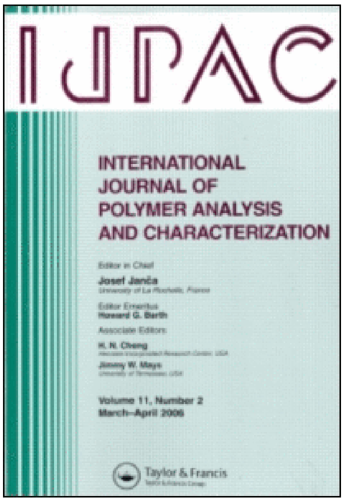

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Application of GPC Coupled with Diode-Array Detector for the Study of Oxidative Changes in Styrene-Butadiene Copolymers

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Application of GPC Coupled with Diode-Array Detector for the Study of Oxidative Changes in Styrene-Butadiene Copolymers

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The combination of GPC with a diode-array detector (DAD) was utilized for the determination of the oxidation course of styrene-butadiene copolymers. This article describes the use of a facile GPC-DAD technique to determine the relative contents of hydroxyl and carbonyl functional groups formed during oxidation along the molecular weight distribution. Hydroxyl and carbonyl groups detection is based on derivatization of these groups resulting in uniquely strongly UV-visible absorbing derivatives. The relative changes in molecular weight distribution were determined simultaneously. The results from the analysis can be valuable information for elucidation of degradation and branching processes during polymer oxidation.

Keywords: Gel permeation chromatography, diode array detection, styrene-butadiene copolymer, oxidation, derivatization

INTRODUCTION

Low-molecular-weight styrene-butadiene copolymers with low contents of styrene (LBS) can be utilized as surface coatings. These materials, besides their advantageous features in coating applications, have also some deficiencies, in particular very limited solubility in commercial

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polar solvents, slow drying rate, insufficient adhesion to the base materials, and some surface flaws of the film. Improvement can be achieved by introducing of polar groups into copolymer macromolecules, for example, by oxidation of a polymer solution. This process also changes molecular structure (owing to a degradation, branching and cross-linking) depending on oxidation conditions. An excessive preliminary oxidation of polymer in solution causes excessive branching and cross-linking and, in addition, the amount of double bonds is substantially decreased at the same time. This process results in a poor quality coating application. Therefore, optimum conditions of polymer oxidation (temperature, oxidation time) are needed.

When examining the thermal oxidation of polymer, determination of functional groups (carbonyl and hydroxyl) can be an advantageous method for elucidation of the degradation and branching processes. In the past, infrared analysis has been utilized for examination of the presence of carbonyl and hydroxyl groups formed in the course of polymer oxidation. However, this technique has failed to provide quantitative levels and has not been able to provide direct information regarding the location of functional groups on macromolecules (pendant or chain end) or dependance on the molecular weight distribution.[1,2] To overcome this problem, gel permeation chromatography (GPC) equipped with a refractive index detector and a diode array detector (GPC-DAD) can be utilized.

This paper describes the use of GPC-DAD to study the changes in the content of carbonyl and hydroxyl groups along the molecular weight distribution of styrene-butadiene copolymer as a function of temperature and time of copolymer oxidation. In order to make possible the detection of carbonyl and hydroxyl groups in the ultraviolet (UV) range, derivatization of the groups into highly UV absorbing groups was applied. By derivatizing the functional groups (not UV absorbing, such as hydroxyl or carbonyl) with a dye or tag reagent, a chromophore with a unique UV or visible response can be generated and a diode-array detector can be utilized which collects instantaneous spectral information from 190–800 nm. Attempts to derivatize carbonyl groups with 4-nitrophenylhydrazine and hydroxyl groups with 4-dimethylaminoazobenzene-4′-sulfonyl chloride were carried out.[3–5] Only insignifant reactivity dependance on the molecular weight and branching level was assumed.

The main aim of this work was coupling the UV tag technique with GPC-DAD to obtain a facile method for the study of polymer oxidation. By coupling the derivatization technique with GPC, any excess tag reagent that interferes with the UV analysis is separated from the polymer during the chromatography (purification is not required). This is another advantage of the method. In addition, the changes in molecular weights and molecular weight distribution were estimated by means of calibration using narrow polystyrene standards.

The relative average contents of carbonyl and hydroxyl groups in oxidized LBS copolymer were also determined by FTIR spectroscopy in order to ascertain the differences in these functional groups contents in dependance on experimental conditions.

EXPERIMENTAL

Materials

Copolymer Characterization

Styrene-butadiene copolymer with low content of styrene (5%) produced through anionic polymerization (LBS) was a product of The Synthetic Rubber Research Institute, Kaučuk, Czech Republic. The 1,2-structure of butadiene segments was dominant. Approximate molecular weights of the copolymer (based on GPC analysis) are presented in Table I.

TABLE I Molecular weight averages of the samples of LBS copolymer oxidized at various temperatures for 6 h including the original LBS (the temperature and time of oxidation are indicated in the sample name). M_n, M_w and M_z are number-average, weight-average, and z-average molecular weight respectively.

Sample name	M_n *(g/mol)*	M_w *(g/mol)*	M_z *(g/mol)*	M_w/M_n
LBS (orig.)	4,600	4,930	5,180	1.07
LBS-135C-2h	2,660	5,600	9,850	2.12
LBS-135C-4h	1,890	6,150	14,450	3.26
LBS-135C-6h	1,570	6,450	17,620	4.10
LBS-140C-2h	3,540	6,240	11,800	1.76
LBS-140C-4h	2,940	8,320	22,350	2.83
LBS-140C-6h	2,740	10,530	28,740	3.84
LBS-145C-2h	3,080	7,490	17,960	2.43
LBS-145C-4h	2,840	14,110	46,620	4.96
LBS-145C-6h	2,770	28,660	129,000	10.35

Chemicals

Xylene, n-butanol, toluene and hydrochloric acid (37%) were obtained from Lachema, Brno, Czech Republic. 4-Nitrophenylhydrazine (NPH), tetraethylene glycol dimethyl ether (tetraglyme), 4-(dimethylamino) azobenzene-4′-sulfonyl chloride (DABSYL-Cl), 1,4-diazobicyclo(2.2.2) octane (DABCO), methylene chloride, and tetrahydrofuran (THF) HPLC grade were obtained from Fluka Chemika-Biochemika.

Oxidation of LBS Copolymer

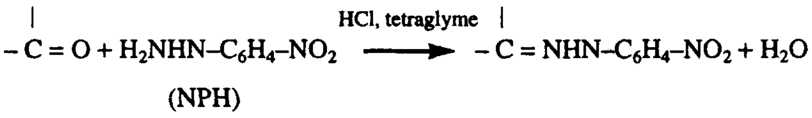
Solution of LBS copolymer (25 wt%) in the mixture of n-butanol and xylene (1:2) was oxidized in duplicated vessel (1-L volume) equipped with a turbine stirrer. The oxidation was made by the air by means of the tube introduced into the intensively agitated solution under the stirrer. The pressure above the solution was kept at 0.35 MPa. The air above the solution was continuously drained off by means of the vent to ensure high oxygen concentration during the oxidation. Experimental temperatures were 135°, 140° and 145°C. Samples of reaction mixture were taken for analysis at 2, 4 and 6 h of oxidation.

Derivatization

Oxidized LBS copolymer samples were derivatized according to the laboratory procedures published in.[3,4] The samples of reaction mixtures from copolymer oxidation were treated by removal of solvents (xylene and n-butanol) by means of vacuum under nitrogen at ambient temperature.

Derivatization of Carbonyl Groups

Reactions were performed in a distillation apparatus assembled using a Wheaton Micro Kit (Wheaton Scientific, Millville, New Jersey). A 5-mL flask of the apparatus (immersed into the silicone oil bath on the heater) was charged with toluene (2 mL), NPH (0.3 g), tetraglyme (0.1 g), hydrochloric acid (0.05 mL) and LBS copolymer (0.3 g). The mixture was refluxed under the nitrogen for 8 h and the water formed during the reaction was removed by azeotropic distillation in order to drive the reaction. The reaction of carbonyl group with NPH is reversible, as shown in Scheme 1.



$$-\overset{|}{C}=O + H_2NHN{-}C_6H_4{-}NO_2 \xrightarrow{\text{HCl, tetraglyme}} -\overset{|}{C}=NHN{-}C_6H_4{-}NO_2 + H_2O$$

(NPH)

SCHEME 1 Reaction of carbonyl group with NPH (hydrazone formation)

Derivatization of Hydroxyl Groups

A 50-mL flat-bottom flask equipped with a magnetic stirrer was charged with LBS copolymer (0.1 g) and methylene chloride (20 mL). The mixture was stirred until the copolymer dissolved. DABSYL-Cl (0.1 g) and DABCO (0.1 g) were added. The mixture was stirred at ambient temperature for 24 h. The reaction is shown in Scheme 2.

$$R{-}OH + ClSO_2{-}C_6H_4{-}N=N{-}C_6H_4{-}N(CH_3)_2 \xrightarrow[\text{-HCl}]{\text{DABCO}} R{-}O_3S{-}C_6H_4{-}N=N{-}C_6H_4{-}N(CH_3)_2$$

(DABSYL-Cl)

SCHEME 2 Reaction of hydroxyl group with DABSYL-Cl

As any excess tag reagent was separated from the copolymer during the chromatography, purification of the copolymer was not done. Reaction mixtures were filtered (0.2 μm) and the solvents were removed by means of vacuum under nitrogen.

GPC Analysis

Chromatographic System

A Waters GPC (Waters Discovery System) equipped with a refractive index detector 410 and a diode-array detector 996 was employed. Four thermostated (30°C) ultraStyragel columns of nominal pores 100, 500, 10^3 and 10^4 Å were used. The mobile phase was THF at a flow rate of 1 mL/min. The data were treated by chromatographic manager Millenium 2010 (all from Waters Corp., Milford, Mass.).

Sample Preparation

All samples (including samples of LBS copolymer without derivatization) were dissolved in THF (0.15% w/v) and toluene was added as an internal standard to correct for variations in the carrier flow rate. The injection volume was 100 μL.

Columns Calibration

For the molecular weight calibration, authentic standards were not available. For this reason, a universal calibration[6] was used. Polystyrene standards with narrow-molecular-weight distribution from Polymer Laboratories (Shropshire, UK) were employed for calibration. Mark-Houwink coefficients for polystyrene ($a = 0.713$, $K = 1.25 \times 10^{-4}$ dL/g) and polybutadiene homopolymer with 70% content of 1,2-structure ($a = 0.693$, $K = 4.03 \times 10^{-4}$ dL/g) as approximate values (the obtained values of LBS molecular weights were not actual due to the different chemical structure of LBS, and also due to the changes during the oxidation) were taken from the literature.[7]

Infrared Spectroscopy

Infrared (IR) spectra were measured on Nicolet 550 spectrometer (Fourier transform infrared). The solvents from the samples were completely removed by means of vacuum under nitrogen at the laboratory temperature. The selected intensities of the carbonyl band (1729 cm^{-1}) and the hydroxyl band (3440 cm^{-1}) were utilized for the determination of approximate relative amounts of these groups. These intensities were related to the band of phenyl groups (2919 cm^{-1}) the content of which was considered to be constant during the oxidation at applied temperatures. It has been shown[8] that oxygen at relatively low temperatures preferentially attacks the α-hydrogens found on the backbone of the styrene polymer or copolymer chain. So the chemically unchanged groups $-C_6H_5$ from the original LBS copolymer macromolecules could be present in various degraded and branched portions.

RESULTS AND DISCUSSION

Molecular weight averages of the samples of oxidized LBS copolymer for 6 h (without derivatization) including the original LBS copolymer are presented in Table I. The temperature and time of oxidation are indicated in the sample name, e.g., LBS-135C-6h means the sample of LBS copolymer oxidized at 135°C for 6 h. Normalized molecular weight distributions are given in Figures 1–4. UV spectra of oxidized LBS copolymer with its derivatives of carbonyl and hydroxyl groups are shown in Figures 5–7. Average relative content (related to the samples with the highest contents of the groups) of carbonyl and hydroxyl groups calculated from the infrared spectra and related to the phenyl group band can be seen in Table II. Three-dimensional (3-D) plots (retention time of GPC vs. wavelength vs. absorbance) of oxidized and derivatized LBS copolymer from GPC analysis are shown in Figures 8–11.

Molecular Weights

It is clear that the changes in the molecular weight distributions are very sensitive to the temperature of oxidation. At 135°C, the fraction of molecules below 2–3,000 g/mol increases during the course of oxidation and

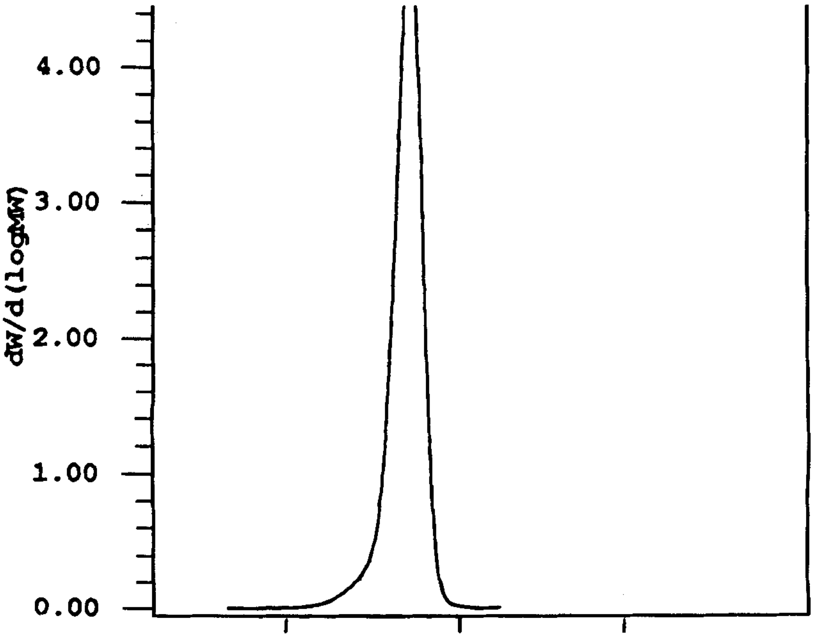


FIGURE 1 Molecular weight distribution of the original LBS copolymer.

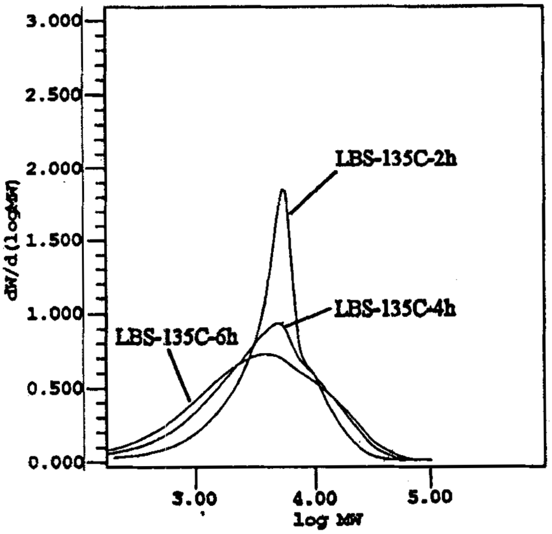


FIGURE 2 Molecular weight distributions of the samples of oxidized LBS copolymer. Dependance on the time of oxidation at 135°C. The temperature and time of oxidation are indicated in the name of sample.

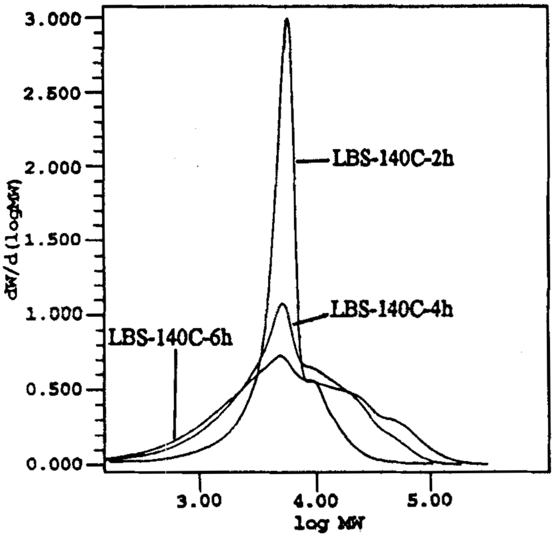


FIGURE 3 Molecular weight distributions of the samples of oxidized LBS copolymer. Dependance on the time of oxidation at 140°C. The temperature and time of oxidation are indicated in the name of sample.

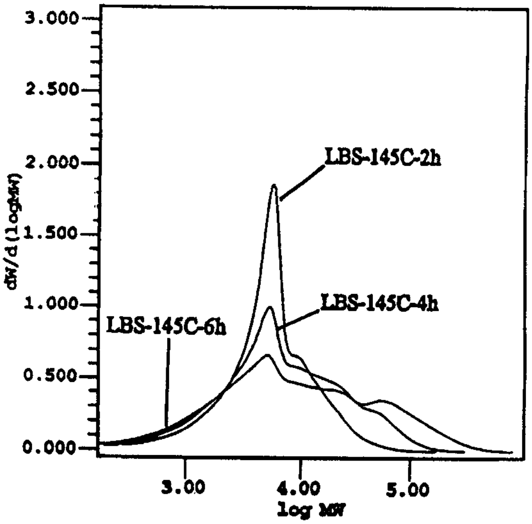


FIGURE 4 Molecular weight distributions of the samples of oxidized LBS copolymer. Dependance on the time of oxidation at 145°C. The temperature and time of oxidation are indicated in the name of sample.

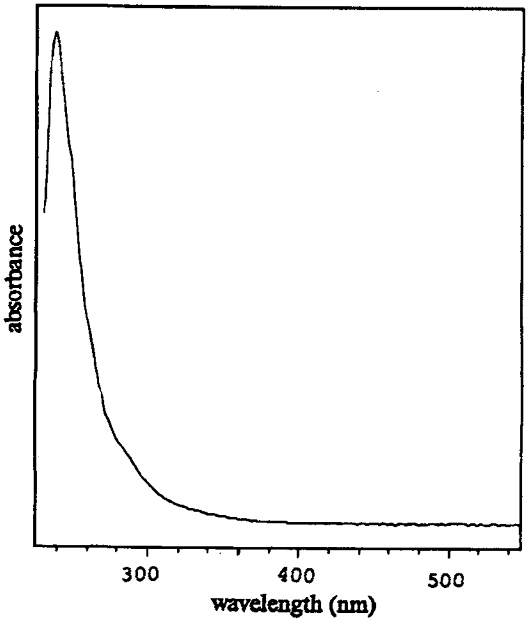


FIGURE 5 UV spectrum of oxidized LBS copolymer (without derivatization).

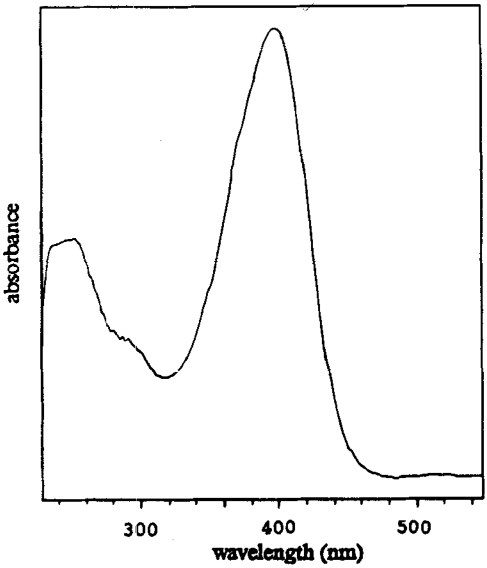


FIGURE 6 UV spectrum of oxidized and derivatized LBS copolymer (derivatization of carbonyl groups with NPH).

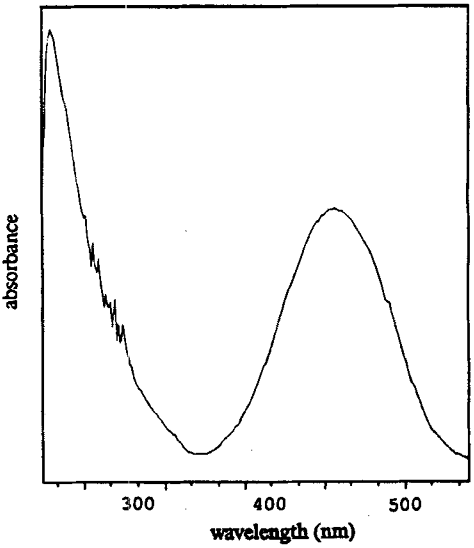


FIGURE 7 UV spectrum of oxidized and derivatized LBS copolymer (derivatization of hydroxyl groups with DABSYL-Cl).

TABLE II Average relative content of carbonyl and hydroxyl groups in oxidized LBS copolymer calculated from IR spectra. The values of absorbance (A_{rel}) are related to the samples with the highest content of either carbonyl or hydroxyl groups. The temperature and time of oxidation are indicated in the sample name.

Sample name	A_{rel} *(carbonyl)*	A_{rel} *(hydroxyl)*
LBS-135C-2h	0.39	0.45
LBS-135C-4h	0.70	0.72
LBS-135C-6h	1	1
LBS-140C-2h	0.11	0.14
LBS-140C-4h	0.18	0.24
LBS-140C-6h	0.23	0.33
LBS-145C-2h	0.16	0.18
LBS-145C-4h	0.25	0.32
LBS-145C-6h	0.31	0.43

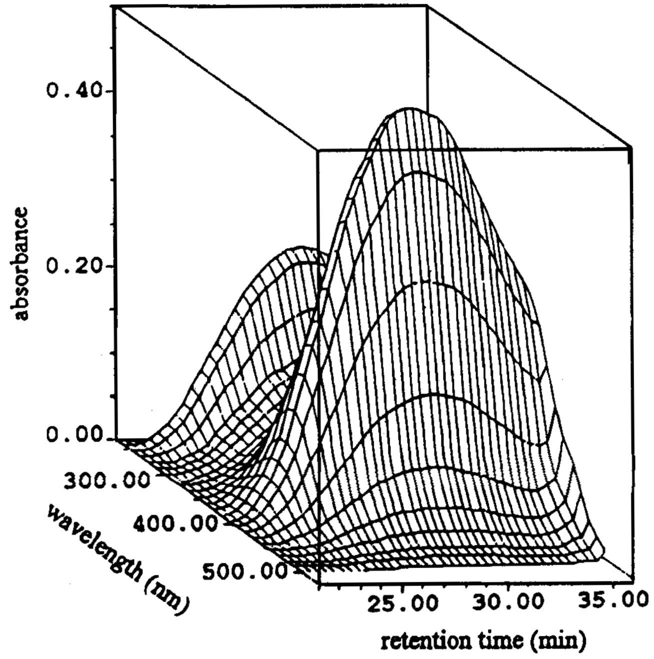


FIGURE 8 Three-dimensional GPC-DAD plot of oxidized and derivatized (carbonyl groups) LBS copolymer (temperature of oxidation: 135°C, time of oxidation: 6 h)

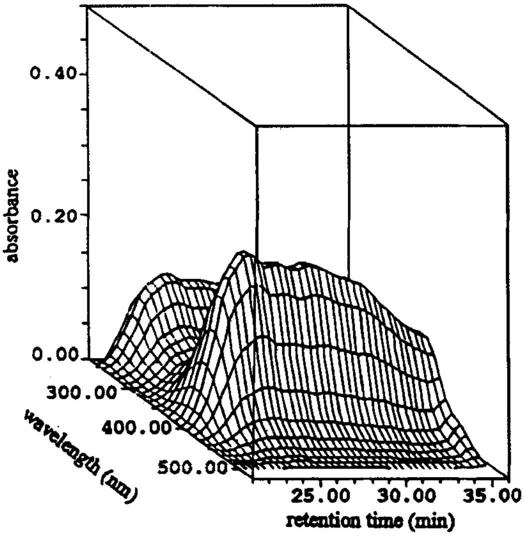


FIGURE 9 Three-dimensional GPC-DAD plot of oxidized and derivatized (carbonyl groups) LBS copolymer (temperature of oxidation: 145°C, time of oxidation: 6 h).

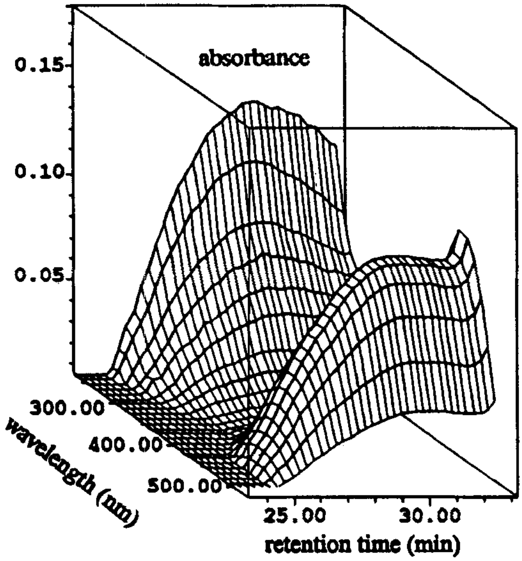


FIGURE 10 Three-dimensional GPC-DAD plot of oxidized and derivatized (hydroxyl groups) LBS copolymer (temperature of oxidation: 135°C, time of oxidation: 6 h).

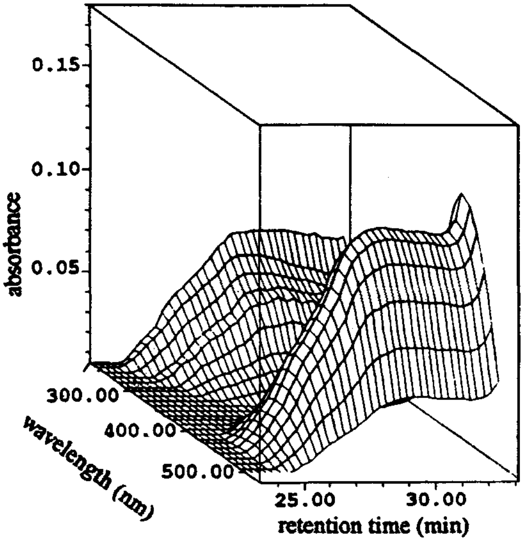


FIGURE 11 Three-dimensional GPC-DAD plot of oxidized and derivatized (hydroxyl groups) LBS copolymer (temperature of oxidation: 145°C, time of oxidation: 6 h).

this increase is higher than the increase in the region above 10,000 g/mol, which implies that the degradation of macromolecules is a dominant process. However, the ratio of degradation and branching (cross-linking) processes is changed in the case of higher temperatures (140°C, 145°C) and branching processes are dominant. Particularly at 145°C, the increase of the fraction above 10,000 g/mol is very high and the increase in the low-molecular region is not significant. In other words, increasing polydispersity M_w/M_n results from a decrease of M_n in the case of a lower temperature and from an increase of M_w in the case of a higher temperature during oxidation (as seen in Table I).

Derivatization

Attempts to derivatize carbonyl and hydroxyl groups in LBS copolymer with NPH and DABSYL-Cl, respectively were succesful, as can be seen in Figures 5–7. It is also apparent that oxidized copolymer (without derivatization) absorbs at 243 nm, implying the formation of new chromophores. This wavelength is different from the wavelength of styrene

(260 nm). With the use of mesityl oxide as a model compound, it appears this absorption is caused by carbonyl groups in the conjugation with double bonds. In the case of derivatized samples, GPC-DAD analyses clearly show NPH hydrazone chromophores (maximum absorbance at 390 nm) and DABSYL chromophores (maximum absorbance at 445 nm). UV spectra were taken at retention times corresponding to the maximum of molecular weight distribution. However, no measurements concerning the complete conversion of carbonyl and hydroxyl groups into their derivatives were made. That means the results cannot be used for the quantitative computations.

Three-Dimensional GPC-DAD Plots

Three-dimensional chromatograms were plotted which show the dependance of the relative amount of carbonyl or hydroxyl groups on the molecular weight in the oxidized LBS copolymer. The samples of LBS-135C-6h and LBS-145C-6h derivatized with NPH and DABSYL-Cl are shown as examples in Figures 8–11. In the case of low temperature oxidation (135°C), the plots clearly show the presence of carbonyl (or hydroxyl) groups particularly in the region of low molecular weights (retention interval 29–35 min corresponding to the fraction below 5,000 g/mol). The amount of carbonyl and hydroxyl groups is relatively high, which results from the values in Table II. However, at higher temperatures of oxidation (145°C), the functional groups are presented also in the region of high molecular weights (retention interval 23–29 min corresponding to the fraction above 5,000 g/mol). It is obvious, particularly in the case of the carbonyl groups in Figures 8 and 9. The amount of carbonyl and hydroxyl groups is relatively low under these temperatures. At higher temperatures, the portion of large macromolecules above 100,000–200,000 g/mol formed by branching and cross-linking processes can be found. The mechanism of the LBS copolymer degradation and branching can be assumed as follows,[9] where RH denotes polymer:

Initiation:
$$RH \rightarrow R\cdot \qquad (1)$$

Propagation:
$$R\cdot + O_2 \rightarrow ROO\cdot \qquad (2)$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \qquad (3)$$

Chain branching and termination:

$$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot + OH\cdot} \qquad (4)$$

$$\mathrm{RO\cdot + RH} \longrightarrow \mathrm{ROH + R\cdot} \qquad (5)$$

$$\mathrm{HO\cdot + RH} \longrightarrow \mathrm{HOH + R\cdot} \qquad (6)$$

$$2\,\mathrm{R\cdot} \longrightarrow \text{inert products} \qquad (7)$$

$$2\,\mathrm{ROO\cdot} \longrightarrow \text{inert products} \qquad (8)$$

$$\mathrm{R\cdot + ROO\cdot} \longrightarrow \text{inert products} \qquad (9)$$

Degradation: $$\mathrm{R\cdot + nO_2} \longrightarrow \mathrm{RCO + ROH + RCOOH + \ldots} \qquad (10)$$

The details of Reaction (10) are given in the literature.[9,10]

Optimal oxidation conditions to obtain a product with good adhesion and a rapid drying rate without tackiness of the resulting coating can be proposed from the results of these analyses. An optimum temperature (in the case of 6 h of oxidation time) is about 140°C. LBS copolymer oxidized under these conditions has only a small portion of degraded molecules with a high content of carbonyl and hydroxyl groups (this portion is responsible for the slow drying rate and tackiness of the coating). The amount of undesirable macromolecules above 100,000–200,000 g/mol is negligible (this portion is probably responsible for poor coating quality, for example, surface flaws). The medium contents of carbonyl and hydroxyl groups are sufficient to guarantee good solubility in polar solvents and good adhesion to the grounds in contrast to the original LBS copolymer as was verified by qualitative application experiments.

CONCLUSIONS

The changes in low-molecular-weight styrene-butadiene copolymers with a low content of styrene during oxidation by the air in solution depends strongly on conditions (temperature and time of oxidation). The significant changes are observed in molecular weight distribution and also in the carbonyl and hydroxyl groups content. Carbonyl and hydroxyl groups formed in the course of copolymer oxidation can be derivatized to highly UV absorbing groups. Three-dimensional GPC-DAD chromatograms of the derivatized samples clearly show the relative content of carbonyl and hydroxyl groups as a function of molecular weight. Optimum conditions for the oxidation of LBS copolymer can be proposed on the basis of GPC-DAD analyses.

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