyzed by SEC, LC–CC and 2D chromatography. SEC shows; (1) a shift of the peak maximum towards lower molar masses, (2) an increase in the amount of higher molar mass components. These results indicate that chain degradation and chain branching occur at the same time. Similar results are obtained by LC–CC, where the elution peak maximum is shifted towards higher elution volumes and a significant peak broadening is obtained. Both effects indicate that the chemical heterogeneity of the block copolymer increases. The elution volume shift is a clear indication for an increase of the styrene/butadiene ratio in the copolymer as a result of the stepwise degradation of the PB block while the PS block remains unchanged.

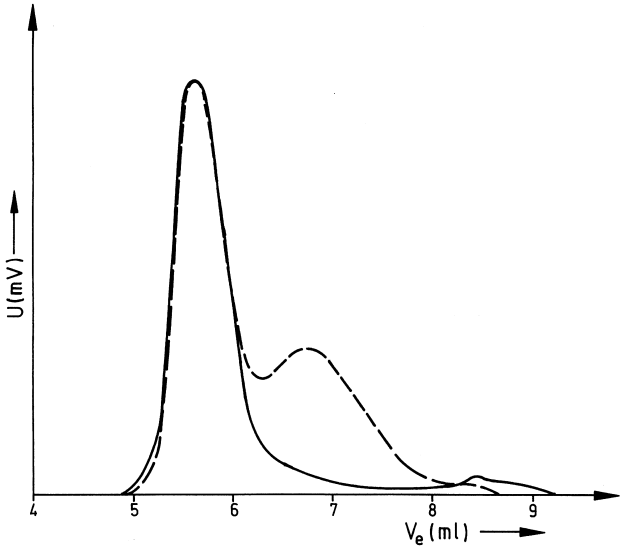

Fig. 5. SEC chromatogram of the graft product; stationary phase: PL Mixed D, eluent: THF, detection: (—) UV 254 nm, (- - -) ELSD.

A clear picture of the structural changes in the block copolymer when treated with the peroxide is given by the 2D chromatography experiment, see contour diagram in Fig. 4. A comparison with the initial contour diagram in Fig. 3 shows that only the additive in fraction 4 remains unchanged. The block copolymer fractions in peaks 1 and 2 exhibits a significant broadening in both the chemical composition (ordinate) and molar mass direction (abscissa). This broadening prevents the PS homopolymer fraction (peak 3 in Fig. 3) from being detected. Instead, a new peak region 3 is obtained which is shifted towards higher elution volumes in the first dimension as compared to the block copolymer peak 1. In agreement with the LC–CC experiment this region 3 can be assigned to block copolymer fractions with a higher styrene/butadiene ratio, which are formed due to the degradation of the PB block. The shift of this region towards lower molar masses supports this assumption. A rough estimation gives a molar mass

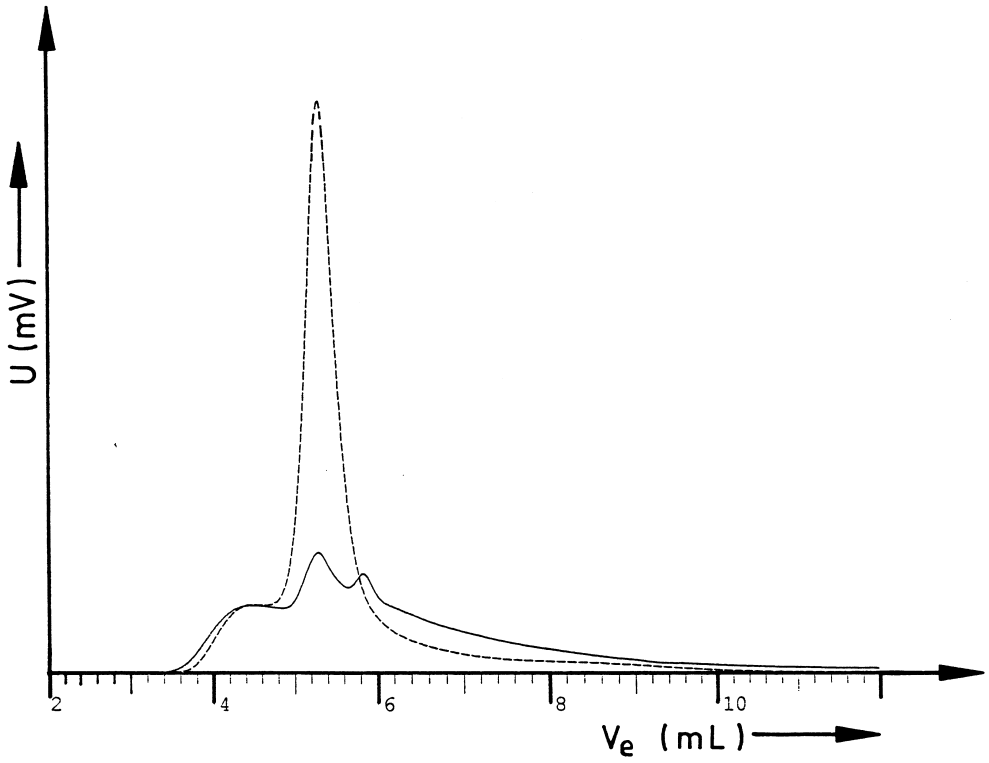

Fig. 6. LC–CC chromatogram of the graft product; stationary phase: Si-300 + 1000 Å, eluent: THF:cyclohexane 15.5:84.5% by volume, detection: (—) UV 254 nm, (- - -) ELSD.

decrease of about 20,000 g/mol, indicating that the average molar mass of the PB block in this region in only 50% of the initial molar mass.

After analyzing the chemical composition of the graft backbone and the behavior of the graft backbone under the conditions of the grafting reaction, a real graft copolymer can be investigated. The preparation of the graft copolymer is also carried out in toluene at 80°C in the presence of dibenzoyl peroxide as the initiator and butyl acrylate together with a small amount of maleic anhydride. The reaction time is 16 h, after this time the reaction mixture is cooled down and the solvent is removed by evaporation. For a first information on the chemical composition of the reaction product, 1D SEC and LC–CC measurements can be conducted. The SEC chromatogram in Fig. 5 shows two elution peaks with different UV activities. While the higher molar mass elution peak appears to be rather uniform when comparing the UV and ELSD traces, the lower molar-mass elution-peak has a very low UV activity. In agreement with the UV behavior of the different components of the graft product, the low molar-mass elution-peak can be assigned to a fraction, comprising mainly butyl acrylate units. Therefore, the high molar-mass elution-peak must contain the graft copolymer and the ungrafted polymer backbone. The LC–CC chromatogram of the graft product in Fig. 6 shows three elution peaks exhibiting different UV activity. Taking the first elution peak as the reference, the second peak has a significantly lower UV activity, while the third peak and the extended tail again have higher UV activities. From the preliminary experiments it is known that PBA elutes at an elution volume at about 5 ml. Accordingly, the second elution peak can be assumed to contain mainly PBA. Considering the behavior of the graft backbone as has been described in Fig. 4, the first elution peak can be assigned to the graft copolymer and ungrafted block copolymer. The third peak and the tail correspond to graft and block copolymer fractions with an increased styrene/butadiene ratio, where the PB block is partially degraded.

The elucidation of the chemical heterogeneity in relation to the molar mass distribution of the graft product components is done by 2D chromatography. It is obvious from Fig. 7, that the contour diagram is much better suited for describing the molecular heterogeneity than single SEC or LC–CC chromatograms. Comparing the ELSD- and UV-based contour diagrams, PBA and the additive can readily be identified as being peaks 5 and 4, respectively. The most intense peak 2 exhibiting the highest molar mass obviously belongs to the graft copolymer, while peak 1 can be assigned to the ungrafted PS–PB block copolymer. In agreement with Fig. 4, the tail in position 3 can be assigned to graft and block copolymer fractions with partially degraded PB blocks.

In addition to the fractions appearing in both the UV and ELSD detectors, a product fraction of very low concentration appears in positions 6, which is only detected by the ELSD. From the position of this fraction in the contour

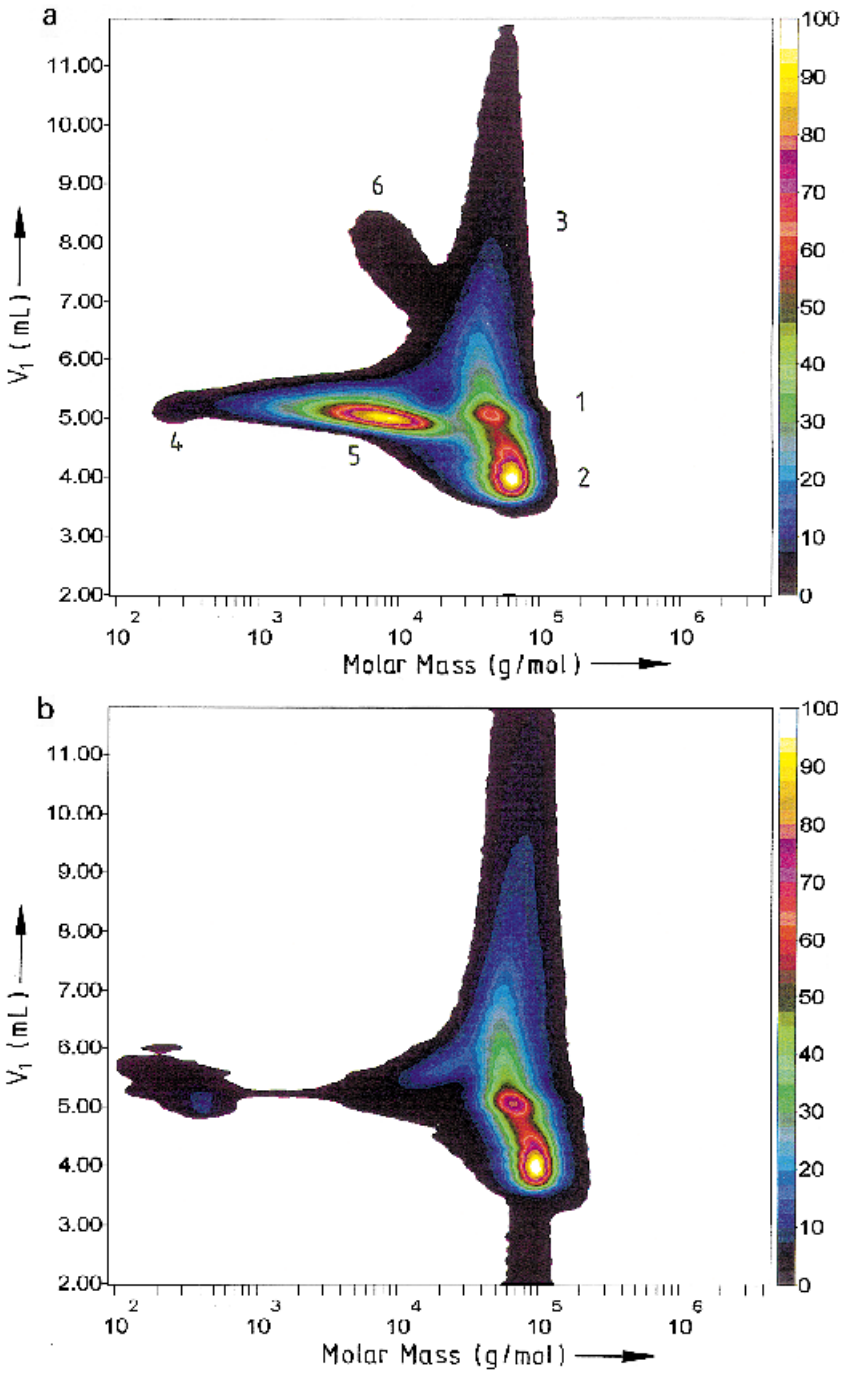

Fig. 7. Contour plot of the 2D separation of the graft product; First dimension: LC–CC (PBA), Second dimension: SEC, detection: (a) ELSD, (b) UV.

diagram it can be concluded, that its molar mass is in the same magnitude as the molar mass of PBA, while the higher elution volume in the first dimension indicates higher polarity as compared to PBA. It has been mentioned in the experimental part that in the grafting reaction butyl acrylate and a small amount of maleic anhydride were used. When maleic anhydride is incorporated into the graft copolymer or the PBA homopolymer, fractions of higher polarity can be formed due to the hydrolysis of the anhydride groups to carboxylic groups. While more polar graft copolymer fractions cannot be detected in the contour plot because they overlap with the fractions in position 3, fractions of butyl acrylate–maleic acid copolymer should appear in the same molar mass range as PBA but shifted towards higher elution volumes. This is the case for the fractions in position 6.

It is obvious that in addition to highly selective separation techniques powerful detection methods must be used to analyze the molecular heterogeneity of complex polymers in detail. UV and ELSD detection indicate changes in

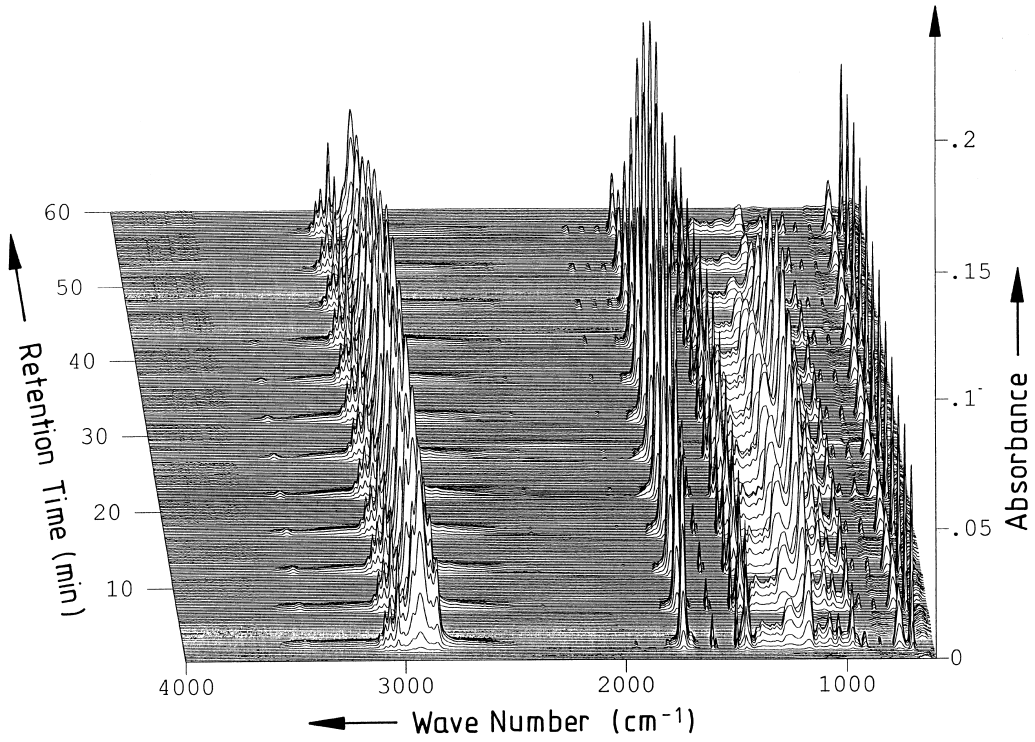

Fig. 8. Waterfall diagram obtained from the 2D separation with FTIR detection.

concentration and UV activity across a chromatographic peak and gives a rough estimate on compositional changes. For a more detailed analysis of the chemical composition of a chromatographic fraction, however, FTIR must be used as a more selective detection technique.

For determining the chemical composition of different fractions of the graft product, 2D chromatography is combined with FTIR spectroscopy via the LC Transform system. The design concept of the interface is briefly described in Refs. [23–25]. The effluent of the liquid chromatography column is split with a fraction going into the heated nebulizer nozzle located above a rotating sample collection disc. The nozzle rapidly evaporates the mobile phase while depositing a tightly focused track of the solute, which can be measured by FTIR. As a result, a complete FTIR spectrum for each position on the disc and, hence, for each sample fraction is obtained.

In the present case, the 2D chromatography system was coupled to the LC Transform, the UV and ELSD detectors by splitting the effluent after the SEC column and directing one branch of the split to the UV–ELSD and the other branch to the LC Transform (split ratio was about 1:1). One major limitation for such an experiment, however, is the very low concentration of a particular fraction to be collected. One has to keep in mind, that a sample amount of about 2 mg is injected into the LC–CC column. The sample is significantly diluted in the first separation step and further diluted when transferred into the SEC system. As a result, fraction amounts in the ng range are obtained, which then shall be analyzed by FTIR spectroscopy. Another limitation is the significantly lower peak resolution in FTIR detection when compared to UV or ELSD detection. Due to the specific spray technique used in the LC Transform, two chromatographic peaks are only separated when their elution volumes are significantly different. Otherwise, one broad elution peak is detected.

The raw data of the FTIR detection can be organized in a "waterfall diagram" representing the single FTIR spectra for a particular number of SEC fractions at different positions of the elution curve, see Fig. 8. This diagram gives a first indication on changes in the chemical composition in different fractions or across a chromatographic peak.

However, for the detailed analysis of the chemical composition of different graft product fractions, specific SEC injects are selected and investigated by FTIR. For example, inject 20 corresponds to an elution volume of 4 ml in the first dimension. For this inject the contour plot in Fig. 7 suggests the presence of the graft copolymer (graft product fraction 2). Similar to the ELSD and UV detector traces, the Gram–Schmidt presentation in Fig. 9 indicates a homogeneous elution peak. The Gram–Schmidt presentation results from the summation of all peak intensities over all frequencies and presents a concentration profile for the total fraction. Chemigrams for a particular component can be obtained when the peak intensity is presented for one specific absorption frequency. The characteristic frequencies for the graft components are 1601, 966 and 1735 cm^{-1} for PS, PB and PBA, respectively. The chemigrams presented in Fig. 9 have the same shape as the Gram–Schmidt curve and indicate that the fraction is

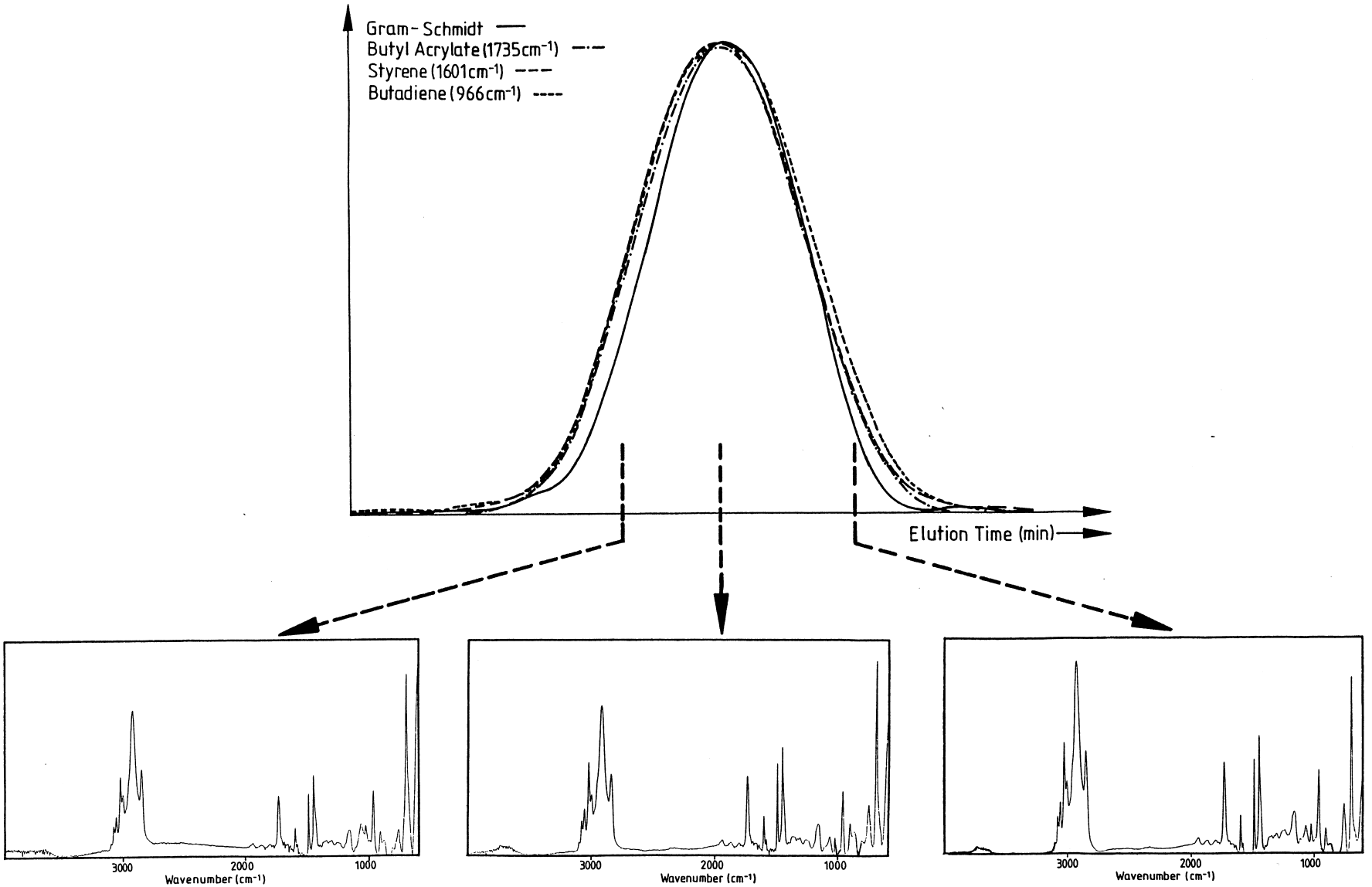

Fig. 9. Gram–Schmidt diagram and chemigrams for PB, PS and PBA together with selected FTIR spectra of inject 20 taken from the 2D separation of the graft product.

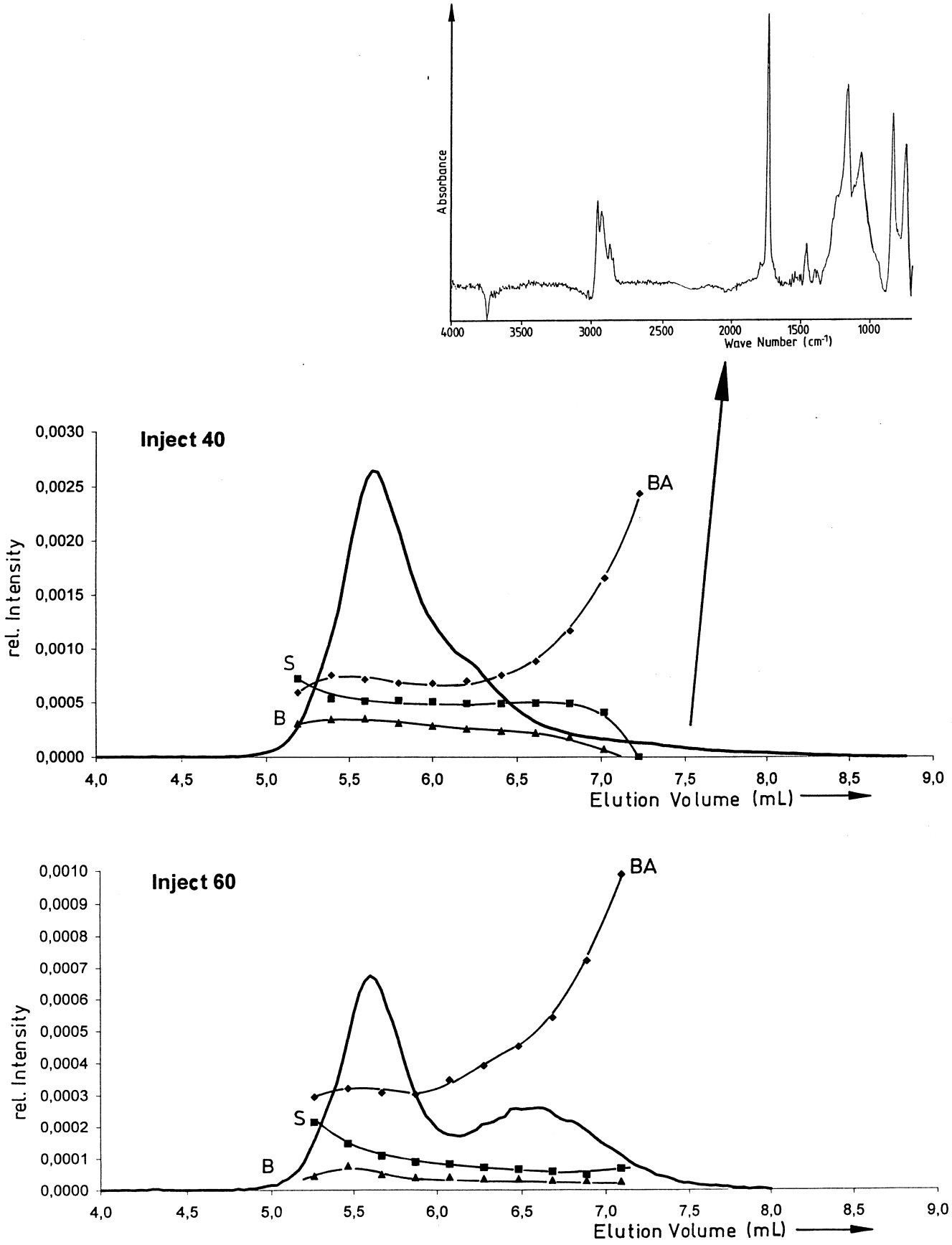

Fig. 10. FTIR analysis of injects 40 and 60 taken from the 2D separation of the graft product.

homogeneously distributed with respect to styrene, butadiene and butyl acrylate. This is also proved by comparing the FTIR spectra at different peak positions.

Similar analyses can be carried out for all injects entering the SEC system from the first dimension. FTIR spectra are accumulated across the elution peaks and can be used for detecting differences in chemical composition. For monitoring changes in the styrene, butadiene, and butyl acrylate content in a particular fraction, relative concentrations are calculated from the ratio of the characteristic frequencies and the C–H valence frequencies. These relative concentrations are plotted across the elution peaks, where S, B, and BA stand for the relative concentration profiles of styrene, butadiene and butyl acrylate units, respectively.

In Fig. 10, the detailed analysis of two injects is presented. Inject 40, corresponding to an elution volume of about 6 ml in the first dimension, exhibits an elution peak with a shoulder and a pronounced tailing at the low molar mass end of the chromatogram. The main part of the elution peaks seems to be homogeneous in composition, indicated by the parallel lines for S, B, and BA contents. Towards higher elution volumes (equal to lower molar masses) the relative concentration of BA units increases, while concentrations of S and B decrease. At the very end of the chromatogram, the inject seems to contain only BA. An FTIR spectrum, taken from the end of the chromatogram does not indicate any absorbances of S and B units, and is solely due to PBA. This is in perfect agreement with our previous assumption that fraction 5 in the contour plot (Fig. 7) is due to PBA homopolymer. Investigating inject 60, where fractions 3 and 6 are eluted, it can be shown that indeed fraction 3 is due to graft copolymer while fraction 6 is mainly due to PBA.

In addition to the previously discussed graft product components 1–5, the contour plot in Fig. 7 indicates a component 6 which was assigned to a small amount of butyl acrylate–maleic acid copolymer. The analysis of injects 50 and 60 by FTIR spectroscopy supports this assumption by indicating O–H absorption peaks in the spectra.

To summarize, 2D chromatography is an excellent tool for the analysis of the grafting reaction of butyl acrylate onto styrene–butadiene copolymers. The graft products can be separated into the components graft copolymer, graft backbone and PBA homopolymer. When FTIR spectroscopy is used as a quasi on-line detector, each component of the graft product can be analyzed with respect to chemical composition. Information on the absolute chemical composition of the different fractions can be obtained when individual spectra are quantified via appropriate calibration curves for styrene, butadiene, and butyl acrylate.

Acknowledgements

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References

[1] Francuskiewicz F. Polymer fractionation, Berlin: Springer, 1994.
[2] Glöckner G. Adv Polym Sci 1986;79:159.
[3] Mori S. Anal Chem 1988;60:1125.
[4] Glöckner G. Trends Anal Chem 1988;7:169.
[5] Tacx JCJF, German AL. Polymer 1989;30:918.
[6] Glöckner G. Gradient HPLC of copolymers and chromatographic cross-fractionation. Berlin: Springer, 1991.
[7] Glöckner G, van den Berg JHM, Meijerink N, Scholte TG. In: Kleintjens L, Lemstra P, editors. Integration of fundamental polymer science and technology. Barking: Elsevier Applied Science, 1986.
[8] Glöckner G, Stickler M, Wunderlich W. J Appl Polym Sci 1989;37:3147.
[9] Augenstein M, Stickler M. Makromol Chem 1990;191:415.
[10] Mori S. J Chromatogr 1990;503:411.
[11] Kilz P. Labor Praxis 1993;6:64.
[12] Kilz P, Krüger RP, Much H, Schulz G. ACS Adv Chem 1995;247:223.
[13] Kilz P, Krüger RP, Much H, Schulz G. PMSE Prepr 1993;69:114.
[14] Trathnigg B, Maier B, Yan X. Proceedings of the Seventh International Symposium on Polymer Analysis and Characterization. Les Diablerets, Switzerland, 1994.
[15] Adrian J, Braun D, Pasch H. LC–GC Int 1998;11:32.
[16] Murphy RE, Schure MR, Mink LP, Foley JP. Proceedings of the International Symposium on Polymer Analysis and Characterization, A7. Sanibel Island, FL, 1995.
[17] Murphy RE, Schure MR, Foley JP. Anal Chem 1998;70:1585.
[18] Krüger RP, Much H, Schulz G. Int J Polym Anal Char 1996;2:221.
[19] Pasch H, Trathnigg B. HPLC of polymers. Berlin: Springer, 1997.
[20] Belenkii BG, Gankina ES, Tennikov MB, Vilenchik LZ. Dokl Acad Nauk USSR 1976;231:1147.
[21] Entelis SG, Enreinnov VV, Gorshkov AV. Adv Polym Sci 1986;76:129.
[22] Pasch H. Adv Polym Sci 1997;128:1.
[23] Wheeler LM, Willis JN. Appl Spectrosc 1993;47:1128.
[24] Willis JN, Dwyer JL, Wheeler LM. Polym Mater Sci 1993;69:120.
[25] Esser E, Pasch H, Montag P. GIT Zeitschr Lab 1996;16:68.