Use of Gradient, Critical, and Two-Dimensional Chromatography in the Analysis of Styrene- and Methyl Methacrylate-Grafted Epoxidized Natural Rubber

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ABSTRACT: The growing number of heterogeneous polymeric species that are being synthesized places increasing demands on existing analytical techniques. Although size-exclusion chromatography (SEC) has established itself as a powerful analytical tool, it has its limits when complex polymers, e.g., graft copolymers, must be analyzed. In this case, complementary techniques such as gradient HPLC and liquid chromatography at critical conditions (LCCC) are more favorable. The present study describes the synthesis and analysis of methyl methacrylate- and styrene-grafted epoxidized natural rubber by different chromatographic techniques. The grafting efficiency was evaluated by gradient HPLC under normal and reversed phase conditions. Methyl methacrylate-grafted ENR50 was further analyzed by LCCC, where separation of the rubber and grafted rubber occurred according to chemical composition but was independent of the molar mass of the methyl methacrylate homopolymers. This was followed by the combination of LCCC and SEC, where separation was achieved in two dimensions. Relevant deductions were made of both the chemical composition distribution and the molar mass distribution of the functional groups of methyl methacrylate-grafted ENR50. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2530–2538, 2003

Key words: high performance liquid chromatography (HPLC); chromatography; rubber; graft copolymers

INTRODUCTION

Size-exclusion chromatography (SEC) is used extensively as a powerful analytical tool for the determination of molar masses and molar mass distributions (MMD). For linear homopolymers, SEC yields true molar masses (when certain requirements are met), while for more complex systems, such as copolymers or branched polymers, different problems are encountered. In the case of polymer mixtures, for example, a serious problem is caused by overlapping molar mass distributions of the different blend components, leading to coelution of the macromolecules of different molar masses. Even more complicated is the analysis of graft copolymers where, in addition to MMD, chemical heterogeneity and branching distributions are encountered. For the evaluation of such heterogeneous polymers, analysis by gradient HPLC, liquid chromatography under critical conditions (LCCC), and two-dimensional chromatography can be useful alternatives or complementary methods to SEC.

Chromatographic separation can be divided into three modes: the exclusion mode, critical mode, and adsorption mode.[1] Critical conditions in the chromatography of homopolymers are defined as those conditions under which entropic exclusion effects are exactly compensated for by enthalpic effects, hence retention is solely governed by small differences in the chemical structure of polymers to be analyzed. Such differences in chemical structure can be due to endgroups or different blocks in segmented copolymers. To date, most work in the area of critical and adsorption chromatography has been carried out on the analyses of block copolymers[2,3] and functional homopolymers.[4] In this study, the focus will mainly fall on the analysis of grafted material.

Graft copolymers are highly complex macromolecular systems due to the chemical composition as well as molar mass drift that can exist in these species. Accordingly, for their analysis, techniques must be used that combine information on chemical composition with information on molar mass. Molar mass

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distributions are usually characterized by size-exclusion chromatography while chemical composition distributions are mostly determined by means of interaction chromatography.[5] In particular, by working at LCCC conditions[6–11] of one of the components of a segmented copolymer, this component can be made chromatographically invisible,[12–14] thus not contributing to the retention and allowing the other components to elute in the size-exclusion mode. Hence, LCCC yields information on the chemical heterogeneity of segmented copolymers.

To analyze both chemical composition and molar mass distributions in copolymers, different chromatographic techniques can be combined. Chromatographic cross-fractionation[15–18] is one such technique, where separations in diverging directions are combined. While one type of separation occurs with regard to chemical composition, the other type of separation is sensitive towards hydrodynamic volume. Thus, by applying and combining different modes of liquid chromatography, it is possible to separate polymers selectively according to hydrodynamic volume, chemical composition, or functionality. In 1993, Kilz et al.[19–21] developed a fully automated two-dimensional chromatographic system. This allows copolymers to be fractionated by interaction chromatography according to chemical composition distribution in the first dimension through the application of a suitable solvent–nonsolvent combination. Fractions are automatically stored in a sample loop and subsequently transferred to the second dimension where it is separated according to hydrodynamic volume via size-exclusion chromatography. During the last few years, numerous automated two-dimensional chromatography applications have been described, including the analyses of polyalkylene oxides, polyesters, and block copolymers.[19–23]

The analysis of graft copolymers, especially of styrene and methyl methacrylate grafted onto epoxidized natural rubber (ENR50), has not received much attention.[24–26] Gelling[27] performed thermal analyses 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.[28] The effect of epoxidation was also investigated by size-exclusion chromatography and the conclusion was drawn that for the soluble fraction, the epoxidation is accompanied by a decrease in molar mass and a change in molar mass distribution.[29]

This article will focus on the use of gradient, critical, and two-dimensional chromatography to evaluate the grafting efficiency of styrene and methyl methacrylate onto ENR50 as well as to determine the homogeneity of the incorporated graft polymer throughout the sample. The different analytical techniques will be discussed and the interpretation of data will be correlated and explained.

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 until required. 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. For HPLC separation, the solvents used were tetrahydrofuran (THF) HPLC-S (Biosolve), acetonitrile (ACN) HPLC-S (Biosolve), cyclohexane (Biosolve), and dichloromethane (DCM) HPLC (Biosolve).

Gradient HPLC

The chromatographic system used for gradient HPLC analyses consisted of a Waters 2690 Separations Module (Alliance), Waters 486 tunable absorbance detector, Polymer Laboratories PL-EMD960 evaporative light scattering detector (ELSD), and the Waters SAT/IN module. The column oven temperature was 35°C and the flow rate of the solvent was 0.5 mL/min. The ELSD was operated at 70°C with an N_2 carrier gas flow rate of 4.9 SLM (standard liters per minute). To achieve separation between the different grafted samples, two different gradient phases had to be used, i.e., normal and reversed phase. Normal phase chromatography separation was achieved on a μBondapak CN column (particle size 10 μm, pore size 125 Å, and column dimensions 150 × 3.9 mm i.d.) combined with a Nova-Pak CN HP precolumn. For reversed phase separations, a Symmetry C_{18} column (particle size 5 μm, pore size 100 Å, and column dimensions 150 × 3.9mm i.d.) was used in combination with a Nova-Pak C_{18} precolumn. Millennium[32] software was used for data acquisition. Table I shows the gradients that were used for both the reversed and normal phase setups.

LCCC

For analysis of ENR50 at the critical point of poly(methyl methacrylate) (PMMA), a Thermo Separations Products, Spectra Series P100, pump was used. This

pump system cannot run solvent gradients, hence the solvent mixture had to be premixed. The solvent mixture for this isocratic run was 63.3% THF and 36.7% cyclohexane by weight and was taken at the critical point. The columns used for the separation were a Knauer Nucleosil 300 CN (particle size 7 μm, dimensions 250 $\times$ 4 mm i.d.) and a Nucleosil 500 CN (particle size 7 μm, dimensions 250 $\times$ 4 mm i.d.) and the column oven temperature was set at 40°C. The detectors used were the Waters 486 tunable absorbance UV detector at a wavelength of 254 nm and the Altech ELSD 500 detector. The flow rate was 1.0 mL/min. Data collection was done with PSS-WINGPC 4 from Polymer Standards Service (PSS; Mainz, Germany).

Two-dimensional chromatography

For the first dimension, the same setup was used as described for the LCCC analysis of ENR50. However, for two-dimensional chromatography the flow rate was set at 20 μL/min. Sample fractions from the first dimension were collected in an eight-port valve system (VICI Valco EHC8W), which consisted of two loops, each having a sample capacity of 100 μL.

The second dimension consisted of a Waters 510 pump delivering a flow rate of 1.5 mL/min. The column used was a Polymer Standards Service SDV (styrene divinyl benzene) column (pore size 5 μm, dimensions 300 $\times$ 8 mm i.d.). The same detectors were used as for the analysis of the ENR50 at the critical point.

For the construction of contour plots, calibration standards had to be injected. These standards were injected into the second dimension. Sample fractions collected in the first dimension are automatically injected into the second dimension and no calculations have to be done for the processing of the contour plots as was necessary in other reported cases.[1,2] Data acquisition and processing were automatically performed by the Polymer Standards Service software: WINGPC 4 and PSS-2D-GPC-Software, respectively.

TABLE I
Gradient Profiles for Reversed and Normal Phase Separation of the Styrene and Methyl Methacrylate Grafted ENR50

Reversed phase				Normal phase		
Time	% solvent			Time	% solvent	
(min)	H_2O	ACN	THF	(min)	DCM	THF
0	50	50	0	0	100	0
12.5	0	100	0	5	100	0
37.5	0	0	100	15	0	100
40	0	0	100	20	0	100
45	50	50	0	25	100	0

Total runtime: 60 min for reversed, 35 min for normal. All gradient changes were linear.

TABLE II
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)
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
M1		8.4		2.8	0.70
M4		4.2		2.8	1.05
M5		12.5		2.8	1.05
M6		8.4		2.8	0.70
M8		12.6		2.8	0.35
M10		12.5		2.8	1.05

General sample preparation

A total of 10 g 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.

Synthesis

The monomer, emulsifier, rubber, and water were stirred continuously for 15 min in a round-bottom flask under an N_2 blanket. The solution was subsequently transferred to a pressure-equalizing dropping funnel. Initiator 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 S3, S5, S6, and S8, as well as for M1, M4, and M5. For samples M6, M8, and M10, 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 are shown in Table II. In all formulations, 47.7 g of ENR50 latex was used.

RESULTS AND DISCUSSION

Due to the fact that epoxidized natural rubber with a degree of epoxidation of 50% was used in the grafting

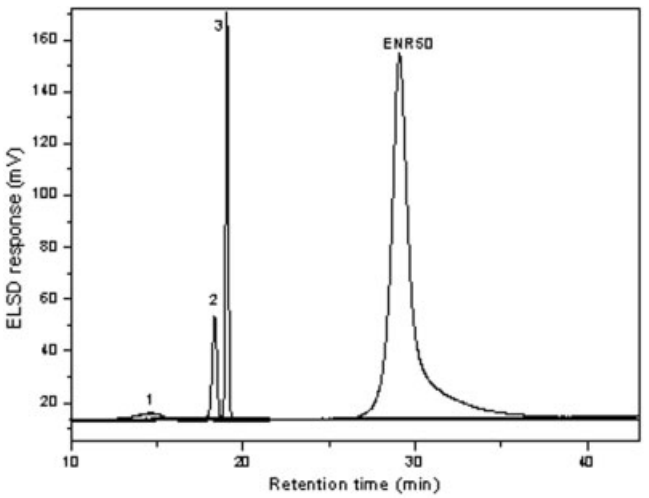

Figure 1 PMMA standards and ENR50 rubber analyzed by gradient HPLC; peak 1, PMMA 625 g/mol; 2, PMMA 9,200 g/mol; 3, PMMA 62,600 g/mol. Column: Symmetry C_{18}; reversed phase gradient; detector: ELSD.

reactions, the presence of epoxy groups in the polymer backbone could lead to the formation of crosslinks when subjected to the reaction conditions used. This could lead to a decrease in the solubility of the rubber, causing complications in the analyses of the grafted products. The degree of epoxidation combined with reaction conditions are therefore the limiting factors in the determination of the grafting efficiency. This has always been the constraining factor in the analyses of epoxidized natural rubber.[29]

Gradient analysis

Separation of standards

For the optimization of the gradient HPLC separation, the polarity of the polymeric species has to be taken into consideration. In the present case, PMMA is more polar than ENR50 and PS. When using a reversed phase column, elution should follow an order of decreasing polarity. Therefore, the PMMA homopolymer should elute first, followed by the copolymer and then the ENR50. In a normal phase system, e.g., silica gel, the order of elution is reversed. Nonpolar species will elute first, followed by polar species. Hence, under such conditions, PS is eluted first, followed by the copolymer and lastly the ENR50.

It was the aim to elute the corresponding homopolymers PMMA and PS first, followed by the graft copolymer and the ENR50 rubber. Accordingly, for the PMMA-grafted system, a reversed stationary phase was chosen, while for the PS-grafted system a normal stationary phase was selected. The elutions of PMMA standards and ENR50 are shown in Figure 1. Note that the elution window for the grafted polymer is 10 min. Elution of the grafted samples will take place from the highest to the lowest incorporated amount of methyl methacrylate.

Figure 2 shows the elution of polystyrene standards under normal phase conditions. PS is much less polar than ENR50 and will therefore elute in a less polar solvent, hence pre-eluting before the ENR50. The separation window for grafted species is 2 min, which is sufficient for such analyses.

Analysis of ENR grafted with MMA by gradient HPLC

Due to the partial insolubility of the ENR50 samples, only the soluble part can be analyzed by liquid chromatography. This factor has to be taken into consideration when chromatographic data is analyzed.

The chromatographic separation of a number of PMMA-grafted rubber samples is shown in Figure 3. The peak at 9.7 min (peak 1) can be attributed to BEROL 291, which is the surfactant used for the methyl methacrylate emulsion reactions. As can be seen from Figure 3, there is a substantial difference in polymer composition between the different samples due to the different reaction conditions used. For M1, M4, and M5 there were limited amounts of PMMA homopolymer in the samples (peak 2), and a new peak appeared between the retention times of the homo PMMA and the ENR50 rubber (peak 4) peaks. The newly formed peak (peak 3) is due to the grafting of MMA onto ENR50. The higher polarity of the MMA molecules will make the grafted polymer more soluble under the conditions of the solvent composition used in the reversed-phase system. The higher the polarity of the polymer, the earlier the polymer will elute under a certain solvent mixture from the column. All

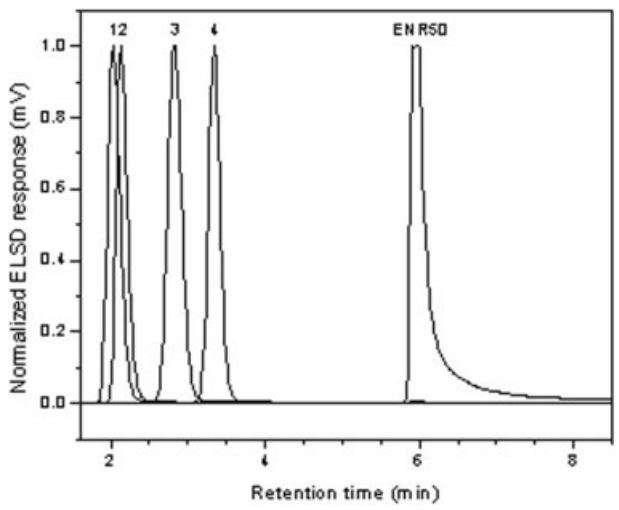

Figure 2 PS standards and ENR50 analyzed by gradient HPLC; peak 1, PS 700,000 g/mol; 2, PS 66,000 g/mol; 3, PS 5,050 g/mol; and 4, PS 500 g/mol. Column: μBondapak CN; normal phase gradient; detector: ELSD.

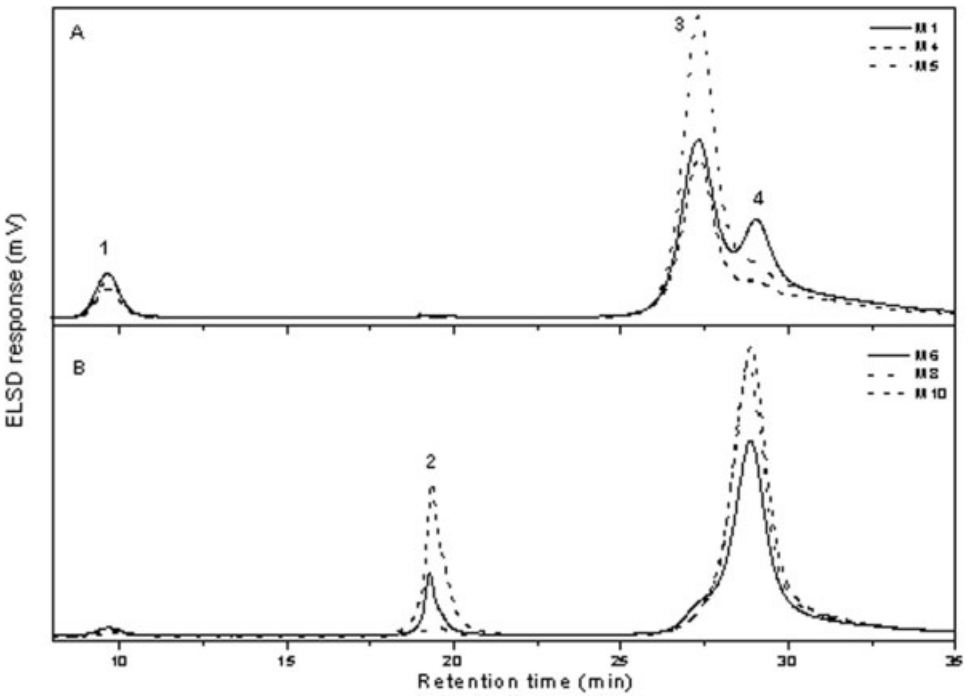

Figure 3 Chromatograms of samples M1, M4, M5, M6, M8, and M10 showing separations obtained by gradient HPLC. Column: Symmetry C_{18}; reversed phase gradient; detector: ELSD.

the peak maxima are shown as retention times, in minutes, in Table III.

The grafting efficiency can be evaluated by comparing the peak intensities of the different components of the grafting products. As can be seen in Figure 3(B), the chromatograms show only peaks for the ungrafted rubber (peak 4) and for PMMA homopolymer (peak 2). A small shoulder at the lower retention time side of peak 4 indicates some grafting but only in very low amount. Accordingly, the grafting efficiency in samples M6, M8, and M10 is very low.

The situation is completely different for the samples shown in Figure 3(A). For these samples, very low or no amounts of PMMA homopolymer are detected. The elution peaks for the graft copolymer (peak 3) exhibit a high intensity while the intensity of nongrafted rubber in peak 4 is much lower. This clearly indicates that the grafting efficiency for samples M1, M4, and M5 is very high.

Reaction conditions for M1, M4, and M5, where the premixed monomer–rubber solution was added to a reactor by means of a pressure-equalizing dropping funnel, gave better grafting than M6, M8, and M10, where the monomer and initiator were added to a rubber-filled reactor. Premixing of the rubber and the monomer before the introduction of the initiator will lead to better mixing of the monomer into the latex phase, resulting in higher graft products.

TABLE III
Tabulation of the Peak Retention Times for the Chromatograms Shown in Figure 3

	Retention times (min)			
Sample code	BEROL 291 (1)[a]	PMMA (2)[a]	grafted ENR50 (3)[a]	ENR50 (4)[a]
M1	9.6		27.3	29.0
M4	9.7		27.3	29.0
M5	9.6		27.3	29.0
M6	9.7	19.3		28.9
M8	9.6	19.4		28.8
M10	9.9	19.3		28.9

Retention time: BEROL291, 9.7 min; ENR50, 29.1 min; PMMA 62,600 g/mol, 19.0 min.

[a] Numbering of peaks as seen in Figure 3.

Analysis of ENR grafted with styrene by gradient HPLC

The chromatographic separation of the reaction products of styrene-grafting onto ENR50 is presented in Figure 4. Very prominent free polystyrene peaks can be seen eluting at 2.3 min (peak 1). This means that much of the styrene monomer that was used in the grafting reaction polymerized to form PS homopolymer instead of grafting with the ENR50. The retention time of the free PS peaks coincides with the retention time of the high molar mass PS standards, thus pointing to and confirming the formation of long PS chains. At 6 min, the rubber peaks can be seen (peak 3), followed by humps from 7 to 11 min. These humps are caused by microgels in the solution that was injected into the column. At 4.67 min, the peaks representing the styrene-grafted ENR50 are obtained (peak 2).

The intensity of the peaks corresponding to the graft copolymer can be traced to the starting conditions of the grafting reactions. Samples S3 and S8 show the largest ELSD peaks. This is because the most monomer and least initiator were used in these reactions, leading to the formation of long PS chains grafted onto the ENR50. These peaks are closely followed by the peak of sample S5. In S5, the same amount of monomer as in S3 and S8 was used but the initiator concentration was higher. The latter leads to the formation of shorter chains. The lowest amount of graft copolymer is obtained for sample S6. The signal for S6 is the smallest due to the intermediate amounts of monomer and initiator used, leading to the formation of many smaller branches. It can therefore be concluded that, although grafting did take place, the efficiency was not very high.

Critical point analysis

LCCC is a very simple experimental technique. Elution is conducted in the isocratic mode where the binary mobile phase is usually premixed. Therefore, LCCC is a very facile technique to be combined with other liquid chromatographic techniques such as SEC.

The application of LCCC to the separation of the PMMA-grafted rubber samples is presented in Figure 5. In this case, chromatographic conditions are used that correspond to the critical point of PMMA. On a polar stationary phase such as cyanopropyl-modified silica, critical conditions can be established using a binary mobile phase of THF–cyclohexane. The critical point corresponds to THF–cyclohexane 63.3%/36.7% by weight. As UV detection cannot be used for PMMA analysis, an ELSD was utilized as an alternative detector giving information on the relevant retention

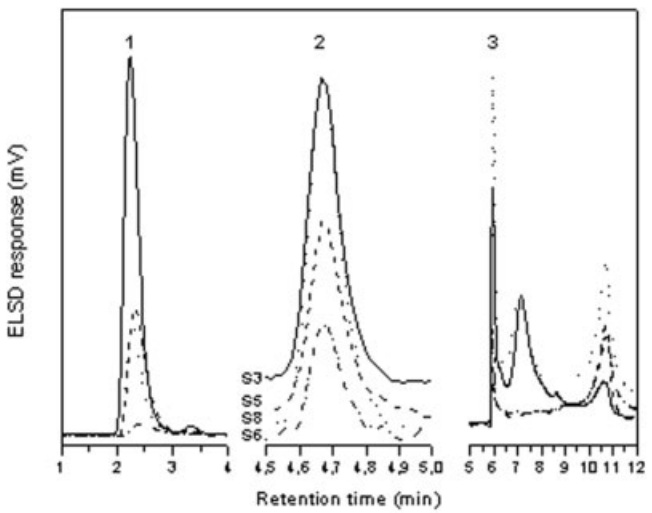

Figure 4 Chromatograms of samples S3, S5, S6, and S8 showing separations obtained by gradient HPLC. Column: μBondapak CN; normal phase gradient; detector: ELSD.

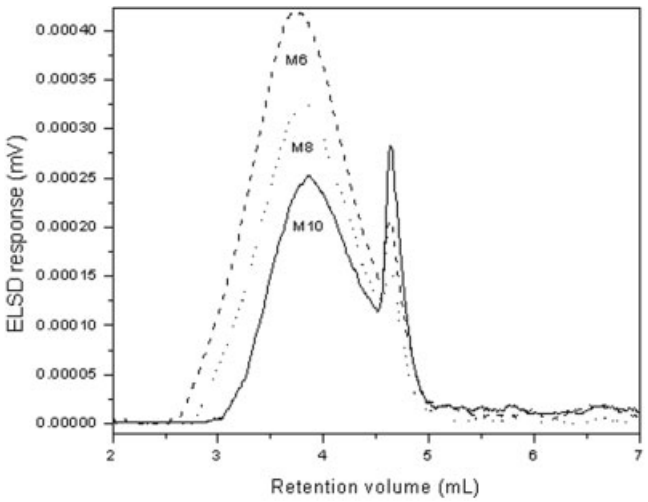

Figure 5 Chromatograms for M6, M8, and M10 in the LCCC mode showing the PMMA homopolymer peak at 4.6 mL and the ENR 50 rubber and grafted rubber peak from 3.7–3.9 mL. Column: Nucleosil CN 300 + 500 Å; eluent: THF–cyclohexane 63.3%/36.7% by weight; detector: ELSD.

data but without the quantitative analysis of the sample composition.

Under the critical conditions that were used, PMMA elutes independently of its molar mass. It appears as a separate peak in the chromatograms while ENR50 and grafted ENR50 co-elute in the size-exclusion region according to molar mass. In Figure 5, the chromatograms for the separation of PMMA-grafted ENR50 under critical conditions are shown. The presence of PMMA homopolymer can clearly be seen for samples M6, M8, and M10, as indicated by the peak at 4.6 mL, as well as the grafted rubber and rubber peaks that are also visible in all the chromatograms. Note that the grafted and rubber peaks shift toward higher molar mass.

In sample M10, the highest concentrations of monomer and initiator were used. This led to the formation of shorter grafts and a decrease in the solubility of the grafted rubber due to increased crosslinking. This corresponds to the low intensity of the graft peaks as well as the low molar mass of this peak. For sample M8, a high concentration of monomer was used but a low concentration of initiator, thus leading to the formation of long graft chains. This can be seen by the slight increase in molar mass of the grafted peak. For sample M6, intermediate concentrations of monomer and initiator were used. The curve for M6 shows the highest intensity of the three peaks. Although the increase in molar mass is marginal, the increased grafting efficiency is evident from the increased detector signal. This was also seen in the gradient HPLC separation of the sample. From the free PMMA peaks, it is evident that grafting efficiency was not good.

Another interesting point that was observed was related to the solubility of the samples. The solubilities

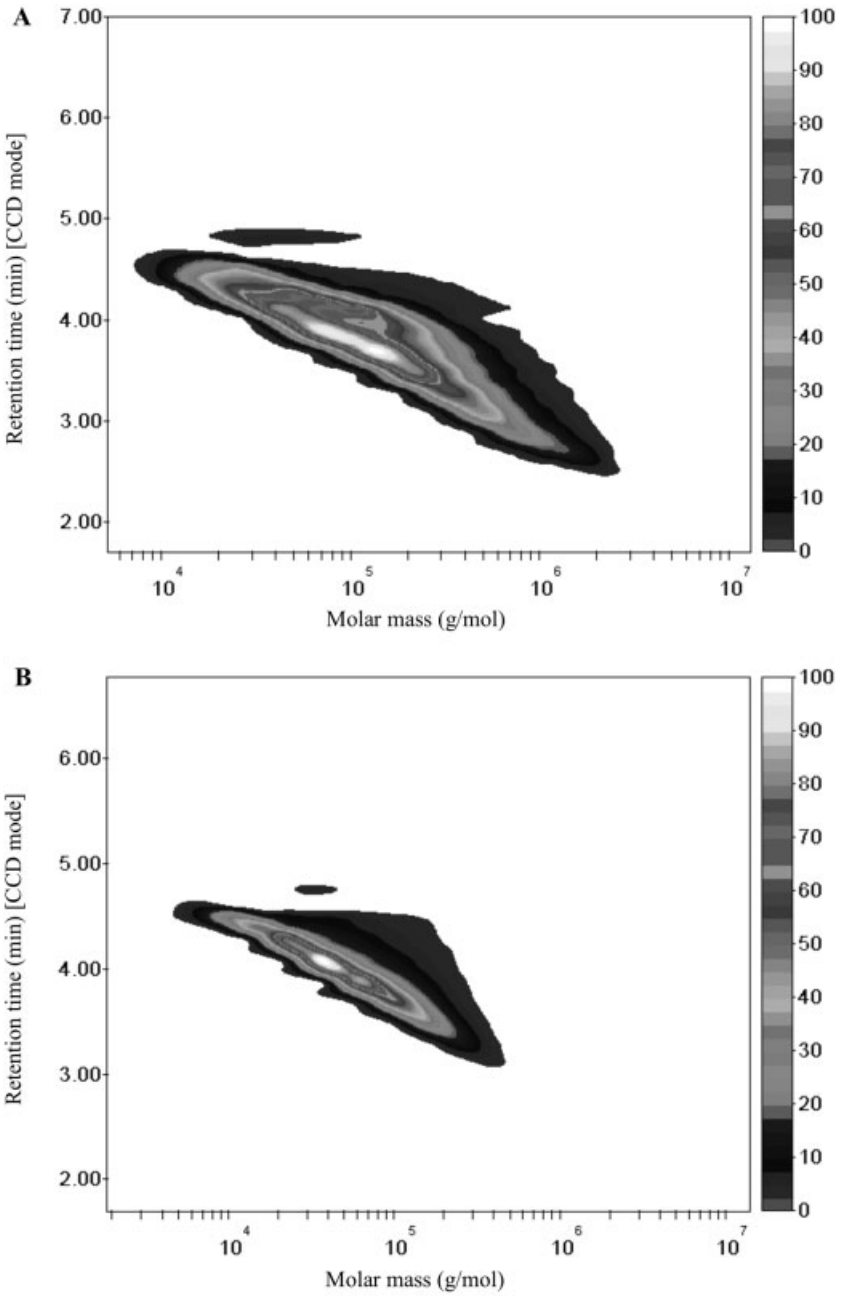

Figure 6 Two-dimensional contour plot of the ENR50 (A) and ENR50 reacted with initiator in the absence of monomer (B), with the scale on the right-hand side indicating the detector signal intensity. First dimension: critical conditions for PMMA; second dimension: SEC; detector: ELSD.

of the samples decreased from M8 down to M10 as the initiator concentration was increased. Sample masses used for analyses were the same throughout, thus proving the crosslinking effect of the initiator.

Two-dimensional analysis

The coupling of LCCC with SEC gives additional information on the chemical composition in relation to the molar mass distribution. Neither LCCC nor SEC alone can give such detailed information on the chemical heterogeneity of the samples as two-dimensional chromatography.

Figure 6(A) shows the two-dimensional contour plot of the initial ENR50 rubber. The shape of the contour plot here indicates that the epoxidation reaction of the isoprene rubber is not a homogeneous reaction. Contour plots are volume-related and not area-based as a result of the color palette being a function of the detector signal intensity.

Figure 6(B) shows the contour plot of the ENR50 rubber reacted with initiator in the absence of MMA.

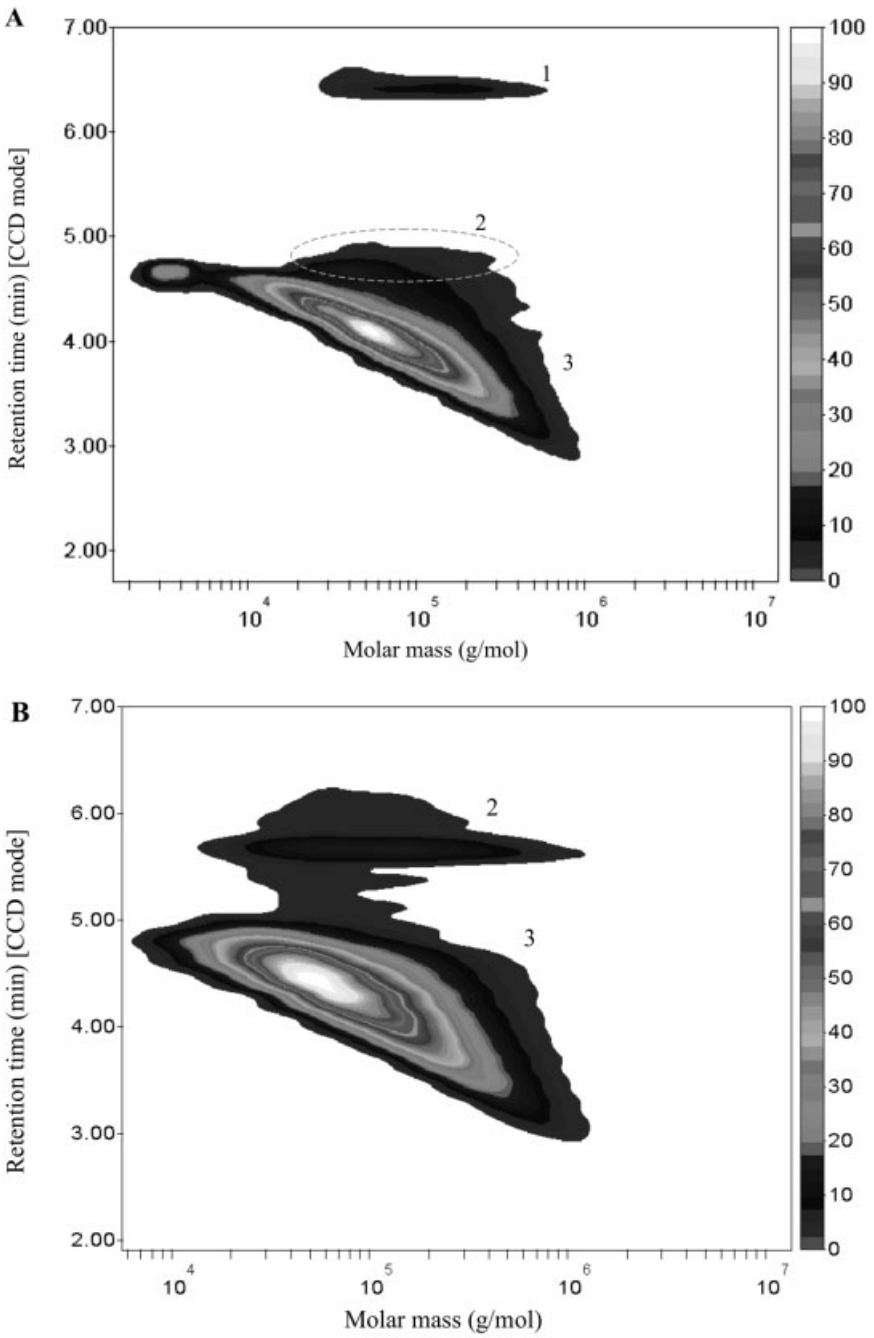

Figure 7 Two-dimensional contour plot of M10 (A) and M5 (B), with the scale on the right-hand side indicating the detector signal intensity. First dimension: critical conditions for PMMA; second dimension: SEC; detector ELSD.

What can clearly be seen here is a narrowing in the molar mass range in comparison to Figure 6(A). The rubber in the high MM region of the sample is no longer visible and the peak maximum has shifted from 1.1×10^5 in Figure 6(A) to 3.7×10^4 in Figure 6(B). Addition of an initiator can cause crosslinking between the rubber molecules. This will preferentially occur in the higher MM polymers, which will lead to partial insolubility. But the initiator can also cause degradation, thus cleaving the polymer chains into shorter segments.

In Figure 7(A), the MMA-grafted ENR50, sample M10, can be seen. Peak 1 is the PMMA homopolymer that is eluted under critical conditions. Peaks 2 and 3 contain the ENR50 grafted with MMA and the ENR50, respectively. If the contour plot shape of the ENR50 in Figure 6(B) is compared to the shape of ENR50 in M10 in Figure 7(A), it can be concluded that the change in the contour plot shape can be attributed to the grafting of MMA onto the rubber. This is evident from the increase in molar mass comparing Figures 6(B) and 7(A).

A second indication that grafting has occurred can be seen in the region marked 2 in Figure 7(A), where the upper part of the region is enlarged (compared to the areas in Fig. 6). It is expected that a grafted polymer sample will move in the direction of higher retention times, i.e., towards the area where the richer PMMA polymer phase will elute. This migration of the PMMA-rich phase will be explained in more detail in M5 in Figure 7(B), where the presence of grafted material has already been proven by gradient HPLC in Figure 3(A), peak 3.

Sample M5 in Figure 7(B) shows two polymer regions eluting in the contour plot. The region marked 3 is the ENR50 that was not grafted during the reaction, whereas the region marked 2 is the grafted ENR50 product. The region marked 2 lies in between that of the ENR50 (Fig. 6) and the PMMA homopolymer [Fig. 7(A)] on the CCD scale. This is a clear indication that grafting has taken place.

CONCLUSIONS

The use of size-exclusion chromatography has found numerous applications in the analyses of polymeric species but the inability to differentiate successfully between species with closely matched hydrodynamic volumes has forced this technique to be either modified or coupled to enhance its capabilities.

Column selection plays an important role in defining the strength of interaction between the solutes and packing material, thus creating the ability to fine-tune separations through polar or nonpolar interactions. By adjusting the solvent composition, the type of interactions between the solutes and column can be changed. This allows selective separation according to hydrodynamic volume or functional groups and, in doing so, it creates even more coupling possibilities with SEC. In this study, it is shown that styrene- and methyl methacrylate-grafted ENR50 can be successfully analyzed by gradient HPLC under normal and reversed phase conditions. This allows the deformulation of the constituting species into grafted and nongrafted parts, thereby making it possible to evaluate the grafting efficiency of the emulsion reaction. By performing liquid chromatography under critical conditions, it was shown that through the correct solvent composition selection it is possible to separate PMMA from the rubber and grafted rubber, independent of the molar mass of the PMMA homopolymers, thereby permitting separation of the rubber and grafted rubber according to the chemical composition distribution of its constituting parts. Finally, it was shown that LCCC and SEC can be combined to give a two-dimensional separation according to chemical composition distribution as well as molar mass distribution. From this, the influence of reaction conditions, the distribution of functional groups, as well as the efficiency of grafting could be mapped as a contour plot, thus indicating the versatility of two-dimensional chromatography.

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