Monitoring the Grafting of Epoxidized Natural Rubber by Size-Exclusion Chromatography Coupled to FTIR Spectroscopy

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ABSTRACT: The evaluation of heterogeneous polymeric species by a selective, dual detector size-exclusion chromatography setup can provide accurate results on the incorporation of specific functional groups in copolymers as a function of the molar mass distribution. However, when non-UV-absorbing species are used in copolymerization reactions, the dual detector method becomes less reliable. By interfacing a Fourier transform infrared (FTIR) spectrometer with size-exclusion chromatography (SEC), the problem can be overcome, making it possible to map non-UV-absorbing species as a function of the molar mass distribution. Coupling takes place via a solvent-evaporation stage, which delivers the mobile phase as a dry, solvent-free polymeric film onto a germanium disk. In this article, styrene and methyl methacrylate were grafted onto epoxidized natural rubber (ENR50) and analyzed by SEC. The accuracy of FTIR as a suitable detector was evaluated by comparing results from a dual detector SEC setup and FTIR coupled to SEC. FTIR proved to be a successful detector for the analysis of non-UV-absorbing species. This was consequently followed by the characterization of methyl methacrylate-grafted ENR50. From the relevant data, Gram–Schmidt and contour plots could be made to indicate the incorporation of methyl methacrylate into the grafted epoxidized natural rubber as a function of the molar mass distribution. J Appl Polym Sci 88: 2539–2549, 2003

Key words: graft copolymers; FT-IR; rubber; functional groups

INTRODUCTION

Size-exclusion chromatography (SEC) has established itself as an important analytical tool for the characterization of polymeric materials. Although SEC can be used to determine the molar mass distributions of homo- and copolymers, this technique does not give much information about the chemical composition distribution and the functionality type distribution of the samples. This is mainly because of separation according to hydrodynamic volume (which is related to molar mass) and the use of nonspecific detectors, e.g., differential refractive index detectors (RI) and evaporative light-scattering detectors (ELSD), which yield only the concentration of samples. UV-absorbing species in a sample can be identified by the addition of a UV-vis detector, but this technique has limited applications due to the small number of polymers that are UV-absorbing. To overcome this problem, other detectors have been interfaced with SEC but, to date, FTIR has proved to be the most powerful detection tool for the identification of specific functional groups or components within polymeric species.

For the analysis and identification of chemically complex polymer systems, e.g., graft copolymers, it is often necessary to separate the copolymer into its different components. Typical separation processes include fractional extraction, fractional precipitation, and column chromatography.[1,2] Up to now, characterization of graft copolymers was mainly carried out by size-exclusion chromatography,[1,3,4] but no information regarding the molar mass of the chemical components of the graft product could be obtained. By coupling selective separation methods, e.g., critical, adsorption, or size-exclusion chromatography, with selective detectors, e.g., UV or FTIR, not only is it possible to separate complex polymers into their constituting components (i.e., based on molar mass or chemical composition), but it is also possible to analyze selectively specific functional groups as a function of these distributions. This provides more information than was previously available.

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In 1971, Ross and Shank[5] introduced infrared spectroscopy coupled to SEC and in 1975 the coupling was performed by using a flow-through cell.[6] In the case of liquid chromatography coupling, the large amounts of solvents required have a negative influence on the IR spectra. The solvents are IR-active, hence the spectra obtained with the SEC–FTIR flow-through coupling gave inferior signal-to-noise ratios. Additionally, solvents that have absorption bands in the same region as the polymer sample make accurate analyses impossible.[7,8]

The newest method of analyzing the SEC fractions by means of FTIR was proposed in 1986 by Gagel and Biemann.[9] In this method an intermediate step is introduced during which the eluent is evaporated from the sample after it leaves the chromatographic system. As solvent is no longer present, the entire IR spectra can now be used for identification.

The FTIR interface allows the combination of high-resolution SEC together with the good identification capabilities of FTIR. In this analysis method, an aerosol is produced by mixing the eluent with N_2 as it exits the liquid chromatograph. This aerosol is consequently sprayed onto a rotating carrier support, which is subsequently placed into a reflective mirror setup, where the disk is rotated at the same speed as in the spraying mode. In this setup, continuous IR spectra of an entire SEC run can be obtained. To collect the spectra, software that was normally used to collect GC–FTIR spectra is used. The advantage of this technique is that the optical module will rotate at the same speed as the collection module, thus giving a direct time relationship between chromatographic separation and collection. This allows a linear relation to be drawn between the normal SEC detection signal and the 3D presentation of the data. In other words, not only will it be possible to follow the incorporation of functional groups, but the molar mass distributions of these groups will also be evident from the 3D plots. Germanium was chosen as the carrier support due to its IR transmission in the range of 450–6,000 cm^{-1} as well as its chemical inertness and nontoxicity. Aluminium foil was placed on the underside of the disk, allowing double absorption through reflection of the IR beam. Further improvements were made to the nebulization of the aerosol[10,11] and later a commercial company started manufacturing and selling analytical instruments that operate on this concept.[12]

In the years following the major contributions to epoxidized natural rubber (ENR) research, not much emphasis was placed on the analysis of these samples. This was mainly due to the fact that the limited solubility of ENR restricted the number of techniques that could be used, forcing NMR and IR spectroscopy to be the main analytical techniques. The availability of analytical data on the grafting of styrene and methyl methacrylate onto epoxidized natural rubber (ENR50) has, to date, been very limited.[13–15] Gelling[16] performed thermal analysis on epoxidized natural rubber and showed the influence of the degree of epoxidation on the glass-transition temperature (T_g). ^{13}C NMR spectroscopy was used to show that the epoxidation process occurs randomly in homogeneous solution as well as in the rubber latex.[17] The effect of epoxidation was also investigated by size-exclusion chromatography and the conclusion was drawn that for the soluble fraction, the epoxidation was accompanied by a decrease in molar mass and change in molar mass distribution.[18]

This article focuses on the combination of chromatographic and spectroscopic techniques for relatively quick and easy analysis of modified ENR. Styrene and methyl methacrylate will be grafted onto ENR via ordinary emulsion polymerization reactions, after which the grafted rubber will be analyzed by SEC as well as FTIR-coupled SEC. The use of an FTIR detector as an alternative detection method for functional groups will also be evaluated.

EXPERIMENTAL

Chemicals

Styrene and methyl methacrylate, obtained from Plascon Research, were washed with a 0.3 M potassium hydroxide solution prior to distillation under reduced pressure. The distilled monomers were stored at −8°C. The epoxidized natural rubber (ENR50) was obtained from the Lembaga Getah Malaysia (Malaysian Rubber Board) in Kuala Lumpur and was in latex form. The latex had a dry rubber content of 59.4% (w/v). Potassium persulfate (KPS; Saarchem) was used as initiator and Berol 291 (nonylphenol ethoxylate nonionic surfactant) and sodium lauryl sulfate (SDS; BDH) were used as surfactants. Distilled deionized water was obtained from a Millipore Milli-Q purification system. HPLC-grade tetrahydrofuran (THF; ACROS) was used in all analytical experiments.

Equipment

FTIR

Samples were analyzed on a Shimadzu FTIR-8101M fourier transform infrared spectrometer. Shimadzu Hyper IR software was used for computer manipulation of the data.

SEC

The SEC system consisted of a Waters 510 HPLC pump, Waters 486 tunable absorbance detector (UV) at 260 nm, Waters 410 differential refractometer (RI), and a TSP (Thermo Separation Products) Spectra Series AS100 autosampler. Five columns and a precol-

umn filter were used and the column oven was set at 30°C. The column set consisted of Waters Ultra Styragel HR1 (10^2 Å), HR3 (10^3 Å), HR4 (10^4 Å), HR5 (10^5 Å), and HR6 (10^6 Å). Polymer Standards Service (PSS) WinGPC Scientific V4.02 was used for data acquisition and data analysis. THF was used as solvent and the flow rate was 1.0 mL/min^{-1}. The volume of the samples injected was 180 μL and the concentration was 3.3 mg/mL^{-1}.

SEC–FTIR

A Lab Connections LC-transform Model 100 was used as FTIR interface in combination with a Waters 510 pump for separation and sample delivery and a Nicolet 460 FTIR as detector. THF was used as solvent and the solvent flow was set at 1.0 mL/min^{-1}; 100 μL of the samples were injected and the columns used consisted of four PLgel columns [PLgel 5 μ Mixed D, PLgel 3 μ Mixed E, PLgel 10 μ (10^5 Å), and PLgel 5 μ (50 Å)] used in series with an effective molar mass ranging from 100 to 1,000,000 Dalton. The germanium disk of the LC transform had a rotation speed of 10°/min^{-1} and the nozzle evaporation temperature was 70°C. The distance between the nozzle and the germanium disk was 8 mm. A flow splitter was used to direct 1/10 of the flow to the germanium disk and 9/10 of the solvent stream to the UV and RI detector. Omnic 3.1 was used for data analysis.

Sample preparation

General sample preparation

Ten grams of the grafted epoxidized natural rubber latex was added to 10 g of water. The diluted latex was continuously stirred with a magnetic stirrer while 200 mL of MeOH was slowly added to facilitate precipitation. The excess MeOH was subsequently decanted from the precipitated rubber, after which a further 100 mL of MeOH was added to rinse out as much water as possible. The precipitated rubber was decanted into a flat-glass evaporating dish and evacuated at room temperature until constant weight.

FTIR

Due to the partial insolubility of ENR, the complete sample, the soluble part, and the gel part of the sample were analyzed by FTIR. FTIR analysis of the complete sample was carried out by incorporation of the dried sample in a KBr matrix, followed by pressing of FTIR disks. Disks were made by mixing 0.02 g of the dried sample and 4.18 g of water-free KBr. The mixture was ground with a pestle and mortar to ensure complete incorporation of the sample in the KBr matrix. FTIR analysis on the soluble part was performed after dripping the sample solution (3 mg/mL) onto a KBr disk and drying.

SEC

For SEC analysis, 10 mg of the dried samples were dissolved in 3 mL of THF. The samples were left overnight in solution and then filtered through a Gelman Glass Acrodisc and a Gelman GHP Acrodisc GF 0.45 μm, in that particular order.

SEC–FTIR

A total of 300 mg of the dried samples were added to 25 mL of THF. The solutions were left in an oven at 50°C for 24 h to obtain maximum solubility. After 24 h, the soluble part was drawn off from the respective solutions with a syringe and filtered through two filters (Gelman Glass Acrodisc and Gelman GHP Acrodisc GF 0.45 μm) into a round-bottom flask. The flask was then connected to a rotary evaporator where all the solvent was drawn off to be able to determine the dried sample mass. A solution concentration of 20 mg/mL^{-1} in THF was required for analysis.

Synthesis

The monomer, emulsifier, rubber, and water were stirred continuously for 15 min in a round-bottom flask under an N_2 blanket. This solution was subsequently transferred to a pressure-equalizing dropping funnel. Initiator (KPS) was added to a second pressure-equalizing dropping funnel, also connected to the main reactor. The reactor was charged with 10 g of water and heated to 82°C under nitrogen flow. Stirring was maintained at 250 rpm. To start the reaction, 2% of the monomer–rubber solution and 10% of the initiator solution (25% in the case of styrene) were added to the reactor, which was kept at 82°C for 15 min. The remainder of the monomer–rubber solution was added over a 4-h period. The reactor was then heated to 85°C for 30 min to ensure completion of the grafting reaction. The above procedure was followed for samples S2, S3, S5, S6, and S8, as well as for M3 and M5. For sample M8, the reactor was charged with ENR50, while MMA and initiator were added over a 4-h period. All other conditions remained the same. Reaction formulations and sample codes are shown in Table I. In all formulations, 47.7 g of ENR50 latex was used.

RESULTS AND DISCUSSION

The presence of epoxy groups in the polymer backbone leads to a change in the solubility of the rubber, hence the degree of epoxidation seems to determine the gel content of the solubilized samples. Due to the fact that 50% of epoxidized natural rubber was used in

TABLE I
Sample Codes and Reaction Formulations for the Grafting of Styrene and Methyl Methacrylate onto Epoxidized Natural Rubber

	Monomer		Surfactant		
Sample code	Styrene (g)	MMA (g)	SDS (g)	BEROL 291 (g)	Initiator KPS (g)
S2	4.2		2.8		0.35
S3	12.6		2.8		0.35
S5	12.5		2.8		1.05
S6	8.4		2.8		0.70
S8	12.6		2.8		0.35
M3		12.6		2.8	0.35
M5		12.5		2.8	1.05
M8		12.6		2.8	0.35

all the synthesis reactions, it was deemed necessary to evaluate the solubility of the samples and to comment on the validity of the analyses of the soluble parts.

In 1981, Ng and Gan[14] reported on the insolubility of epoxidized natural rubber. Although epoxidized natural rubber can be crosslinked by conventional methods, e.g., sulphur, it can also occur that two epoxidized polymeric chains get linked through the formation of an ether linkage.[14,19] The latter can happen spontaneously due to acid-catalyzed ring opening, which can occur as a result of the acidic reaction conditions during the epoxidation of natural rubber.[16] This leads to increased insolubility of epoxidized natural rubber with a higher epoxide percentage.

The occurrence of crosslinks in ENR50 plays a very important role in the investigation of the validity of the SEC and FTIR analyses. By comparing the FTIR spectra of the complete (E1), gel (E2), and soluble (E3) parts of the ENR50 sample, it can be concluded that the only difference between the samples is the presence or lack of the crosslinked ether linkage (Fig. 1).

The band at 3,280 cm^{-1} is due to the formation of ring-opening products (stretching bands of OH groups). The band at 1,060 cm^{-1} is assigned to a THF ring, also formed during the ring-opening side reaction (Scheme 1). The epoxide groups show characteristic bands at 870 cm^{-1} (asymmetrical ring stretching) and 1,250 cm^{-1} (symmetrical ring stretching). The bands at 2,850 cm^{-1} are due to CH_2 (symmetrical) groups and at 2,972 cm^{-1} due to CH_3 groups. The band at 2,910 cm^{-1} is caused by the CH_2 (asymmetrical) groups. The bands at 1,450 and 1,370 cm^{-1} are caused by ethyl (CH_2CH_3) and methyl (CH_3) groups, respectively. The strong band appearing at 1,720 cm^{-1} is also caused by ring-opening products (ester carbonyl groups). The very strong band at 1,650 cm^{-1} is caused by the cis-alkene functional groups (Me—C═CH—) and is also a ring-opening product. A summary of the IR absorption bands for the abovementioned functional groups can be seen in Table II.

The solubilized sample (E3) will not show the ring-opening products due to the fact that the presence of these products usually lead to crosslinking. This explains the absence of bands at 1,650 and 1,550 cm^{-1}.

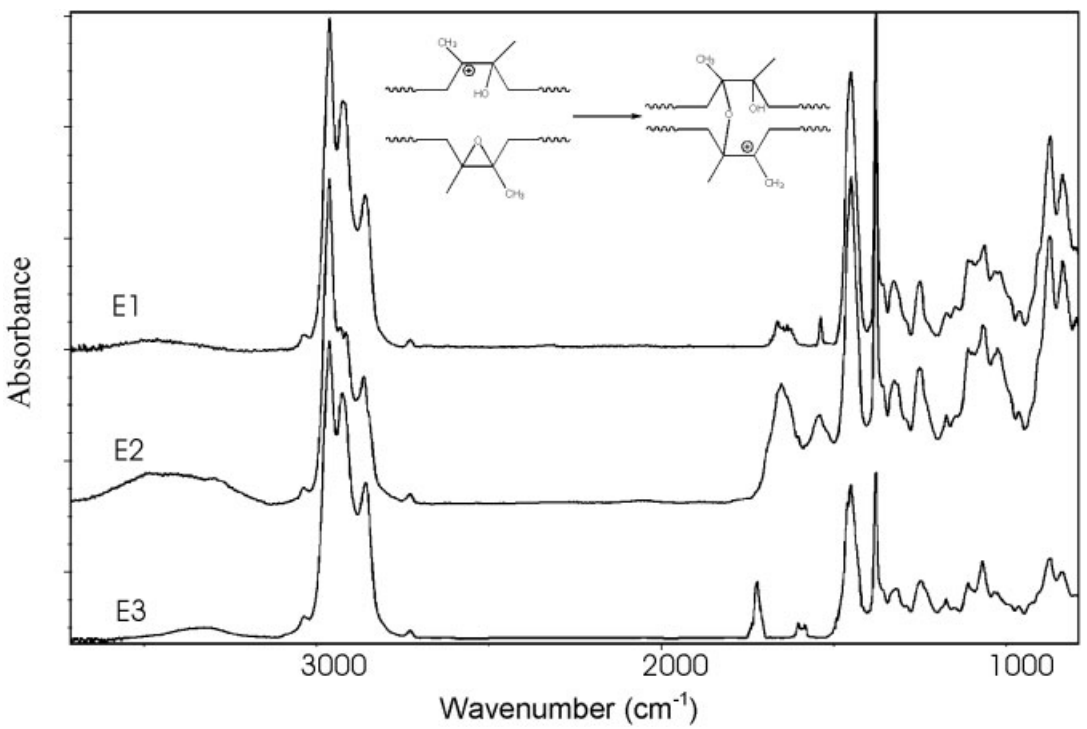
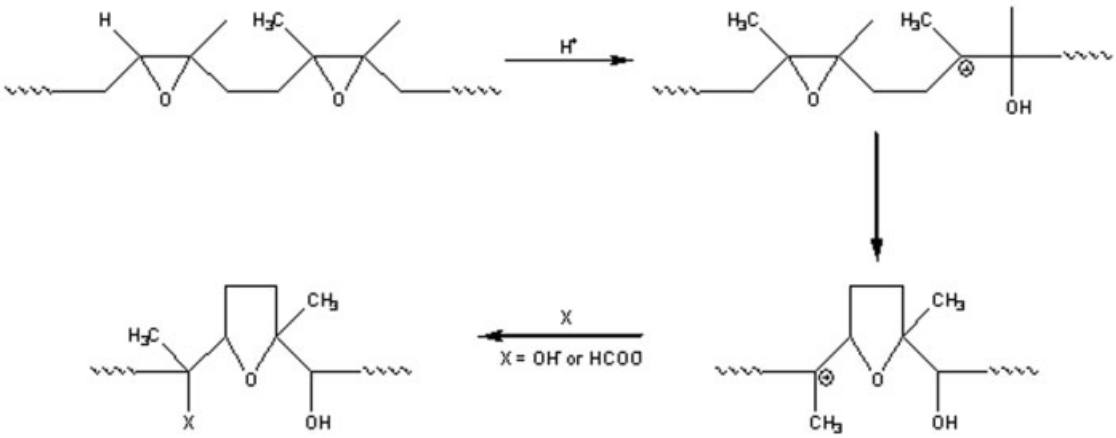


Figure 1 FTIR spectra of the different components of solvated ENR50 rubber showing the structural differences due to the presence of ring-opening products.



Scheme 1

The only ring-opening bands visible in the solubilized sample can be seen at 3,600–3,200 and 1,720 cm^{-1}. These bands are due to hydroxyl and carbonyl groups, which will still be soluble. However, in the original ENR50 sample (E1) and gel ENR50 sample (E2), bands are visible at 1,650 and 1,550 cm^{-1}. These bands are caused by ring-opening products that will lead to the formation of an ether linkage between two polymer backbones. Hence, the only difference between the original and the solubilized sample is crosslinking.

The infrared spectra for the styrene and methyl methacrylate-grafted ENR50 as well as the nongrafted ENR50 are shown in Figure 2. Band 2 (M5) corresponds to the carbonyl absorption band at 1,730 cm^{-1} used for the identification of MMA and band 1 (S3) is the absorption band for the styrene at 698 cm^{-1}. These absorption bands are used for the quantification of MMA and styrene in the graft products.

Size-exclusion chromatography is most frequently used for the determination of molar mass distributions of polymeric samples. However, when different detectors are combined, more information becomes available and thus a better understanding of the polymeric sample is possible. When using a dual detector setup, a differential refractive detector is usually combined with a UV detector, thereby giving more insight into the chromophore-containing polymer, i.e., the distribution of the active species as a function of molar mass will become evident. The absence of UV-absorbing species makes this technique obsolete, as in the case of poly(methyl methacrylate).

Size-exclusion chromatography results for the individual grafted samples can be seen in Table III. The initiator influence, in the absence of monomer, on the molar mass of ENR50 can clearly be seen (sample ENR-i). This is caused by secondary reaction products, which result in crosslinking, hence a decrease in solubility as well as the molar mass of the soluble fraction. The decrease in molar mass of the grafted samples is also a direct influence of the above.

In Figure 3, the styrene content, as a function of the molar mass distribution, can be seen for styrene-

TABLE II
Functional Groups Used in This Study and Their Associated Wave Numbers

Wave number (cm^{-1})	Functional group	Spectral range (cm^{-1})	Bond mode	Peak intensity	Bond
700	Ring	710–690	Bend	Strong	ϕ—R
870	C—O—C	980–815	Asymmetrical ring stretching	Strong	3-ring ether (epoxide group)
1,060	C—O—C	1,080–1,060	Asymmetrical ring stretching	Strong	5-ring ether
1,250	C—O—C	1,280–1,230	Symmetrical ring stretching	Medium	3-ring ether
1,370	CH	1,370–1,365	Deformation	Medium	C—$(CH_3)_3$
1,450	CH	1,485–1,445	Deformation	Medium	R′—CH_2—R″
1,452	CH	1,485–1,445	Deformation	Medium	R′—CH_2—R″
	Ring	1,465–1,430	Stretching	Medium	ϕ—R
1,550	NO_2	1,570–1,520	Asymmetrical stretching	Strong	C—NO_2
1,650	CC	1,662–1,631	Stretching	Medium	CH═CH
1,720	C═O	1,740–1,715	Stretching	Strong	C═C—CO—O—R
2,850	CH	2,863–2,843	Symmetrical stretching	Strong	R′—CH_2—R″
2,910	CH	2,936–2,916	Asymmetrical stretching	Strong	R′—CH_2—R″
2,972	CH	2,972–2,952	Asymmetrical stretching	Strong	R—CH_3
3,280	OH	3,400–3,200	Stretching	Variable	Hydrogen bond (broad peak)

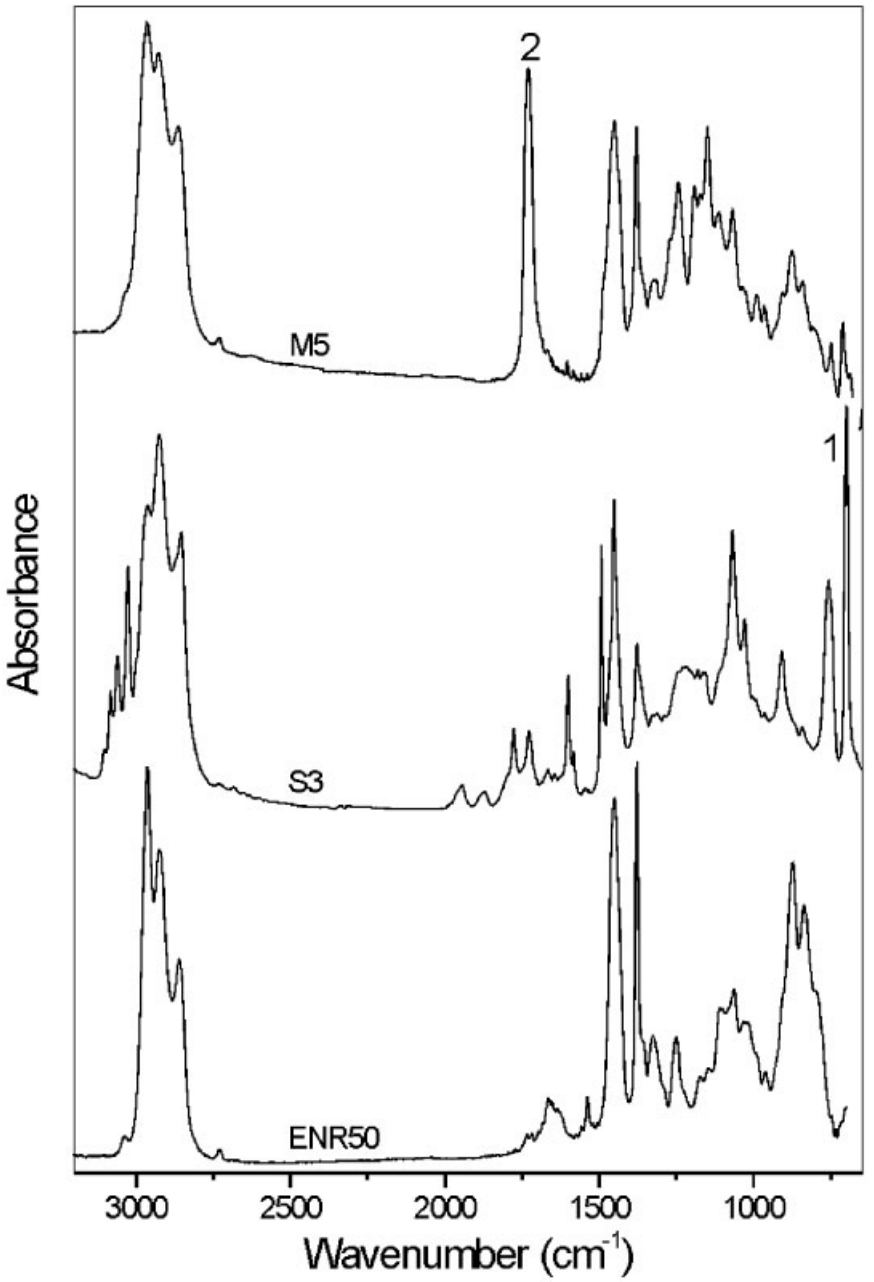


Figure 2 Infrared absorbance spectra of ENR50 grafted with methyl methacrylate and styrene, respectively, as well as ungrafted ENR50. Bands 1 and 2 indicate the characteristic absorbance bands for styrene and methyl methacrylate, respectively.

grafted ENR50. Because the time delay between the two detectors is automatically subtracted, it is apparent that a shift in peaks will indicate a shift in the distribution of the styrene content. If the UV peak shifts to the right [Fig. 3(C)] of the RI peak, it is an indication that more styrene is present in the higher molar mass molecules than in the lower molar mass molecules. When it shifts to the left, the opposite is true. Complete overlapping of peaks indicates that the styrene fraction is well represented over the entire molar mass distribution region of the graft polymer [Fig. 3(B)].

In the case of methyl methacrylate-grafted ENR50, the dual detection method could not be used due to the weak UV absorption of methyl methacrylate. Thus, although adequate molar mass distributions for the grafted samples could be obtained, nothing could be concluded about the methyl methacrylate distribution.

By combining size exclusion and infrared spectroscopy, this analytical gap can be bridged, thus making it possible to collect a complete molar mass distribution and to analyze selectively certain components in a polymeric sample. SEC–FTIR analysis was performed

TABLE III
Size-Exclusion Chromatography Data of the Grafted Samples with Respect to Their Soluble Part

Sample	$M_w \times 10^{-4}$ (g/mol)	$M_n \times 10^{-4}$ (g/mol)	M_w/M_n
ENR50	27.76	4.90	5.67
ENR-i	7.00	3.20	2.19
S2	2.58	1.22	2.11
S3	14.81	4.92	3.01
S5	9.95	3.17	3.14
S6	3.66	1.00	3.65
S8	9.82	2.55	3.85
M3	46.63	15.87	2.93
M5	12.11	3.49	3.47
M8	17.58	3.91	4.49

to evaluate the styrene and methyl methacrylate distributions throughout the grafted samples. Separation according to molar mass was the first step in this analysis technique. On exiting the SEC, fractions of the sample were automatically deposited on a germanium disk as dry, solvent-free spots, which were then inserted into an FTIR spectrometer for further analysis. The fractions collected were therefore a complete representation of the molar mass distribution of the sample in question and, on doing FTIR analysis, the styrene and methyl methacrylate content, as a function of the molar mass distribution, could be mapped. The data collected is not an exact representation of an ordinary SEC analysis but is called a Gram–Schmidt representation of the separation. This representation can be defined as a graphic representation of series data that shows how the relative infrared response changed over the duration of the experiment.

In other words, the Gram–Schmidt representation is the total infrared absorption as a function of time, where the time axis of the trace can be correlated to the molar mass of the sample (high molar masses elute earlier than low molar masses). By using computer software, it is possible to look at the infrared signal at any point on the Gram–Schmidt representation. This allows the opportunity to evaluate the ratio between the styrene (698 cm^{-1}) and ENR50 (1,452 cm^{-1}) bands at different time intervals, thereby making it possible to represent the relative styrene content as a function of the molar mass distribution. In Figure 4, the relative styrene content as a function of time is shown. It is noteworthy that the accuracy of the styrene : ENR50 ratios will diminish before and after the actual polymer retention time due to the fact that very little polymer can be collected for FTIR analysis, thus causing low signal-to-noise ratios.

From S3 [Fig. 4(A)], it follows that there is more styrene present in the high molar mass fraction (low retention time) of the sample. The styrene content steadily decreases with an increase in retention time, pointing to a lower incorporation of styrene at lower

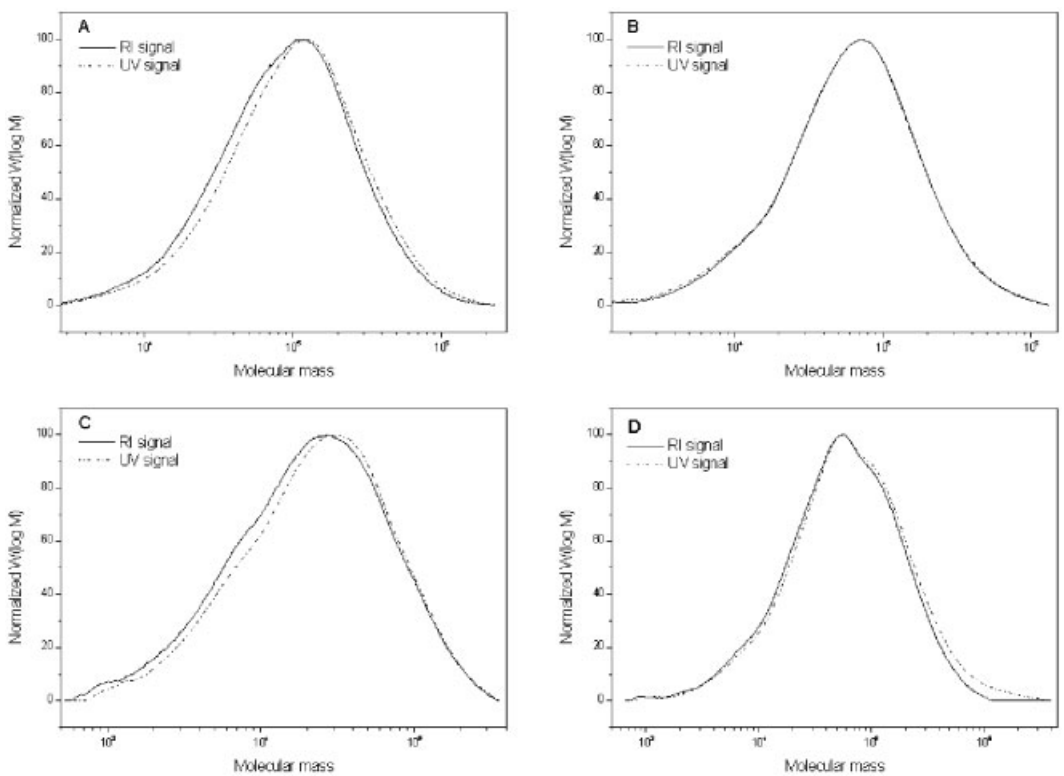


Figure 3 Dual detector analyses of styrene-grafted ENR50 showing the incorporation of styrene as a function of molar mass distribution: samples S3 (A), S5 (B), S6 (C), and S8(D).

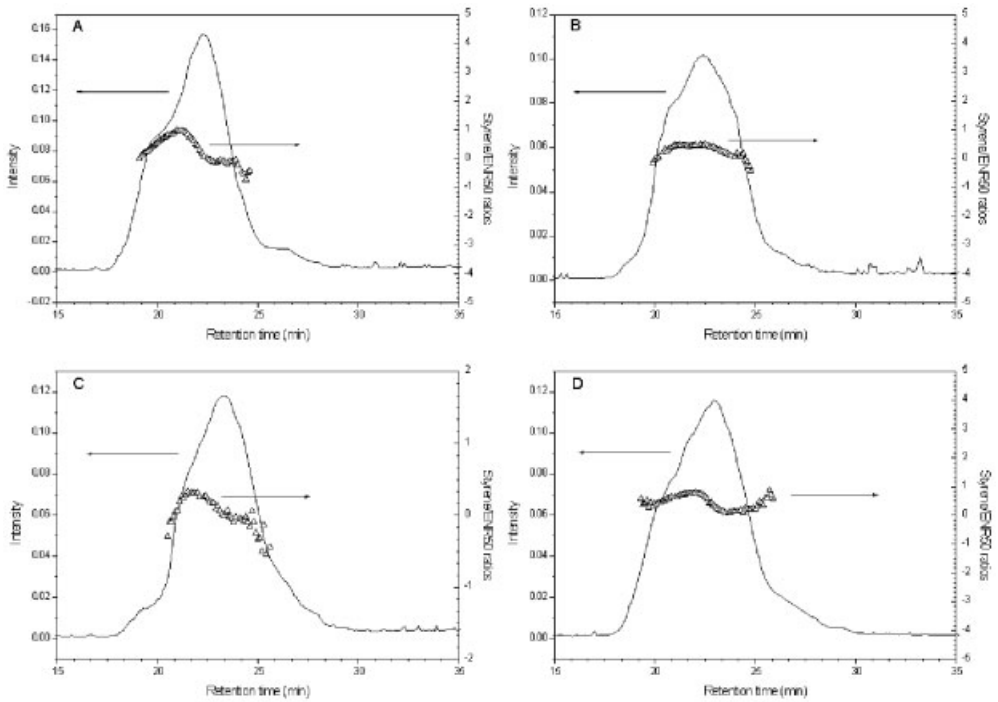


Figure 4 SEC–FTIR analyses of styrene-grafted ENR50 showing the incorporation of styrene as a function of the molar mass distribution: samples S3 (A), S5 (B), S6 (C), and S8 (D).

molar mass. This trend can be correlated with the dual detector SEC analysis, as shown in Figure 3(A). The SEC trace also shows a shift of the UV signal to the higher molar mass region. A similar deduction can be made for S6 [Fig. 4(C)]. For S5 in Figure 3(B), the UV and RI signals show a complete overlap. Again, this is confirmed in Figure 4(B), where the styrene : ENR50 ratio indicates an even incorporation throughout the molar mass distribution. For S8 in Figure 4(D), a more or less homogeneous distribution of styrene over the entire molar mass distribution can be seen. This deduction is exactly mirrored in the SEC traces. Figure 3(D) shows a small decrease in UV absorption in the low molar mass region, followed by an increase in the UV absorption in the high molar mass region. However, the peak maxima for both detectors are exactly the same.

As already mentioned, detection of samples containing PMMA by means of UV is nearly impossible owing to the coincidence of the absorption spectra for PMMA and THF. In this instance, SEC could only be used for the determination of molar mass distribution and not for the detection of PMMA incorporation, as was the case for the polystyrene as shown in the elugrams in Figure 3.

The use of SEC–FTIR made the detection of methyl methacrylate possible by using the absorption wave number for the carbonyl group in comparison to the Gram–Schmidt curve. Figure 5(A), sample code M3, shows clearly that the chemigram (1,800–1,700 cm^{-1}) for the carbonyl absorbance in poly(methyl methacrylate) has a higher intensity in the low molar mass region of the Gram–Schmidt distribution. From this it can be concluded that the SEC–FTIR will give the same distribution profile as the dual detection of the styrene-grafted copolymers, where RI and UV detectors were used. Figure 5(B) shows the increase in poly(methyl methacrylate) relative to the ENR50 content in the sample as the molar mass in the samples decreases.

Data from the SEC–FTIR runs can also be presented as contour plots showing the absorbance of the IR bands versus the elution profile of the SEC run. The information obtained is similar to that of the Gram–Schmidt and the chemigram, but with a better overview. Absorbance bands of more than one compound in the system can be compared directly to other compounds. The intensity of absorbance of the functional groups is indicated as a color-coded bar, which is displayed to the right of the contour plot. The dashed line in all contour plots indicates peak maximum values.

Sample M5, in Figure 6, shows clearly that the poly(methyl methacrylate) is only present in the low molar mass region. Band 2, showing the region for the carbonyl group (1,750 cm^{-1}), tails off toward the high molar mass region, implicating that the presence of poly(methyl methacrylate) slowly decreases with an increase in ENR50 chain lengths. For sample M8, in Figure 7, this could not be seen. Here, band 2 can be observed for the duration of the sample elution. This sample showed no tailing of the carbonyl band, indi-

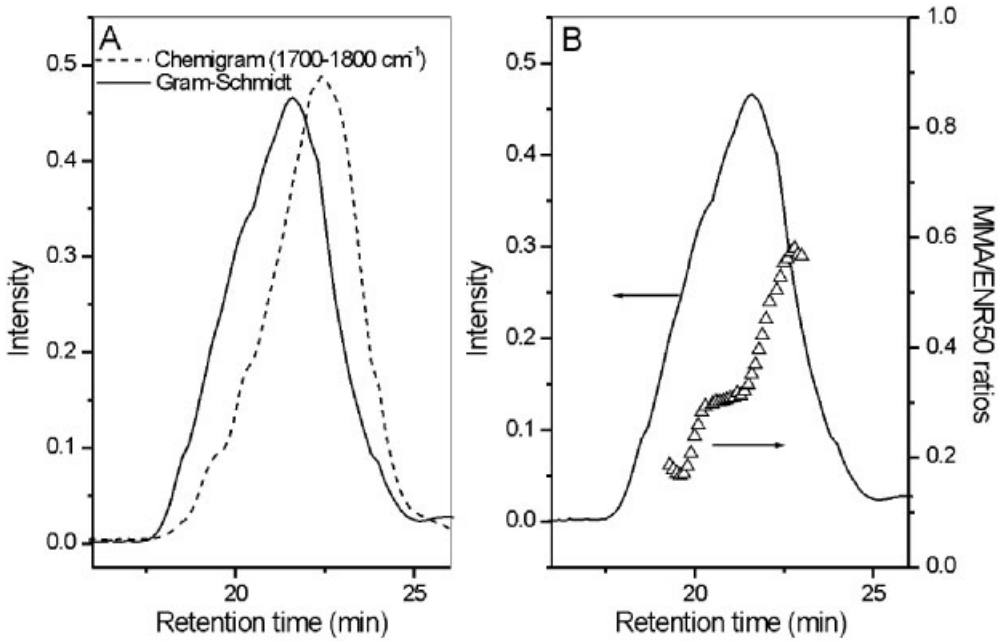


Figure 5 SEC–FTIR analyses of methyl methacrylate-grafted ENR50 (sample M3) comparing (A) the absorption of the carbonyl band of MMA to the total IR absorption as a function of retention time and (B) the ratio of the MMA–ENR50 absorption bands to the total IR absorption as a function of retention time.

cating that the poly(methyl methacrylate) was evenly distributed throughout the polymer system. The same can be seen in Figure 8 for the styrene-grafted samples, where the polystyrene is also spread evenly throughout the MMD. This spread is not that clearly visible for the PMMA because the styrene absorbance band is narrower and more defined than the MMA absorption band in Figure 2.

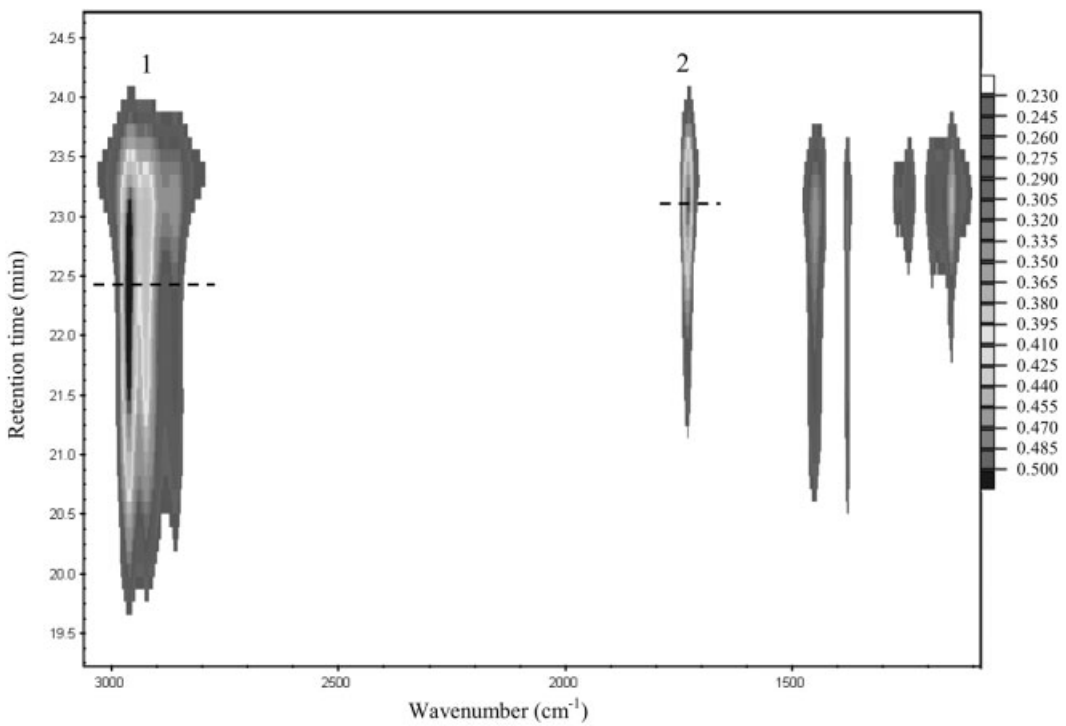


Figure 6 Contour plot of M5 showing the molar mass distribution of functional groups as obtained by SEC–FTIR, with the dashed lines indicating maximum peak intensity. Band 1 is the absorption of the CH_2 groups and band 2 is the absorption of the carbonyl group from the MMA.

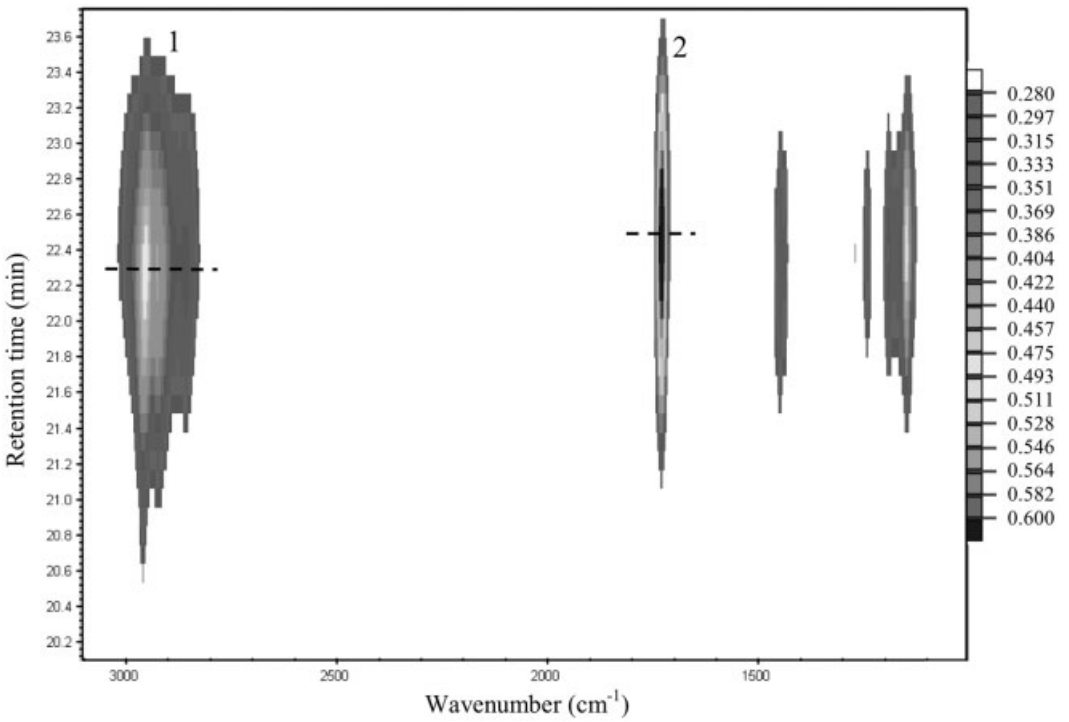


Figure 7 Contour plot of M8 showing the molar mass distribution of functional groups as obtained by SEC–FTIR, with the dashed lines indicating maximum peak intensity. Band 1 is the absorption of the CH_2 groups and band 2 is the absorption of the carbonyl group from the MMA.

Looking at bands marked 1 and 2 in Figures 6 and 7, further comparable deductions on the concentrations of the compounds can be made. In Figure 6, band 1 shows a higher color intensity than band 2, but in Figure 7, band 2 has the higher color intensity, indicating that sample M8 has a higher poly(methyl

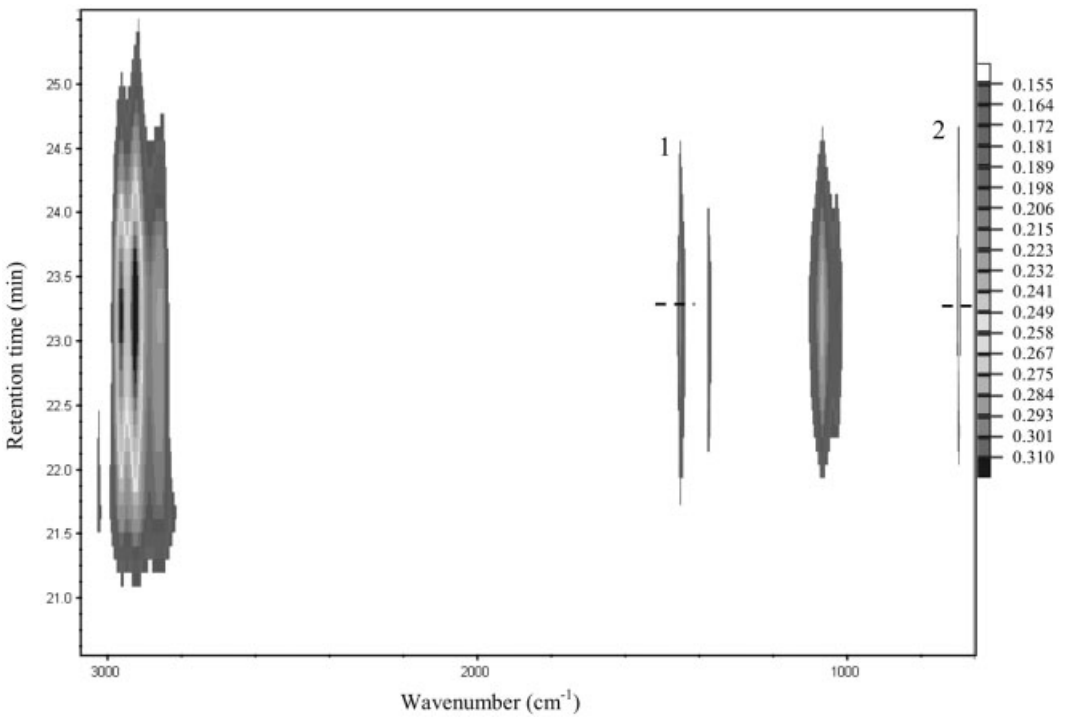


Figure 8 Contour plot of S2 showing the molar mass distribution of functional groups as obtained by SEC–FTIR, with the dashed lines indicating maximum peak intensity. Band 1 is the absorption at 1,452 cm^{-1} of the CH groups present in both the rubber and styrene and band 2 is the absorption of the aromatic structure in styrene at 698 cm^{-1}.

methacrylate) content compared to sample M5. From the above, it can therefore be concluded that SEC–FTIR can be used to identify the incorporation of a functional group as a function of the molar mass distribution.

CONCLUSIONS

Although FTIR coupled to SEC has been established as a well-known analytical technique, the application of FTIR as an analytical detector has not yet reached its fullest potential. This technique has only scarcely been documented, mostly due to the unawareness of researchers of its outstanding capabilities. In this article, it has been shown that the LC transform can be used as a detector for the analysis of the incorporation of styrene in styrene-grafted ENR50 by comparing it to the classical dual detection method. This therefore creates an opportunity for the analysis of UV-inactive species which, to date, have been impossible to analyze. To illustrate the capability of SEC–FTIR, methyl methacrylate-grafted ENR50 samples were analyzed and the results were displayed as either chemigrams or as ratios of the functional groups. To show the versatility of this technique, the data were also displayed as a contour plot in which all the dimensions of the two interfaces were combined. Not only is this type of representation visually pleasing, but both incorporation of functional groups as well as the molar mass distributions can be viewed simultaneously.

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