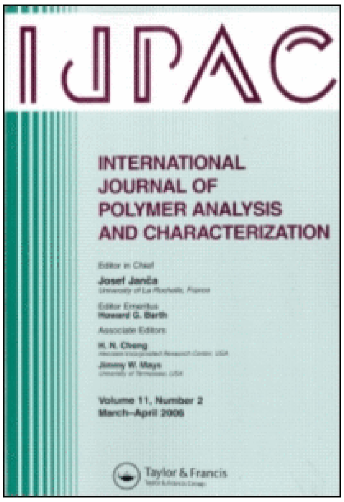

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Epoxidation of Polydienes Investigated by MALDI-TOF Mass Spectrometry and GPC-MALDI Coupling

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Abstract: Polybutadienes (PB) and polyisoprenes (PI) with various molecular weights and polydispersities were epoxidized applying two different synthetic routes. The degree of epoxidation was determined by means of matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS). It has been found that the degree of functionalization of polybutadiene is generally lower than that for polyisoprenes. Additionally, PB shows lower degrees of epoxidation at higher masses, whereas the level of functionalization of PI was unaffected by the molar mass. Coupling of gel permeation chromatography (GPC) with MALDI-TOF mass spectrometry was successfully used for the investigation of epoxidized polymers with higher masses. Using mass spectra of single fractions, the degree of epoxidation could be determined and applied for a calibration of GPC.

Keywords: MALDI-TOF MS; Polyisoprene; Polybutadiene; Epoxidation; Double bonds; Coupling methods

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INTRODUCTION

The functionalization of macromolecules plays an important role in the modification and improvement of polymer properties. It offers the possibility to easily modify inherent polymer properties. The introduction of new functional groups can be performed by using plasma or chemical treatment, for example. In contrast to the less selective plasma treatment, which is based on breaking of covalent bonds of the polymer backbone (C–C, C–H) by highly reactive radicals or ions,[1,2] the modification of existing functional groups by chemical processes represents a much less violent and therefore chemically defined strategy. These functional groups can either be end groups of a polymer chain or reactive groups within the polymer.

Due to the presence of one remaining double bond per monomer unit after polymerization, polydienes (polyisoprene (PI) and polybutadiene (PB)) represent a proper class of polymers for polymer analogous reactions. Their unique elastomeric properties make these polymers indispensable for the production of synthetic rubber. After vulcanization using elemental sulphur, highly flexible and chemically inert materials can be obtained. In order to avoid the formation of toxic side products by thermal degradation of amine-containing stabilizers, alternate solutions for cross-linking have to be found for rubber products intended for contact with food and potable water.[3,4]

In principle, double bonds can be modified in different ways by electrophilic addition. Alkenes/olefins are known to add Br and Cl at room temperature; these reactions proceed very fast without activation by radiation. Moreover, other reactions at double bonds, for instance, with $KMn0_4$, $Os0_4$, borane, or HCl, are also possible. However, the majority of these reagents do not react selectively and quantitatively or cause side reactions and degradation effects.

The most common attempts to modify double bonds that have been published comprise epoxidation reactions. Various procedures using different agents have been described.[5–12] The scheme of epoxidation is shown in Figure 1. The formed epoxides could be hydrolyzed either to mono-hydroxides using acidic peroxides or to vicinal hydroxides using alkaline agents.

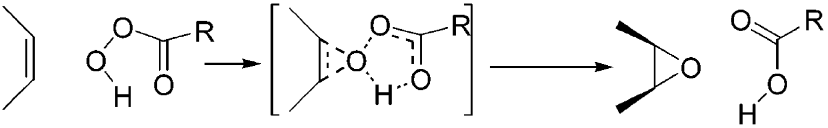

Figure 1. General scheme of epoxidation of double bonds.

In general, functionalization can be achieved using organic peroxiacids (Prileshajev reaction). For better manageability and safer use these peroxyacids are often formed in situ by means of acids (formic, acetic, or benzoic) and hydrogen peroxide.[13–17] As a result of epoxidation the pure original acid is formed again, which can act as catalyst for additional side reactions, e.g., hydrolysis, degradation, or cross-linking.[18,19]

Many different solvents for the reaction (e.g., ethers, acetone and chloroform-benzene, chloroform-dioxan mixtures) have been described. The epoxidation of low molecular weight, unsaturated compounds in non-polar solvents, such as chloroform, generally gives excellent yields.[20] Using benzene, toluene, or xylene as solvent, the epoxidation of bacterial polyesters could be carried out without any side reaction.[21]

Depending on the position of the double bond in a polymer chain the rate of epoxidation is quite different. Olefinic groups located in the middle of the monomer unit show a 25 times higher rate than vinyl double bonds.[15]

The rate of epoxidation by in situ formed peracids is comparatively low. Therefore, compared to the reaction using peracids, generally a lower degree of functionalization can be expected. However, this technique easily offers the possibility of maintaining different extents of expoxidation simply by changing the ratio of acid to hydrogen peroxide.[22] According to Heublein et al.[16] formed products exhibit a high purity. However, one main disadvantage of the use of peroxides is its limited stability. Therefore, m-chloroperbenzoic acid (MCPBA) has been suggested as a reagent for the determination of olefinic bonds. Reported yields of epoxidation vary from 50 to 100%.[23–26] First experiments using low molecular weight compounds with several double bonds (e.g., squalene) showed that complete epoxidation could be achieved.[23] Therefore the use of MCPBA seemed to be an auspicious way to functionalize double bonds to a high degree.

The formed epoxides can be identified by several spectroscopic and chromatographic methods. Changes of molecular weight can be determined by means of gel permeation chromatography (GPC). The quantitative bromination of a polybutadiene with an original molecular weight of 1000 g/mol would result in a product with much higher mass (4000 g/mol). In contrast to that, epoxidation shifts M_w only from 1000 to 1300 g/mol. Nevertheless, any chemical variation of a comparatively nonpolar polymer by polar and/or bulky compounds results in a change of its behavior in solution. Therefore, any calibration of GPC done for polydienes cannot properly be used for the corresponding functionalized products. GPC can give only a rough estimation of the degree of functionalization.

Spectroscopic methods (e.g., nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy) represent a useful way to determine the degree of functionalization. Using an incremental method the increase of glass transition temperatures of biological polyester by stepwise epoxidation was used for the determination of the degree of functionalization.[21]

Formed functional group epoxides can be determined by conventional chemical analysis. Epoxide groups were analyzed by titration with hydrobromine acid using specific indicators (crystal violet).[22]

Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry can be also applied for detecting epoxidation. This method has been established as a useful tool to determine molecular weight and functionality simultaneously. An overview of this method and its specific application to the analysis of synthetic polymers is given in Schrepp and Pasch.[27] For the first time the epoxidation of a nonpolar model compound (squalene) was investigated exemplarily by MALDI-TOF mass spectrometry.[23] After successive addition of MCPBA the formation of products with various numbers of epoxides was detected. Complete functionalization could be obtained by an excess of MCPBA. Additional peaks at higher masses indicated possible cross-linking of formed products. A possible mechanism was proposed.

For polydisperse synthetic polymers (polydispersity PDI >1.2), it has been concluded from theory that the molecular weight distribution provided by MALDI mass spectrometry (MS) does not resemble the distribution as obtained by GPC.[28–30] This is caused by the fundamental difference between recording the number fraction versus m/z (as in MS) and the weight fraction versus the logarithm of the molecular masses (as in GPC). As a consequence, the high-mass tail of the polydisperse distribution disappears much earlier into the base line noise of the MS than into the noise of the GPC system, thus yielding incorrect calculation of the molecular weights. Hyphenation of GPC and MALDI mass spectrometry can overcome the limitations and be a powerful tool for polymer characterization.[31–38] It enables the separation of a broad distributed sample into many narrow distributed fractions.

Since MALDI mass spectrometry provides absolute molecular weights, it can be simultaneously used to calibrate the GPC instrument.

EXPERIMENTAL

Epoxidation by MCPBA

The epoxidation was performed in a four-neck round-bottomed flask equipped with nitrogen inlet, cooler, thermometer, and dropper. The flask was dried and filled with nitrogen. A 185 mg amount of (0.8 mmol) of MCPBA, dissolved in 5 mL dried chloroform, was added stepwise at room temperature to a solution of 0.5 g polydiene dissolved in 1 mL toluene. The solution was stirred with a small magnetic stirrer. The temperature of the reaction mixture was kept constant using a cooling bath. Samples for MALDI-TOF mass spectrometry were taken from the original solution without any purification.

Epoxidation by In Situ Formed Peracids

The epoxidation was performed in a three-neck round-bottomed flask equipped with nitrogen inlet, cooler, and dropper. The flask was filled with nitrogen. Afterwards, 0.2 mL of H_2O_2 (30% solution in water) was added stepwise at room temperature to a solution of 0.2 g polydiene dissolved in 10 mL chloroform. To this mixture 0.36 mL of formic acid was added. The temperature of the reaction mixture was kept constant using a cooling bath. Samples for MALDI-TOF mass spectrometry were taken from the original solution without any purification.

MALDI-TOF Mass Spectrometry

The MALDI-TOF experiments were performed using a Bruker Reflex III mass spectrometer (Bremen, Germany) equipped with a nitrogen UV laser emitting at 327 nm. The mass spectra were recorded in the reflector mode of the MS. The pulse length was 3 ns. Formed ions were accelerated at 20 kV.

Different matrices have been described for suitability for MALDI-TOF mass spectrometry of nonpolar polydienes, e.g., 1,8,9-trihydroxyanthracene (dithranol), trans-3-indoleacrylic acid (IAA), and 1,4-bis (5-phenyloxazol-2-yl) benzene (POPOP).[39] Excellent spectra for the systems of both PI and PB could be obtained only using dithranol. Therefore, 10 mg of dithranol were dissolved in 1 mL of tetrahydrofurane (THF). Then 50 μL of this solution was mixed with 20 μL of the polymer solution taken from the reaction mixture.

In order to enable the ionization of nonpolar polydienes, 1 μL of a solution of silver trifluoroacetate (AgTFAA) (2,2 mg in 1 mL THF) was also added. The formation of ions of the epoxidized samples was promoted by the addition of sodium or potassium trifluoroacetate.

Finally, 1 μL of the premixed matrix-analyte solution was dropped onto the MALDI target. After evaporation of the solvent the sample was inserted into the mass spectrometer. Two hundred shots, recorded at different spots of the probe, were accumulated for one spectrum. The instrument was calibrated using a polymethylmethacrylate (PMMA 2000) standard polymer.

GPC Chromatography

For GPC investigations a PL210 high-temperature system (Polymer Labs, U.K.) equipped with an internal refractive index (RI) detector was used. The investigation was performed at 35°C using THF as solvent. The flow rate was 1 mL/min. Various 1,4-polyisoprene standards were used for calibration (Polymer Labs, U.K.). The sample concentration amounted to around 1 mg/mL. Samples were taken from the reaction flask without purification.

Coupling GPC/MALDI-TOF MS

A commercially available interface, LC 500 (LabConnections, U.S.A.), was used. The chromatographic eluent was sprayed via a heated capillary (125°C) onto the MALDI target using a nitrogen stream (20 L/h). The target itself was pre-coated with a matrix film (dithranol, 4 mg/mL in THF) deposited in a previous run. After finishing the preparation the sample target was transferred into the MALDI-TOF mass spectrometer. Mass spectra were recorded at max 14 positions (outer periphery of the target).

Polydienes

Investigated 1,4-polydienes were obtained as polymer standards from Polymer Labs (U.K.) and Sigma-Aldrich (Germany).

RESULTS AND DISCUSSION

Characterization of Polydienes as Received

In Figure 2(a), (b) typical MALDI mass spectra of original polyisoprene PB 960 and polybutadiene PI 940 are shown. A series of peaks with peak-to-peak distances of 54 Da (PB) and 68 Da (PI) can be seen (Figure 2(c), (d)). Due to the addition of silver to the original samples typical silver isotopic patterns can be found. A less intense second series of peaks could be detected too, which differs by +16 Da from the main series. Obviously, the original sample contained impurities of a second polydiene having a different end group. After subtraction of 107 Da (Ag) and 13 × 68 Da (13 repeat units) from a mass of 1050,1 Da a residual mass of 58 Da for PI was calculated. The same result was found for PB. This residual mass exactly corresponds to one hydrogen (1 Da) and an additional t-butyl group (57 Da). Thus, beside the exact molar mass and the number of repeat units, the spectra provide additional information on the type of polymerization applied for these polydienes (anionically living polymerization).

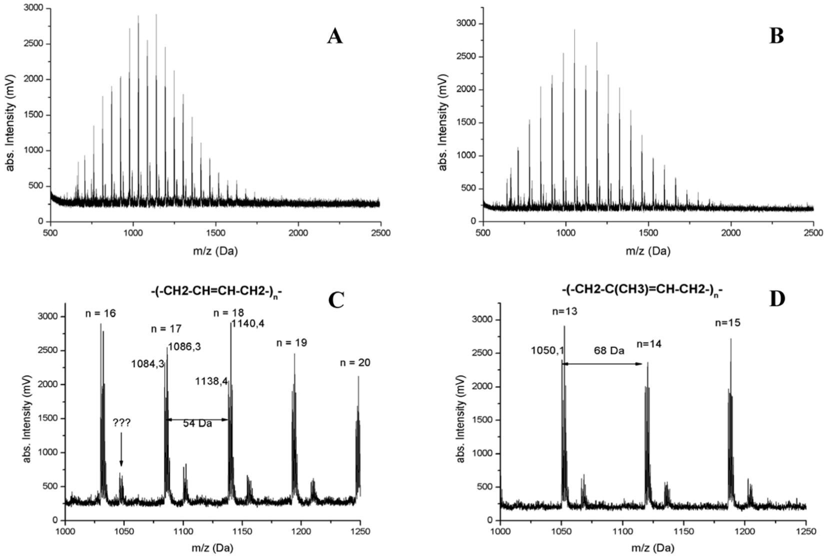

Figure 2. Original MALDI mass spectra of PB 960 (a) and PI 940 (b) (enlarged view presents typical repeat units of PB (c) and PI (d)).

Epoxidation Using MCPBA (PB 960 versus PI 940)

The result of the epoxidation applying MCPBA is shown in Figure 3(a)–(d). After one-hour epoxidation the mass distribution shifted towards higher masses (maximum M_p shifted from 1050 to 1200 Da). A detailed inspection of spectra is given in Figure 3(c), (d). The previously mentioned additional peaks at +16 Da were detected again.

For determining the degree of epoxidation a simple calculation was performed. The molar mass of a peak (M_{peak}) is determined by the number of repeat units (y), the number of formed epoxide groups (x), the mass of the adduct ion (M_{adduct}), and the masses of end groups (M_{end}). It can be expressed in a simple equation:

$$M_{peak} = y \times M_{repeat} + x \times M_{epoxide} + M_{end} + M_{adduct} \qquad (1)$$

This equation can be transformed as follows:

$$x = \frac{M_{peak} - y \times M_{repeat} - M_{end} - M_{adduct}}{M_{epoxide}} \qquad (2)$$

Using Equation (2), the epoxidation was found to be nearly complete for PI after one hour. In contrast to that, PB was not completely epoxidized. A distribution of reaction products (see Figure 3(c)) from 80 to 100%

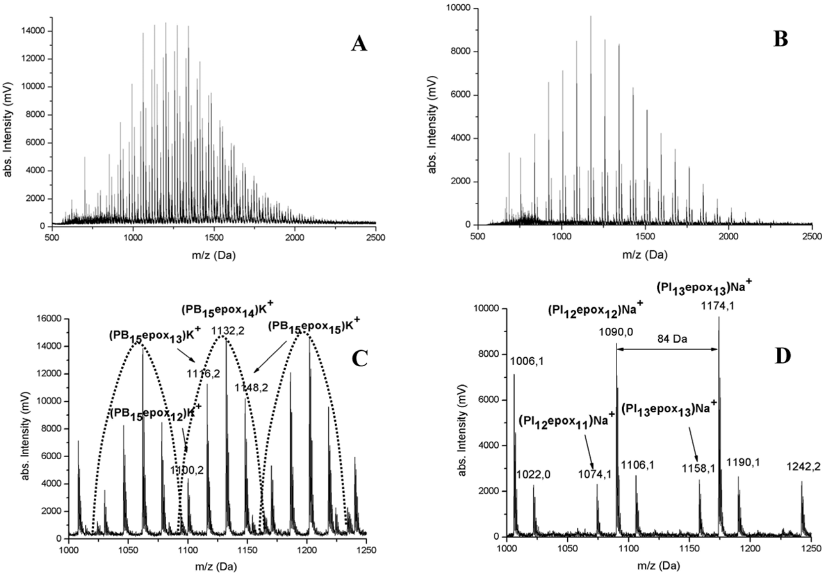

Figure 3. MALDI mass spectra of PB 960 (a) and PI 940 (b) after epoxidation using MCPBA for one hour (enlarged view presents mass numbers and peak attribution of PB (c) and PI (d)).

degree of functionalization was found. Any further addition of MCPBA and longer reaction times (up to 18 hours) did not change the result. The reason for this particular behavior can be deduced from the structural difference of both polymers. In the case of PI the additional methyl group induces a polarization of the double bond (+I effect), which could support the electrophilic attack of the peroxyacid.

Epoxidation of PB 960 Using H_2O_2

Thus, as an alternative synthetic route, the epoxidation of the less reactive PB using MCPBA was compared to its hydrogen peroxide functionalization. The results can be seen in Figure 4(a)–(d). The typical peak pattern for the original PB 960 ionized with silver is shown in Figure 4(a). The peak-to-peak distance is 54 Da, which corresponds to a single repeat unit of $-CH_2-CH=CH-CH_2-$. After one and three hours of epoxidation using hydrogen peroxide MALDI spectra were recorded (see Figure 4(b), (c)). Both spectra show several series of peaks having a difference of +70 Da. The formation of these series was much more pronounced after three hours of epoxidation. However, any addition of H_2O_2 did not increase the degree of functionalization (after four hours). In Figure 4(d)

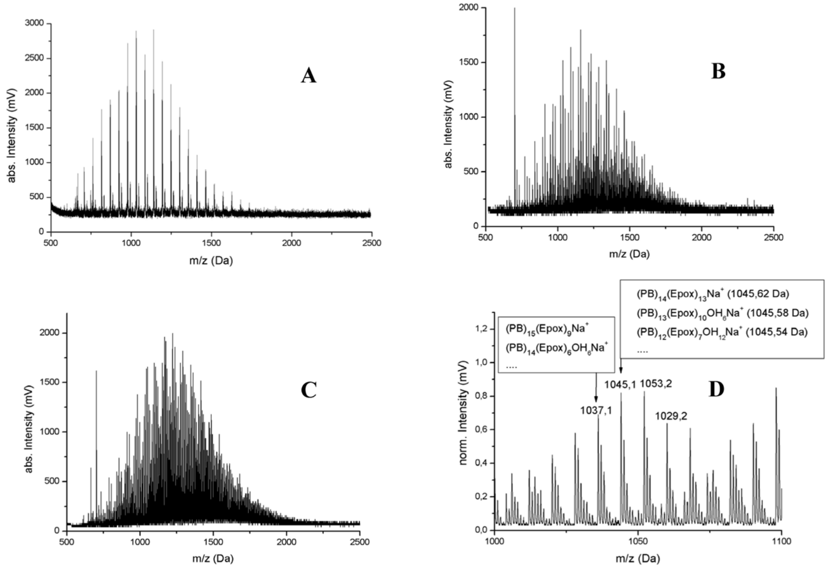

Figure 4. MALDI mass spectra of PB 960 (a) after epoxidation using hydrogen peroxide (after one hour (b), three hours (c)) and possible attribution of structures (d) to two peaks.

possible structures were attributed to some of these peaks. Besides peaks corresponding to nearly completely epoxidized homologous, an additional series of signals differing by +8 Da were detected. Their intensity increased by increasing functionalization time. Surprisingly, these peaks might be attributed to structures having a much lower degree of functionalization. Any significant shift of the molar mass distribution (MMD) towards lower masses, which would indicate a possible degradation of the polymer, was not observed. The maximum degree of epoxidation of these additional species was calculated to be lower than 60%. A reasonable explanation for that behavior could be seen in a partial hydrolysis of formed epoxides into hydroxyl groups. For a more detailed analysis the mass resolution of the MALDI mass spectrometer was too poor. Nevertheless, compared to the epoxidation using MCPBA the functionalization of double bonds using hydrogen peroxide seems to be effective. However, the reaction seems to propagate under hydrolysis of formed epoxides into hydroxyl groups.

Epoxidation of PI 1350 Using MCPBA

In Figure 5(a), (b) MALDI mass spectra before and after epoxidation of PI 1350 using MCPBA are shown. For better resolution a cut of the mass

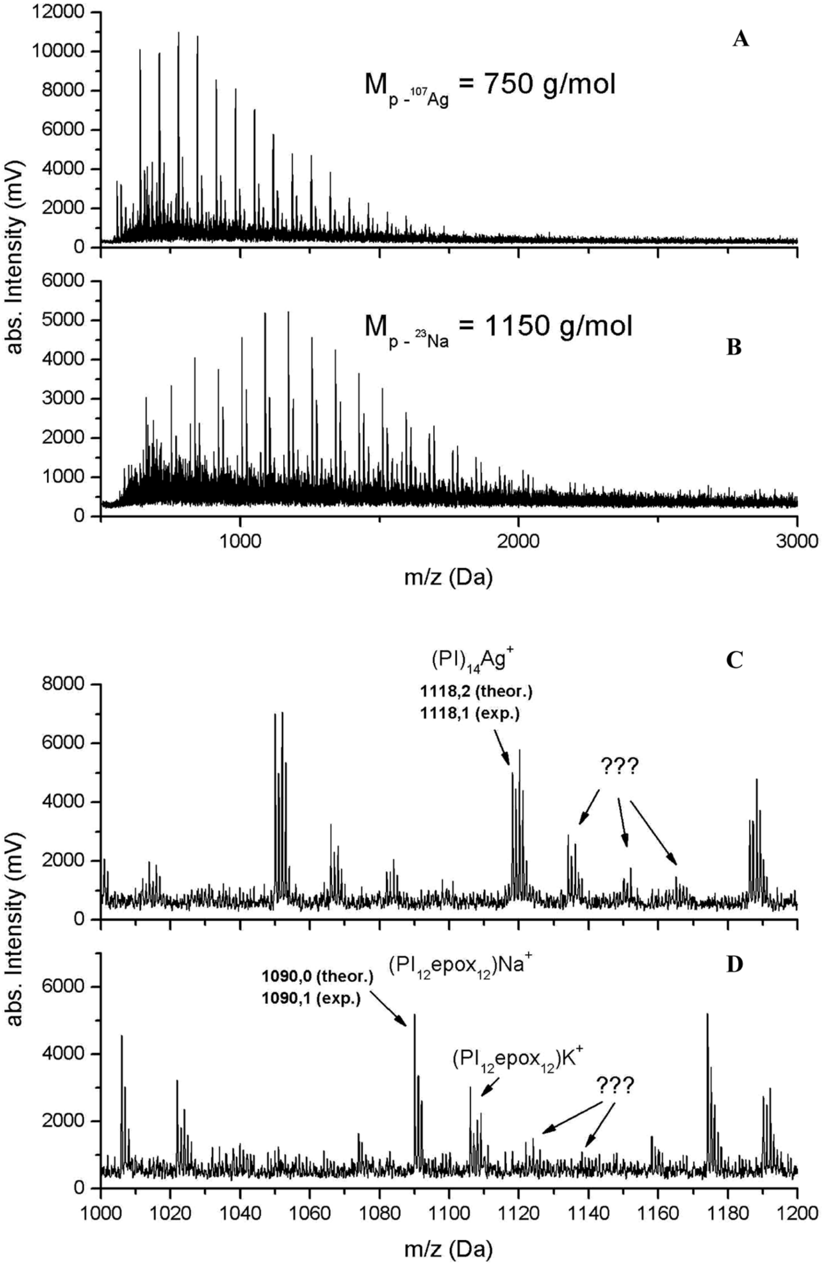

Figure 5. MALDI mass spectra before (a) and after epoxidation (b) of PI 1350 using MCPBA (enlarged view (c), (d) presents mass numbers and attribution of structures before and after epoxidation).

spectra is shown in Figure 5(c), (d). A nearly complete epoxidation was observed after only 1.5 hours. The measured MMD strongly differs from expected values. The maximum of the MMD was 750 Da (corresponds to 12–13 repeat units). After functionalization this maximum should have been shifted by +200 Da. However, the maximum was found to be at 1150 g/mol, which is much higher than calculated but still lower than the manufacturer's Mp of 1350 Da. This discrepancy might be attributed to different ionization probabilities of rather nonpolar polydiene on one hand, compared to the very polar epoxidized product on the other hand. Additionally, in Figure 5(a), (c) various additional peaks series can be seen. Their intensities did not change by increasing laser power (indicates laser-induced in-source fragmentation). In addition, these peaks show the typical silver isotopic pattern. Thus, the original polyisoprene 1350 obviously seemed to be contaminated by additional products (probably PI with different end groups and/or with functionalized double bonds). GPC chromatography was not able to differentiate between these products. Nevertheless they strongly influence the mass determination and led to wrong GPC data.

Epoxidation of Broadly Distributed PB 1500

In contrast to previously investigated polymers having very narrow molar mass distributions, polybutadiene 1500 represents a polymer with a broad MMD. This results in some characteristics that have to be regarded. In principle, MALDI can be used for a correct reproduction of the MMD of a polymer only under certain conditions. The most important requirement is a polymer polydispersity below 1.2. If polymers with higher MMD are investigated by MALDI, spectra always show a strong increase of the intensity in the low molar mass region. No Gaussian-like peak distribution will be seen. One reason can be found in an electronic saturation of the detector by low molar mass ions. In order to obtain absolute values for broad polymer distributions, MALDI-TOF mass spectroscopy has to be coupled with chromatographic methods, like GPC. This enables the collection of fractions with comparatively low MMD, which can be measured exactly by MALDI mass spectrometry. Additionally, the obtained absolute molar mass values can be used to calibrate the GPC. Typical spectra of a broadly distributed PB 1500 before and after epoxidation using MCPBA can be seen in Figure 6(a)–(c). With the exception of the original sample the quality of the spectra was relatively poor. In contrast to previous epoxidation experiments no shift of the MMD towards higher masses can be observed. This is due to the fact that functionalization results in a change of the absolute molar mass but not in a change of the MMD. The functionalized

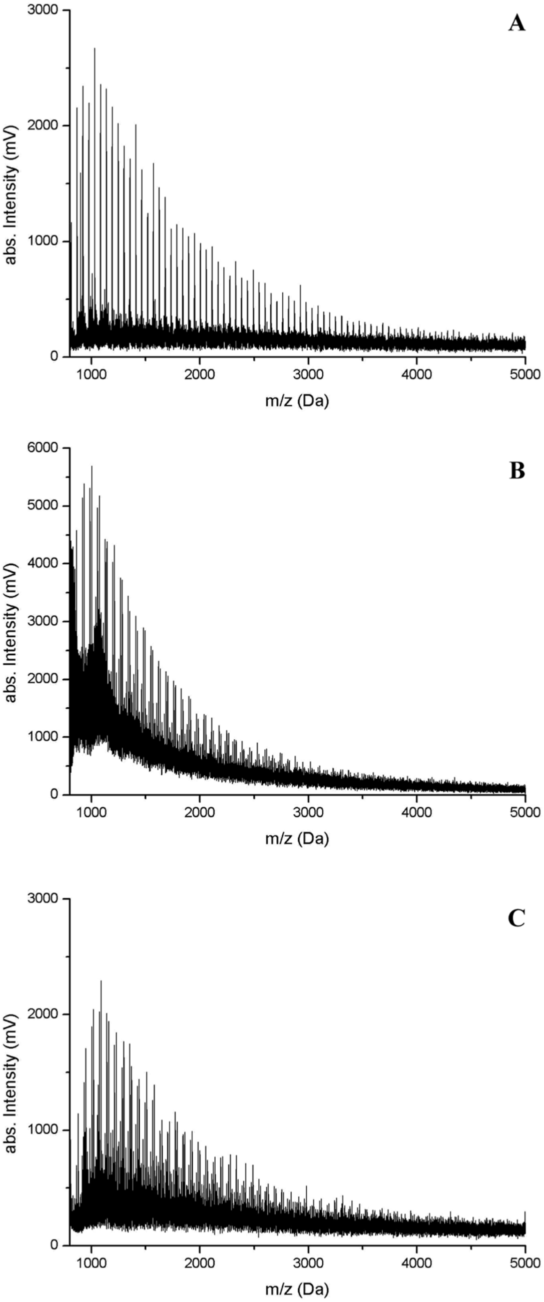

Figure 6. MALDI mass spectra of broadly distributed PB1500 using MCPBA before (a) and after epoxidation for one hour (b) and three hours (c).

polymer remains broadly distributed, and spectra therefore show the typical exponential decay toward higher masses.

A closer view is given in Figure 7(a)–(c). Initially, the typical peak pattern of polybutadiene ionized with silver can be observed again (Figure 7(a)). The peak-to-peak distance corresponds to 54 Da, which is the mass of a single repeat unit of $-CH_2-CH=CH-CH_2-$. The spectra recorded after one hour (Figure 7(b)) show several additional series of peaks differing by 16 Da within a distribution and 70 Da between two distributions. After three hours epoxidation the spectrum changes again (Figure 7(c)). Some additional peaks (+16 Da) appeared. Simultaneously, the intensity of peak series observed in Figure 7(b) decreased. Any further addition of MCPBA did not change that result. The annotation shown in Figure 7(c), reveals an average degree of epoxidation of about 60%.

Epoxidation of Higher Molar Mass PB and PI

The MALDI mass spectra of PB 2350 before and after functionalization with MCPBA are presented in Figure 8(a)–(d). Similar to PB 960, a shift of the MMD towards higher masses can be observed. However, in contrast to PB 960 the spectra contain many more series of peaks. A closer view of the spectra is presented in Figure 8(c), (d), which shows the spectral region between 2500 and 2700 Da (of the original polymer) and between 3050 and 3250 Da (after functionalization). In Figure 8(c) the typical peak pattern for polybutadiene ionized with silver can be seen again. The peak-to-peak distance is 54 Da. A peak detected at 2452.8 Da can be attributed to a polybutadiene with 44 repeat units ($[H\text{-}(PB)_{44}\text{-t-butyl}]^{107}Ag^+$), which shows a theoretical mass of 2452.9 Da, calculated using the XMASS® software tool (Bruker, Germany). This result impressively demonstrates the accuracy of the MALDI calibration performed with PMMA 2000.

After one hour the spectrum in Figure 8(d) was recorded. Although the resolution of the spectra is poor in comparison to previously illustrated mass spectra, it shows several series of peaks differing by +16 Da within a distribution and with a difference of +70 Da between two distributions. Because NaTFAA was added, major peaks were supposed to represent sodium adducts. Similar to PB 960, a high degree of functionalization was assumed. In the case of 100% epoxidation the expected structure $(PB)_{44}(epox)_{44}Na^+$ should exhibit a molar mass of 3162,9 Da. However, the mass of the attributed peak was found to be 3161,2 Da. In conjunction with detecting additional peaks at +16 Da (respectively +32, +48 Da), which theoretically correspond to utterly impossible degrees of epoxidation $[(PB)_{44}(epox)_{45\ldots48}Na^+]$, the assumption of

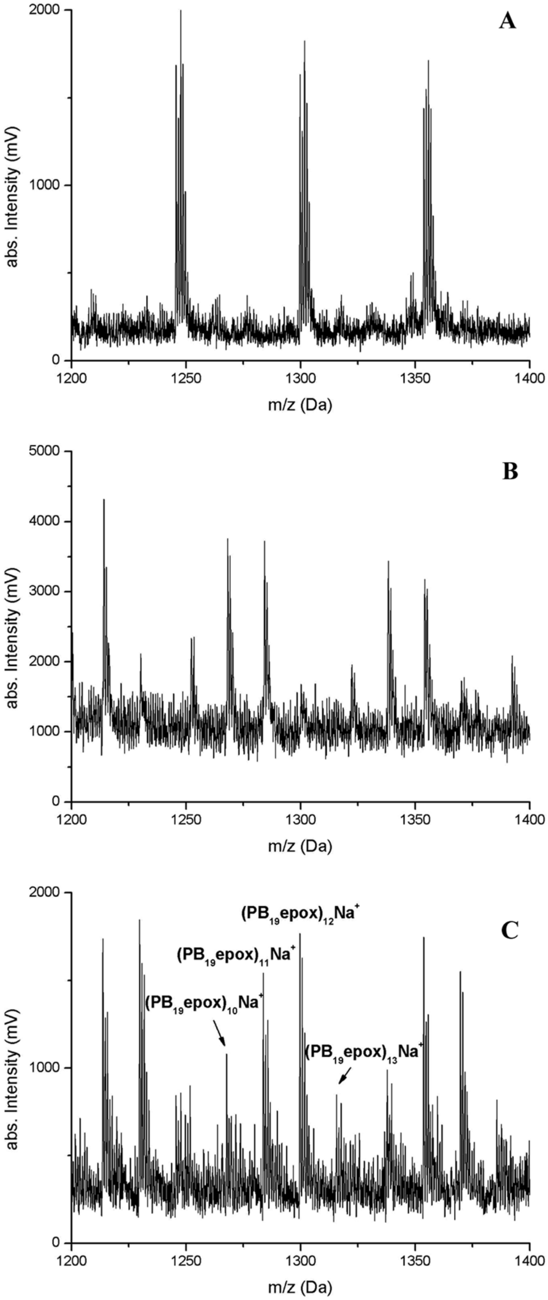

Figure 7. MALDI mass spectra (enlarged view) of broadly distributed PB1500 using MCPBA before (a) and after epoxidation for one hour (b) and three hours (c); possible structures are attributed to peaks.

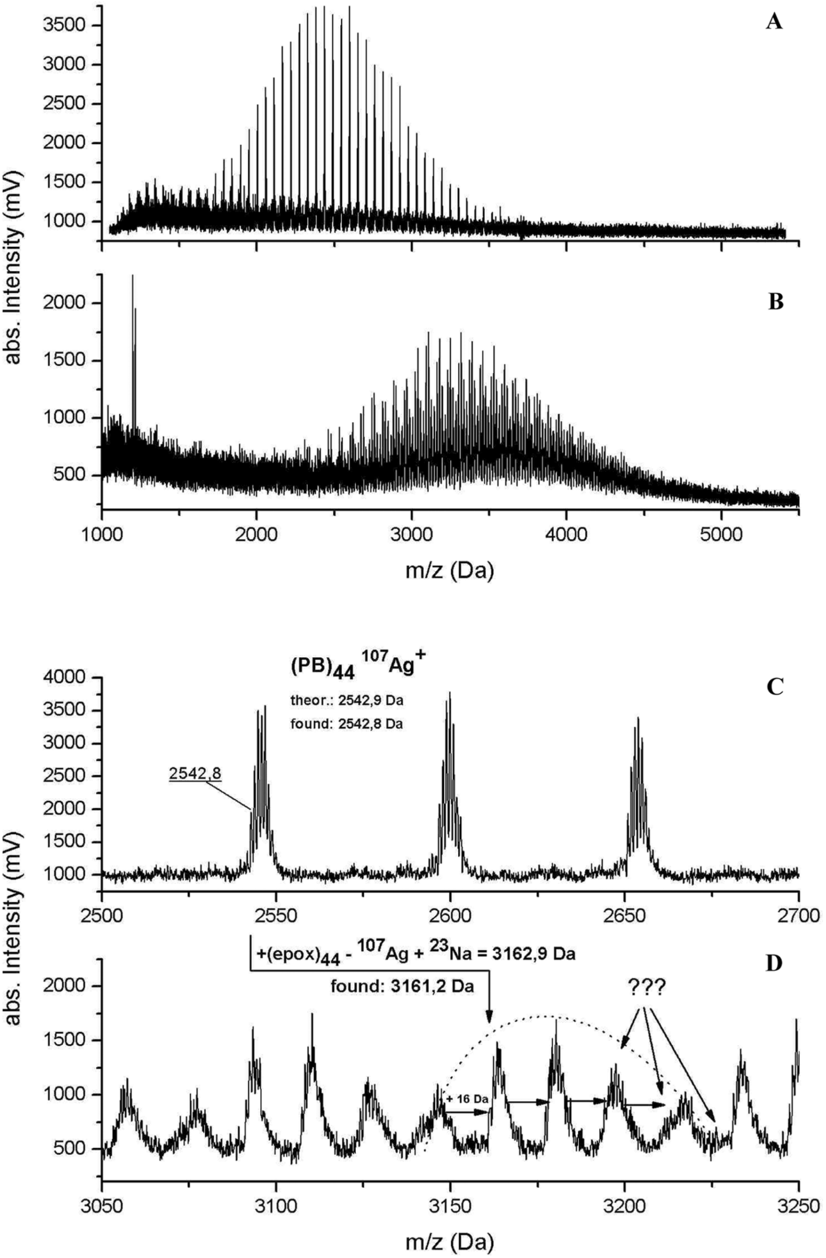

Figure 8. MALDI mass spectra of PB 2350 before and after functionalization with MCPBA for one hour (enlarged view presents mass numbers and peak attribution of PB (c) and PI (d)).

Table I. Structure, composition, and mass variation of epoxidized PB 2350 (for a single peak at 3161.2 Da).

Structure	No_{PB}	$No_{epoxides}$	$Mass_{theoret.}$	Variation
$(PB)_{44}(epox)_{44}Na^+$	44	44	3162.8	+1.6
$(PB)_{47}(epox)_{34}Na^+$	47	34	3163.9	+2.7
$(PB)_{49}(epox)_{27}Na^+$	49	27	3161.1	−0.1
$(PB)_{52}(epox)_{17}Na^+$	52	17	3163.1	+1.9

nearly complete functionalization had to therefore be refused. In Table I various structures of epoxidized polybutadienes and their theoretical masses and compositions are listed. Considering the comparatively high resolution and the accurate calibration of the mass spectrometer only the structure $(PB)_{49}(epox)_{27}Na^+$ can be attributed to this peak. Therefore, the degree of epoxidation averages 55%. This is significantly lower than for PB 960, but similar to PB 1500. It can be explained by an increasing steric hindrance of the electrophilic attack with increasing length of polymer chain.

In contrast to PB 2350 the epoxidation of PI 3190 using MCPBA could be performed almost completely. The resulting MALDI mass spectra of the original polyisoprene and after epoxidation are shown in Figure 9(a)–(d). The maximum peak distribution of the untreated sample shifted from approximately 2400 to 2900 Da of the epoxidized sample. This corresponds very well to the estimated epoxidation of approximately 32 double bonds.

Within the low molar mass region of the original spectrum in Figure 9(a) silver adducts can be observed. The formation of these adducts has often been observed and can be suppressed by optimizing the matrix-analyte-silver salt ratio. Since the intensity of adducts was comparatively low and they did not interfere with the polymer distribution, optimizing experiments were not performed. The MALDI mass spectrum of the epoxidized PI 3190 (Figure 9(b)) shows a significantly lower signal-to-noise ratio compared to the spectrum of the original sample. However, it has to be kept in mind that samples were always taken from the reaction mixture without any purification. Furthermore, the concentration of the reaction mixture was lower than for the original sample and the addition of MCPBA (respectively, the formation of benzoic acid during the reaction) strongly influences the quality of MALDI spectra ("signal quenching").

An insight of the spectrum is seen in Figure 9(c), (d). The peak-to-peak distance of the original polyisoprene is 68 Da, which is according to the expected monomer unit ($-CH_2-C\ (CH_3)=CH-CH_2-$). After epoxidation the spectrum in Figure 9(d) was recorded. Two series of

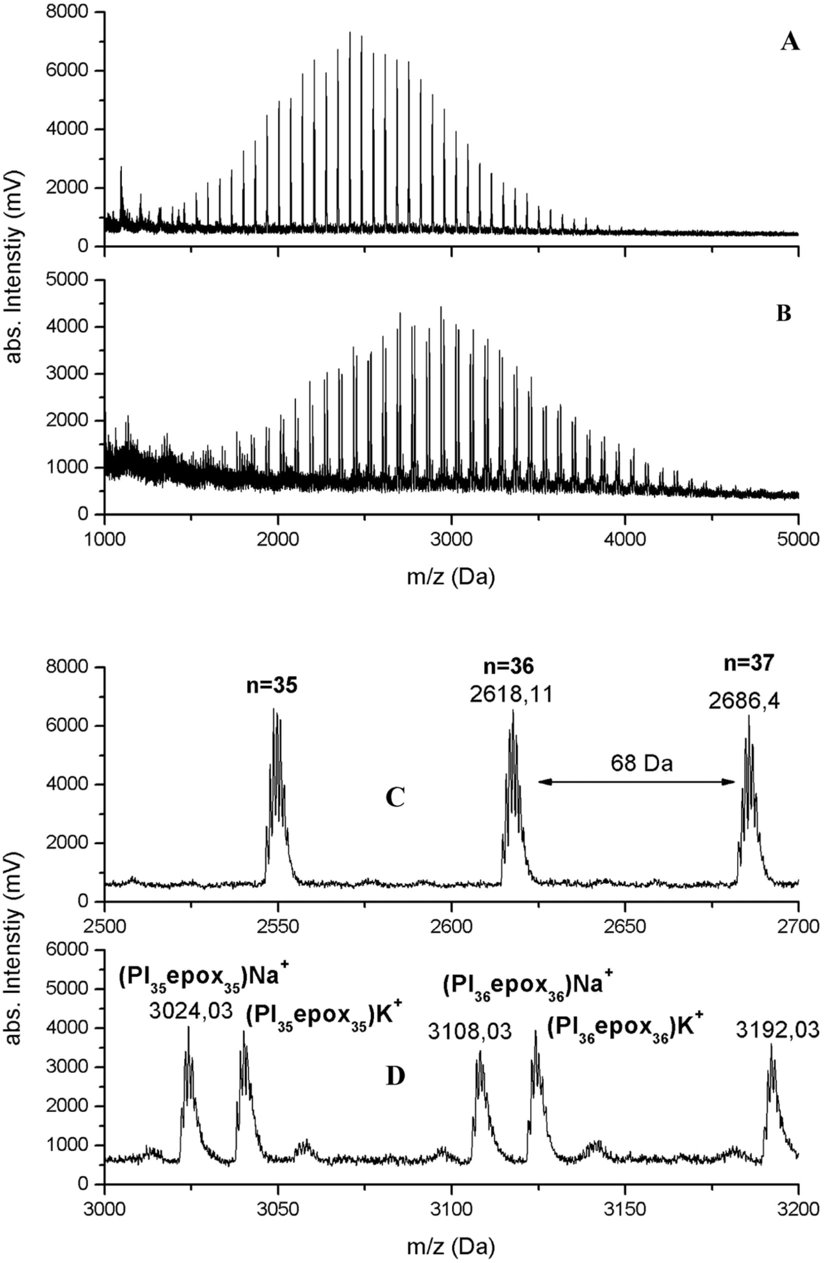

Figure 9. MALDI mass spectra of PI 3190 before and after functionalization with MCPBA for one hour (enlarged views (c) and (d) present mass numbers and peak attribution).

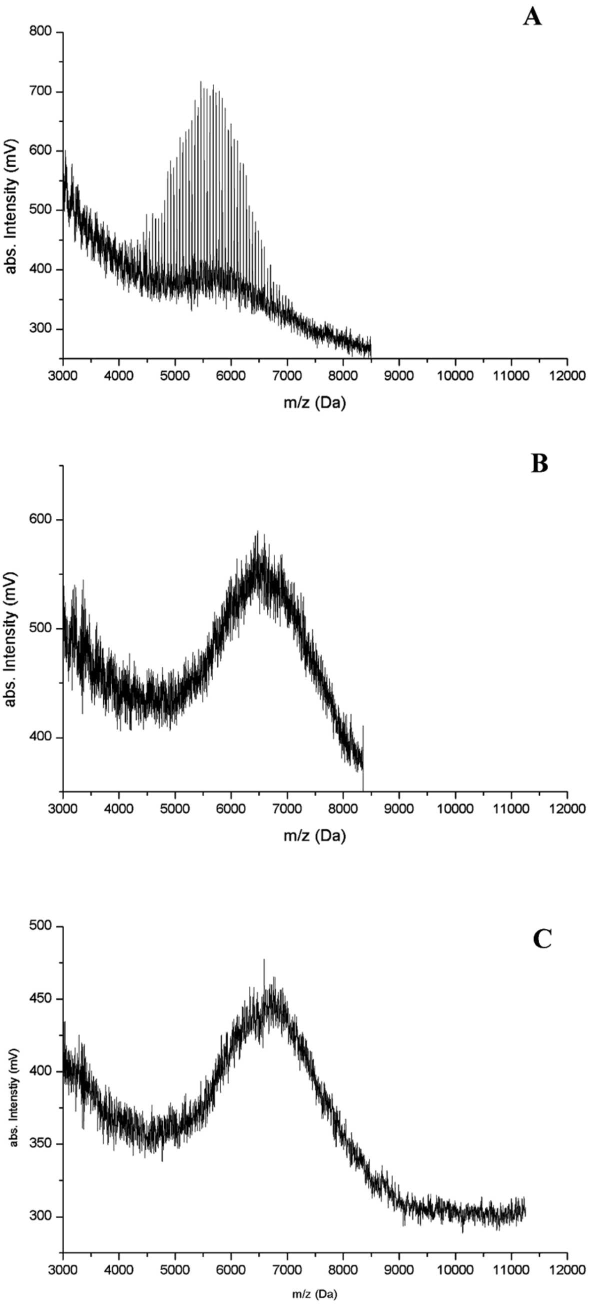

Figure 10. MALDI mass spectra of PB 5000 before (a) and after functionalization with MCPBA for one hour (B) and for 20 hours (c).

peaks can be seen that differ by 16 Da. Due to the nature of ionization in MALDI mass spectrometry and because of the lack of an additional salt, these peaks could be attributed to sodium and potassium adduct ions representing completely epoxidized polyisoprene chains.

For the following experiments a higher molar mass PB 5000 was investigated. The original spectrum (ionized with AgTFAA) is shown in Figure 10(a). Although working in a molar mass region above 5000 Da, the peak resolution is excellent. The theoretical molar mass of a polybutadiene with 100 repeat units, tert-butyl end group, and silver adduct ion is 5569 Da, which corresponds very well to the measured masses.

The spectra after epoxidation using MCPBA are presented in Figure 10(b), (c). These spectra were of poor quality, with no distinct peaks suitable for the determination of the degree of epoxidation. This discrepancy is due to the fact that the number of possible species increases with the degree of polymerization. The resolution of the MALDI mass spectrometer is determined by the mass of a single peak divided by its full width at half-peak maximum (FWHM). The higher the measured masses are the broader the peaks become. At a certain "critical" peak-to-peak distance (which is 16 Da after functionalization, in contrast to 54 Da of the original sample) these peaks could no longer be resolved.

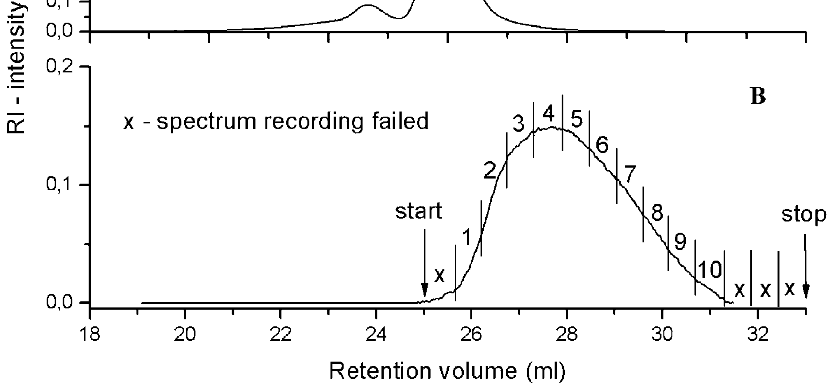

Figure 11. GPC plots of PB 5000 before (a) and after epoxidation (b) using MCPBA (fraction marks are indicated in (B)).

Coupling GPC/MALDI-TOF Mass Spectrometry

The results of the GPC investigation of PB 5000 is shown in Figure 11(a), (b). In Figure 11(a) two peaks can be seen, one for PB 5000 (at 26 mL elution volume) and an additional small peak at 24,5 mL, which corresponds to a doubling of the molar mass. Anionic polymerization often results in the formation of side products with higher masses. These products can be formed by either radical side reactions and/or at the beginning of the anionic polymerization itself. Especially monomers with conjugated electron systems (such as butadiene) are able to form dianions. The chain growing results in polymers showing doubled molar masses.

In Figure 11(b) the chromatogram after epoxidation for one hour is shown. In contrast to the original chromatogram the curve was shifted towards higher elution volume, respectively lower molar masses. Simultaneously, the peaks became broader and more asymmetrical. This result is diametrical to MALDI data (Figure 10), showing an increase of the molar mass during epoxidation. The reason could be seen in the GPC principle. GPC is based on entropic separation. The introduction of

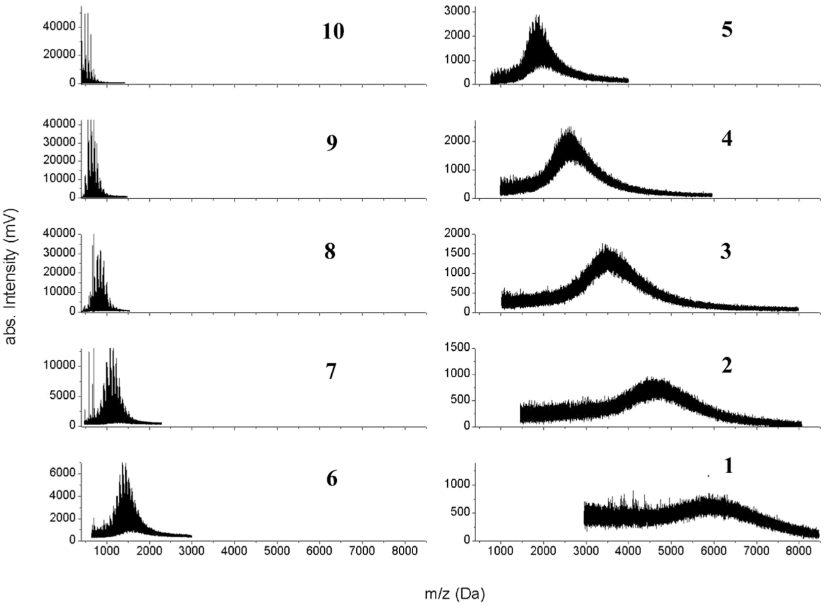

Figure 12. Series of continuously recorded MALDI mass spectra after GPC-MALDI coupling (epoxidation for one hour using MCPBA); numbers in the mass spectra are identical with fraction number in Figure 11.

epoxide groups during functionalization led to a drastic increase of polarity. These epoxides are supposed to interact with the stationary phase. Hence, the retention of these polar polymers is restricted by additional enthalpic interactions. This has been known for many other polar polymer systems, like polyethylene-glycols and polyacrylic acids, which have to be investigated using more polar (aqueous) solvent systems.

In order to get more detailed insight, after functionalization GPC was coupled to MALDI. Spectra were continuously recorded from 25 to 33 mL elution volume. In Figure 12 10 MALDI mass spectra are shown related to their elution volumes (fractions are indicated in Figure 11(b)). The maximum of the first chromatographic fraction is about 6000 Da. From fraction 7 (maximum about 2700 Da) to fraction 1 (maximum at 500 Da) well-resolved spectra with single-peak resolution could be obtained. This makes it possible to determine the degree of epoxidation depending on the length of the polymer. The results are shown in Figure 13(a)–(d). Independent of the molar mass of fractions some double bonds of the PB 5000 remained non-epoxidized. Any increase of the reaction time and/or further addition of MCPBA only led to minor changes.

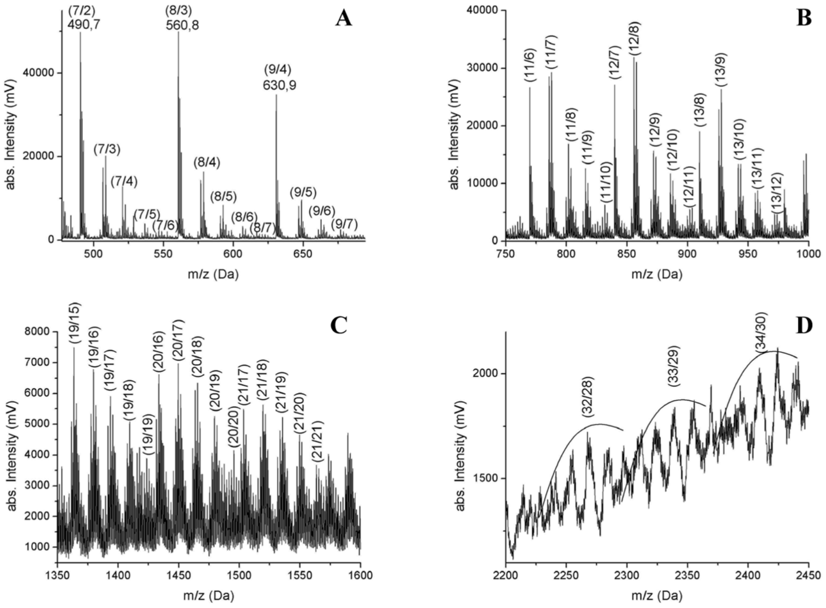

Figure 13. Degree of epoxidation depending on the length of the polymer; (a) fraction 10, (b) fraction 8, (c) fraction 6, (d) fraction 4 (enlarged view of spectra seen in Figure 12).

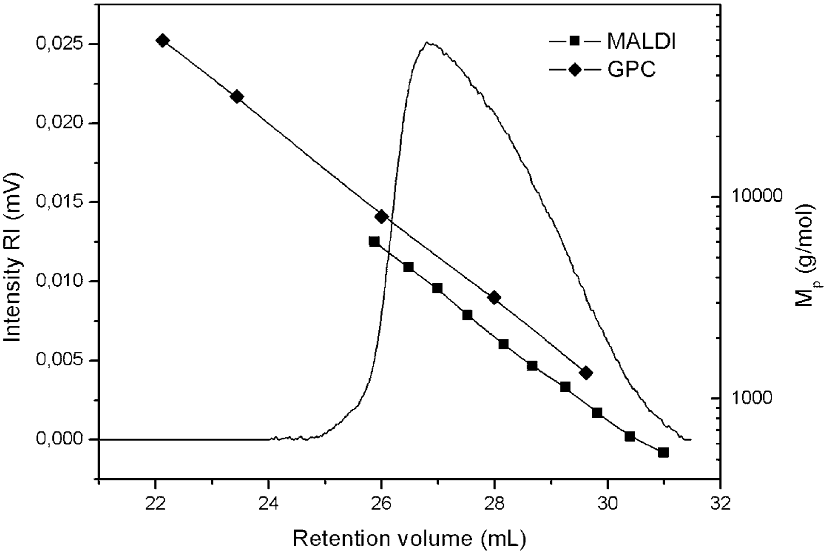

Figure 14. GPC-chromatogram and calibration curves of PB 5000 after functionalization with MCPBA for one hour. Calibration was performed using PI standards as well as by means of Mp data obtained from MALDI mass spectra after fractionation by GPC.

The MALDI data (Mp) obtained from spectra shown in Figure 12 were used to create a calibration curve. Simultaneously, GPC itself was calibrated using PI standards. Both calibration curves were compared in Figure 14. They exhibit a similar slope but show strong differences in terms of absolute masses. This could be explained by a different hydrodynamic volume of functionalized polymers. Although their chain length is shorter compared to non-functionalized polymers (e.g., PB 2700 = 50 repeat units, PB_{func} 2700 = 40 repeat units) the introduction of approximately 40 epoxide groups results in an increase of polarity, which possibly led to an expansion of the whole polymer coil. Therefore, functionalized polymers elute at lower retention times than non-functionalized polymers.

CONCLUSIONS

The epoxidation of various polydienes was performed using two agents (MCPBA, H_2O_2,). Structure and reactivity of the reagent used for epoxidation strongly affect the degree of functionalization. Using MCPBA, polyisoprenes could be completely epoxidized. Similar to MCPBA, epoxidation with hydrogen peroxide results in nearly completely functionalized products. However, side products indicating a partial hydrolysis of epoxides were formed too. The degree of epoxidation is strongly influenced by the nature of polydiene polymers. Polyisoprenes could be completely epoxidized, whereas polybutadienes showed lower degrees of epoxidation. This effect is due to the main structural difference between PI and PB. The additional methyl group of PI causes a +I effect, which results in a polarization (increase of electron density) of the double bond. This result is not influenced by the molar mass. PI always shows a 100% epoxidation, whereas higher molar mass PB remains incompletely functionalized.

The coupling of GPC with MALDI mass spectrometry was used successfully for the investigation of epoxidized polymers with higher masses. Single mass spectra of fractions were recorded that could be used for exact determination of the degree of epoxidation of higher mass polymers and an accurate calibration of GPC.

Due to its excellent resolution, MALDI was able to provide exact information on the degree of epoxidation as well as on the molar mass of reaction products.

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