

# Derivatization of Carboxyl-Terminated Polybutadiene for Determining Relative Functionality Distribution

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**ABSTRACT:** A new and highly efficient method for determining relative carboxyl group distribution in carboxyl-terminated polybutadiene has been developed using practical synthetic and analytical techniques. Using oxalyl chloride, samples of carboxyl-terminated polybutadiene were rapidly transformed to acid chlorides that were then chemically derivatized with benzyl alcohol, 4-nitrobenzyl alcohol, and 3,5-dinitrobenzyl alcohol. This provided quick and quantitative conversion to the corresponding benzyl ester derivatives. Each new derivative was fully characterized by nuclear magnetic resonance and Fourier transform infrared spectroscopy. The benzyl ester modified polymers were investigated in detail to determine their relative carboxyl group concentrations. To do this, gel permeation chromatography combined with ultra violet/refractive index dual

detection was employed. The 4-nitrobenzyl ester, having the highest extinction factor at 270 nm provided the best UV data for analysis. The ultra violet/refractive index data of four separate polymer samples were plotted as a function of molecular weight. The data were compared with a theoretical plot (carboxyl group = two for all molecular weights) to illustrate the relative carboxyl concentration over the entire molecular weight range. Supplemental characterization of the 4-nitrobenzyl modified polymer was carried out using matrix-assisted laser desorption ionization coupled with time of flight mass spectrometry. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 691–698, 2012

**Key words:** esterification; polybutadiene; gel permeation chromatography; modification; MALDI

## INTRODUCTION

Carboxyl-terminated polybutadiene (CTPB, polymer 1) liquid polymers are widely used as elastomeric binders in nondetonable solid propellant formulations,<sup>1–4</sup> and as additives to epoxy resins to increase toughness.<sup>5–10</sup> The final mechanical properties of these systems are directly correlated to the carboxyl ( $-\text{CO}_2\text{H}$ ) concentration in the CTPB. 1,3-Butadiene polymerizes through the one and four carbons (1,4-regiochemical addition) and to a lesser extent at the 1,2-regiochemistry (Fig. 1). Both polymerization mechanisms produce allylic sites along the polymer chain that are susceptible to hydrogen radical abstraction leading to branching.<sup>11</sup> This results in functionality counts both higher and lower than the theoretical end-cap value of two. Thus, determining

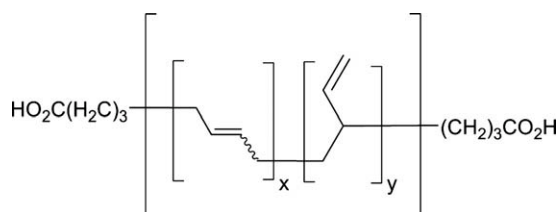
carboxyl concentration is not just an issue of end-group analysis, but one of determining where the functionality resides and if it is distributed evenly over all molecular weight fractions.

Establishing the absolute functionality of CTPB is a challenging exercise in analytical chemistry. This is because direct detection of carboxyl groups in high molecular weight polymers, where the functionality concentrations are generally low, is very difficult. Consequently, analytical data need to be correlated to well-known standards to obtain accurate functionality information. Earlier work by R. D. Law depicts a method for determining CTPB functionality using a combination of laboratory manipulations.<sup>12–14</sup> The process described involves gel permeation chromatography (GPC) analysis of polymer fractions recovered from stepwise elution over partially deactivated silica gel. Carboxyl content is then determined by fitting the IR spectra of each fraction to a calibration curve derived from titrating the whole polymer with KOH. The procedure is very time consuming and tedious,<sup>13</sup> and involves eluent mixtures containing carbon tetrachloride; a solvent that has become expensive to purchase and creates highly undesirable waste streams. A number of variations of this method have also been reported<sup>4,15</sup> including a more recent example containing nuclear magnetic resonance (NMR) spectroscopic analysis.<sup>11</sup>

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**Figure 1** Structure of carboxyl terminated polybutadiene (CTPB) showing the three possible chemical linkages (1,4-cis/trans and 1,2-regiochemical addition). The propylene carboxyl function originates from the glutaric acid peroxide polybutadiene initiator/terminator.

The difficulty in direct detection of carboxyl groups in CTPB compelled us to explore new, more practical, approaches for assessing their abundance in high molecular weight polymers. Since CTPB is a critical component in the production of rocket boosters, and the cure chemistry and properties of the cured elastomer are directly related to crosslink density, we had a keen interest in developing a fast and accurate method for determining (1) the level of end-cap and branching, and (2) if this ratio is constant over the entire range of polymer molecular weights. To accomplish this set of tasks, we leveraged the carboxyl reactivity to add an aromatic ultraviolet (UV)-chromophore to the polymer to serve as a readily detectable carboxyl group indicator. UV spectroscopy is ideally suited for this type of analysis due to its extremely low detection limits. By combining GPC analysis with a UV and refractive index (RI) dual-detection system, we were able to obtain all the data necessary to ascertain carboxyl group concentrations in samples of CTPB relative to a known CTPB standard. Similar methods have recently been used to determine compositional heterogeneity of copolymers.<sup>16</sup>

Herein, we report a time and chemically efficient method for derivatizing CTPB with an aromatic UV-chromophore. The modified polymer is then subjected to GPC-UV/RI analysis sequentially with a known derivatized CTPB standard to provide rapid and thorough assessment of relative carboxyl group distribution as a function of polymer molecular weight. The new analytical technique is particularly useful for monitoring lot-to-lot changes in CTPB.

## EXPERIMENTAL

### Derivatization of carboxyl-terminated polybutadiene (polymer 1)

#### General

Synthetic transformations were carried out using standard Schlenk techniques. Anhydrous  $\text{CH}_2\text{Cl}_2$ , oxalyl chloride (2M in  $\text{CH}_2\text{Cl}_2$ ), reagent grade benzyl alcohol, 4-nitrobenzyl alcohol (99%), 3,5-dinitrobenzyl alcohol (98%), and 4-(dimethylamino)pyridine (DMAP, 99%) were purchased from Aldrich Chemical

Company and used as received. ACS reagent grade methanol was acquired from Fisher Scientific and used without further purification. Distilled water was generated in house. CTPB (polymer 1, commercially known as Hycar) was obtained from Noveon (Lubrizol) and used as received. Additional analytical samples of CTPB came from Rohm and Haas. NMR data were collected on a JEOL Eclipse + 400 MHz spectrometer; the chemical shifts are reported in  $\delta$  (ppm) relative to residual solvent ( $\text{CDCl}_3$ ,  $\delta^1\text{H}$  7.25,  $^{13}\text{C}$  77.0). Fourier transform infrared (FTIR) spectra were collected on a Thermo Scientific Nicolet 6700 FTIR spectrometer.

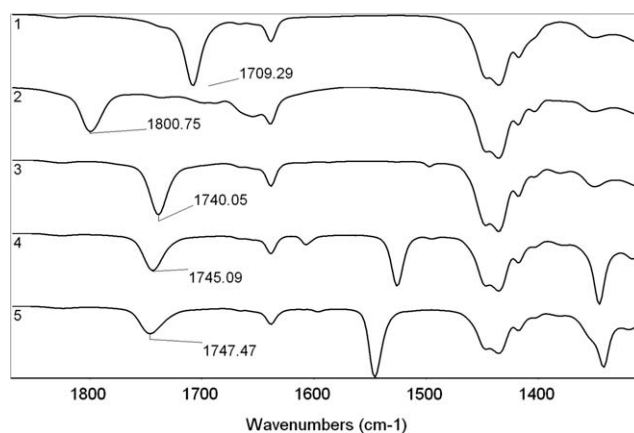
### Synthesis of acid chloride-terminated polybutadiene (polymer 2)

To a stirring solution of polymer 1 (1.00 g, theoretical 0.52 mequiv  $-\text{CO}_2\text{H}/\text{g}$ ) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added oxalyl chloride (0.4 mL, 0.73 mmol, 2M in  $\text{CH}_2\text{Cl}_2$ ). Dimethylformamide (DMF, 1–2 drops) was added and mild effervescence immediately occurred and slowed after  $\sim 30$  min. Conversion of polymer 1 to polymer 2 was confirmed using FTIR spectroscopy (Fig. 2) by noting a shift for the carbonyl  $\text{C}=\text{O}$  peak from  $1709\text{ cm}^{-1}$  (polymer 1,  $-\text{CO}_2\text{H}$ ) to  $1800\text{ cm}^{-1}$  (polymer 2,  $-\text{COCl}$ ). The mixtures were allowed to react for 90 min after the addition of DMF to allow time for complete conversion.

### Synthesis of ester-terminated polybutadiene derivatives

#### Benzyl ester-terminated polybutadiene (polymer 3)

While stirring the  $\text{CH}_2\text{Cl}_2$  solution of polymer 2 (described earlier), solid DMAP (127 mg, 1.04 mmol)



**Figure 2** FTIR spectra (transmission mode) of (top to bottom): (1) carboxyl-terminated polybutadiene (polymer 1) in  $\text{CH}_2\text{Cl}_2$ ; (2) acid chloride-terminated polybutadiene (polymer 2) in  $\text{CH}_2\text{Cl}_2$ ; (3) neat benzyl ester-terminated polybutadiene (polymer 3); (4) neat 4-nitrobenzyl ester-terminated polybutadiene (polymer 4); (5) neat 3,5-dinitrobenzyl ester-terminated polybutadiene (polymer 5). Labeled signals correspond to carbonyl  $\text{C}=\text{O}$  stretching frequencies ( $\text{cm}^{-1}$ ) for each polymer.

and benzyl alcohol (0.1 mL, 1.04 mmol) were added. After 2 h, the solution was transferred to a separatory funnel and washed with water (25 mL), saturated  $\text{Na}_2\text{CO}_3$  (25 mL), water (25 mL), and brine (25 mL). The organic phase was added in one portion to methanol (200 mL). The resulting white emulsion was concentrated (100 mL) by slow evaporation over a period of 2 days. During this time, the polymer separated from the solvent as a brown viscous liquid. The methanol was decanted from the polymer, and the product layer was rinsed with additional methanol ( $3 \times 20$  mL). The polymer was dissolved in a minimal amount of  $\text{CH}_2\text{Cl}_2$  ( $\sim 10$  mL) and concentrated under reduced pressure to give polymer 3 as clear orange/brown viscous liquid (860 mg, 82%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 7.3 (m, 5H aromatic), 5.6–5.2 (m, 67H), 5.1 (s, 2H, benzyl  $-\text{CH}_2-$ ), 5.0–4.8 (m, 15H), 2.3–1.1 (m, 160H). Selected peaks  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 173.5 (ester  $\text{C}=\text{O}$ ), 65.9 (benzyl  $-\text{CH}_2-$ ). See Figure 2 for FTIR spectrum.

#### 4-Nitrobenzyl ester-terminated polybutadiene (polymer 4)

While stirring the  $\text{CH}_2\text{Cl}_2$  solution of polymer 2 (described earlier), solid DMAP (127 mg, 1.04 mmol) and 4-nitrobenzyl alcohol (160 mg, 1.04 mmol) were added. After 2 h, the solution was transferred to a separatory funnel and washed with water ( $2 \times 5$  mL) gently to prevent emulsions, and then brine (5 mL). The organic phase was added in one portion to methanol (200 mL). The resulting white emulsion was concentrated (100 mL) by slow evaporation over a period of 2 days. During this time, the polymer separated from the solvent as a brown viscous liquid. The methanol was decanted from the polymer, and the product layer was rinsed with additional methanol ( $2 \times 20$  mL). The polymer was dissolved in a minimal amount of  $\text{CH}_2\text{Cl}_2$  ( $\sim 10$  mL) and concentrated under reduced pressure to give polymer 4 as clear brown viscous liquid (620 mg, 58%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 8.2 (d,  $J = 8.8$  Hz, 2H aromatic), 7.5 (d,  $J = 8.4$  Hz, 2H aromatic), 5.6–5.2 (m, 69H), 5.1 (s, 2H, benzyl  $-\text{CH}_2-$ ), 5.0–4.8 (m, 14H), 2.4–1.1 (m, 158H). Selected peaks  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 173.2 (ester  $\text{C}=\text{O}$ ), 64.5 (benzyl  $-\text{CH}_2-$ ). See Figure 2 for FTIR spectrum.

#### 3,5-Dinitrobenzyl ester-terminated polybutadiene (polymer 5)

The synthesis was carried out identical to polymer 4 above but using 3,5-dinitrobenzyl alcohol (206 mg, 1.04 mmol) in place of 4-nitrobenzyl alcohol. After workup, recovery by evaporation of the  $\text{CH}_2\text{Cl}_2$  yielded polymer 5 as clear brown viscous liquid (690 mg, 63%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 8.9 (apparent triplet,  $J = 2.2$  Hz, 1H aromatic), 8.5 (apparent doublet,  $J = 1.8$

Hz, 2H aromatic), 5.6–5.2 (m, 73H), 5.2 (s, 2H, benzyl  $-\text{CH}_2-$ ), 5.0–4.8 (m, 16H), 2.4–1.1 (m, 170H). Selected peaks  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 173.0 (ester  $\text{C}=\text{O}$ ), 63.5 (benzyl  $-\text{CH}_2-$ ). See Figure 2 for FTIR spectrum.

#### Gel permeation chromatography-UV/RI analysis of polymers 3, 4, and 5

GPC analysis was carried out on a HP1090 instrument with a diode array detector, Wyatt miniDawn<sup>®</sup> LS-detector, and RI-detector. The GPC size separations were accomplished using Waters<sup>®</sup> HR5E, HR4E, and HR1 ultra-styragel columns (each 300 mm  $\times$  7.8 mm) with high-performance liquid chromatography/UV grade tetrahydrofuran (THF), obtained from Aldrich Chemical Company, as the mobile phase. The THF was degassed by filtering through a 0.2 ( $\mu\text{m}$  polytetrafluoroethylene filter prior to use. The diode array detector was setup to collect the UV spectrum from 220 to 400 nm. Responses from the UV detector at 270 nm and RI detector were exported into the Wyatt miniDawn<sup>®</sup> LS software so point-by-point UV/RI ratios could be plotted over the size separation of the polymer derivatives.

Samples were obtained directly from the esterification reactions and diluted with additional  $\text{CH}_2\text{Cl}_2$  to 25 mg (reaction solution mass)/mL (additional  $\text{CH}_2\text{Cl}_2$ ) and then filtered through a 0.45 ( $\mu\text{m}$  polytetrafluoroethylene filter prior to injecting 100  $\mu\text{L}$  into the GPC.

#### MALDI-TOF/MS characterization of polymer 4

A Waters<sup>®</sup> Synapt<sup>™</sup> matrix assisted laser desorption ionization (MALDI)-time of flight (TOF) mass spectrometer (MS) with a 9 kV reflectron flight tube was used for all analyses. The MALDI source employed a Lumanova<sup>®</sup> 355 nm nitrogen laser, with 3 ns pulse widths, fired at 200 Hz. Laser energy was held constant slightly above the ion detection threshold at approximately 50  $\mu\text{J}/\text{pulse}$ . Ions were detected with a microchannel plate detector held at  $-1700$  V. All polymer signals were detected in the positive mode as copper-ion adducts in the form  $[\text{M} + \text{Cu}]^+$  from the addition of CuI to the sample matrix. Collisional cooling gas at the source was maintained at 2.5 mL/h. Quadrupole trap gas was adjusted to maintain the trap pressure between 5.3 and  $5.8 \times 10^{-3}$  mbarr. Summed spectra from 3 min of manual scan at  $m/z$  400 to 8000 were processed for each sample using MassLynx<sup>™</sup> v4.1 software.

#### Sample preparation

All preparatory reagents were purchased commercially and used without further purification. All *trans*-retinoic acid, 2,5-dihydroxy benzoic acid, and

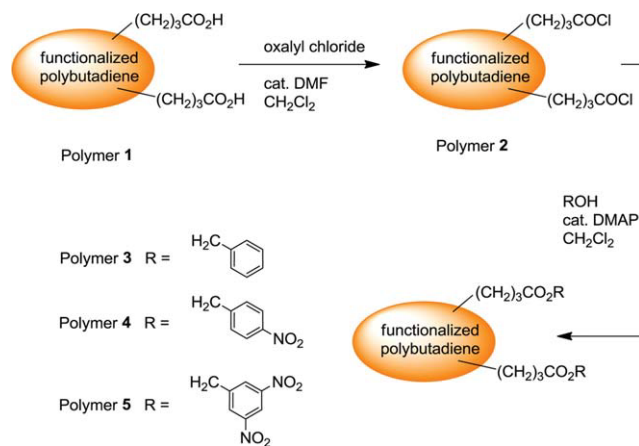
CuI were acquired from Alfa Aesar. Spectroscopic grade THF was obtained from Aldrich Chemical Company, and distilled water was generated in house. A 100  $\mu\text{L}$  aliquot of the  $\text{CH}_2\text{Cl}_2$  esterification reaction solution of polymer 4 was evaporated to dryness under a stream of  $\text{N}_2$ . The resulting solid was washed quickly with distilled water (400  $\mu\text{L}$ ). The water was decanted, the remaining solid dissolved in THF (5 mg/mL), and then combined with a solution of CuI (10 mg/mL THF/ $\text{H}_2\text{O}$ , 1 : 1, v/v) and a solution of retinoic acid matrix (50 mg/mL THF) in a 1 : 1 : 2 ratio (v/v/v), respectively. A CTPB standard, along with a sample from the original 100  $\mu\text{L}$  aliquot of polymer 4 (non-water rinsed) were prepared and analyzed in parallel to check for the presence of hydrolysis (de-esterification).

## RESULTS AND DISCUSSION

A common challenge in rocket propellant development and processing is identifying the source of discrepancies discovered in the physical or mechanical properties of a propellant. For example, if a propellant comprised of a well-known ingredient formulation does not meet established performance criteria it is necessary to determine the root cause of the failure. In CTPB based systems, the degree of functionality is often a contributing factor due to variations in crosslink density which directly impacts the mechanical properties. Presented here is an analytical tool that provides functionality comparisons between two or more samples of CTPB. Key to this technique is that the samples be analyzed sequentially on the same instrument. A sample of CTPB with known performance properties is esterified and then used to create a GPC-UV/RI profile that serves as a baseline of comparison for other "unknown" samples analyzed using an identical method. It is not necessary to establish the exact functionality of the "known" sample because it is used simply as a reference standard by which to compare the "unknown" sample to determine if it has more, less, or equal functionality. A theoretical profile of ideal CTPB where the carboxyl concentration = 2 for all molecular weights can also be created and utilized as a supplemental baseline of comparison. The GPC-UV/RI data is used to determine whether mechanical property changes directly correlate to functionality variations between different lots of CTPB.

### Chemical derivatization

Samples of CTPB (polymer 1) were individually derivatized with benzyl-, 4-nitrobenzyl-, and 3,5-dinitrobenzyl alcohol to afford the corresponding benzylic ester-terminated polybutadienes: polymers 3, 4, and 5, respectively. The alcohols were chosen to



**Scheme 1** Sequence of carboxyl group modification leading to chromophore-modified CTPB: polymers 3, 4, and 5. The propylene carboxyl function originates from the glutaric acid peroxide polybutadiene initiator/terminator. The diagram illustrates a system having an idealized functionality of two. [Color figure can be viewed in the online issue, which is available at [www.wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

assess our hypothesis that the intensity of the UV signal of the resulting esters would increase in proportion to the number of aromatic nitro groups, thereby lowering the functional group detection limit. To reduce the risk of decomposing, the polymer backbone with mineral acids typically used in esterification reactions, polymer 1 was first converted to an acid chloride-terminated polybutadiene (polymer 2), which spontaneously condenses with the selected benzyl alcohols under mild conditions to give polymers 3, 4, and 5 (Scheme 1).

A 0.4 mol-equiv excess (with respect to theoretical  $-\text{CO}_2\text{H}$  concentration) of oxalyl chloride is used in the reaction with polymer 1 to ensure complete conversion to polymer 2 and to account for any carboxyl groups exceeding the theoretical concentration. In the presence of a catalytic amount of DMF, the quantitative conversion of polymer 1 to polymer 2 is achieved in minutes. The reaction progress is followed with FTIR spectroscopy<sup>4,15</sup> by monitoring the shift in the carbonyl  $\text{C}=\text{O}$  peak from  $1709\text{ cm}^{-1}$  (polymer 1) to  $1800\text{ cm}^{-1}$  (polymer 2), (Fig. 2). Effervescence of gaseous coproducts ( $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{HCl}$ ) serves as a visual cue that the reaction is progressing. In this work, both sets of observations were in good agreement with each other. FTIR data showed the reaction was complete after approximately 30 min, which was consistent with cessation of the effervescence. However, following literature precedent of similar transformations,<sup>17</sup> stirring continued for a total of 90 min before proceeding to the esterification step.

Treatment of polymer 2 individually with benzyl-, 4-nitrobenzyl-, and 3,5-dinitrobenzyl alcohols gives essentially quantitative conversion to polymers 3, 4,

and 5 respectively. Each of the alcohols are used in stoichiometric excess (2 mol-equiv with respect to theoretical  $-\text{CO}_2\text{H}$  concentration) to ensure complete modification of the polymer and to consume any unreacted oxalyl chloride. DMAP is added in a 1 : 1 molar ratio with respect to oxalyl chloride to both facilitate the esterification of polymer 2 and to scavenge HCl given off in the process; in all cases the DMAP HCl byproduct remains in solution. The esterification reactions are also tracked with FTIR spectroscopy by monitoring the shift in the carbonyl  $\text{C}=\text{O}$  peak from  $1800\text{ cm}^{-1}$  (polymer 2) to  $1740\text{ cm}^{-1}$  (polymer 3),  $1745\text{ cm}^{-1}$  (polymer 4), and  $1747\text{ cm}^{-1}$  (polymer 5), (Fig. 2). The FTIR data indicated complete esterification with all three alcohols transpired after approximately 20 min. Nevertheless, reactions were allowed to proceed for a minimum of 90 min before any further manipulations were carried out.

Polymers 3, 4, and 5 can be obtained in their pure forms for NMR analysis by aqueous work-up. The  $\text{CH}_2\text{Cl}_2$  reaction solution of polymer 3 is washed with water and aqueous sodium bicarbonate to remove residual DMAP, DMAP HCl, and any unreacted oxalyl chloride. We observed that washing the reaction solutions of polymers 4 and 5 with sodium bicarbonate forms inseparable emulsions. Consequently, only water is used to wash polymers 4 and 5. However, due to their increased hydrophilicity (polar nitro groups) and reactivity, we find it best to minimize both the amount of water used and the contact time. The increased hydrophilicity/reactivity of polymers 4 and 5 did result in lower isolated yields compared to polymer 3.

Addition of the aqueous-washed  $\text{CH}_2\text{Cl}_2$  solutions of polymers 3, 4, and 5 to methanol does not immediately precipitate isolable products. Partial evaporation of the methanol in a fume hood over a period of 2 days causes separation of the polymers from the solvent. Decanting the remaining methanol removes the contaminants and gives the desired products in the form of thin films or small droplets. To recombine the products into quantifiable portions, and to remove residual methanol, the residues are redissolved in  $\text{CH}_2\text{Cl}_2$  and then isolated by concentration under reduced pressure.

To supplement the FTIR data and further verify the success of the syntheses, polymers 3, 4, and 5 were characterized by NMR spectroscopy. In the  $^1\text{H}$ -NMR spectra ( $\text{CDCl}_3$ ) of polymers 3, 4, and 5, the aromatic protons ( $\delta$  8.9–7.3), the benzylic methylene protons ( $\delta$  5.2–5.1), and the butadiene protons ( $\delta$  5.7–5.2, 5.1–4.8, 2.5–1.0) are observable. The relative degree of end-group modification was determined by assessing the ratios of polymer butadiene protons to aromatic protons. In theory, exhaustive esterification would culminate in the aromatic groups being

**TABLE I**  
 **$^1\text{H}$ -NMR Integrations of Ester-Terminated Polybutadienes**

Polymer	Aromatic protons <sup>a</sup>	Polybutadiene protons
3	5	242
4	4	241
5	3	259

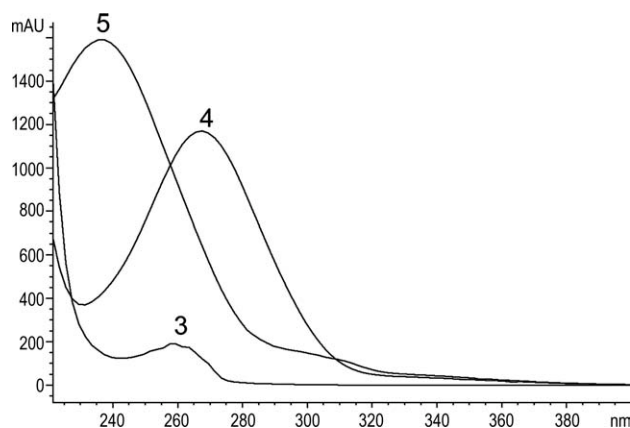
<sup>a</sup> Integrations of aromatic protons set to equal their actual value.

directly proportional to the initial carboxyl concentrations. The integrations of the aromatic proton signals were set to their actual values (aromatic proton integrations = five for polymer 3; four for polymer 4; three for polymer 5). Results show that incorporation was consistent regardless of the alcohol. In the  $^1\text{H}$ -NMR spectrum of polymer 5, the benzylic methylene proton signal overlaps the vinylic protons of the butadiene chain. Thus, reported integrations were determined by subtracting two from the total integrated area between  $\delta$  5.7–5.2. The ratios of polybutadiene protons to aromatic protons from the  $^1\text{H}$ -NMR spectra of polymers 3, 4, and 5 can be seen in Table I. The larger discrepancy in the integration values observed in polymer 5 compared to polymers 3 and 4 is likely a consequence of the signal overlap and is believed to be artificially high.

Analysis of polymers 3, 4, and 5 with GPC-UV/RI and MALDI-TOF/MS did not require the same degree of purification as described for NMR analysis. Both techniques are capable of disregarding low molecular weight impurities such as DMAP, DMAP HCl, and unreacted alcohol so that focus can be directed only on the compounds of interest. Therefore, analytical samples for these techniques were prepared directly from the  $\text{CH}_2\text{Cl}_2$  reaction solutions. Following the completion of the esterification reaction, the derivatized polymers were analyzed at intervals ranging from 1 h to 7 days and they showed no evidence of decomposition or changes in chemical composition.

### Gel permeation chromatography-UV/RI spectroscopy

GPC was used to evaluate the carboxyl functionality across the entire molecular weight distribution of the modified polymers. The UV spectra of polymers 3, 4, and 5 (Fig. 3) were used to select the derivative with optimal response and high wavelength maximum. This is necessary to detect the functional group at high polymer molecular weights, given that longer polymer chains (higher mass) reduce the UV response as a consequence of lower functional group concentrations. The dinitro functionality of polymer 5 led to the shortest wavelength  $\lambda$ -max, yet strongest



**Figure 3** Overlaid UV spectra (200–400 nm) of polymers 3, 4, and 5.

absorption band of the three ester derivatives. However, its absorbance near 240 nm is not practical for routine analysis in THF since it tails well into the low 200 nm area. We found that polymer 4, with a  $\lambda$ -max at  $\sim 270$  nm, provides a more unique wavelength and was, therefore, chosen as the optimal derivative for evaluating the CTPB functionality. Polymer 3 gave the lowest UV response (i.e., weakest extinction coefficient) of all three derivatives between 200 and 400 nm.

A CTPB standard prepared in-house with measured molecular weight distribution ( $M_n = 3050$  Da,  $M_w = 6280$  Da) and Mark-Houwink constants ( $a = 0.787$ ,  $K = 0.013543$ ) was used to convert the size separations to the molecular weight distribution parameters  $M_n$ ,  $M_w$ , and polydispersity (PD) index. The CTPB samples used in this study gave the following average values using this standard:  $M_n = 3898$  Da,  $M_w = 8286$  Da and  $PD = 2.13$ . From this, a correlation of the molecular weight of polymer 4 and the GPC retention time (RT, min) was established and is shown in Equation 1.

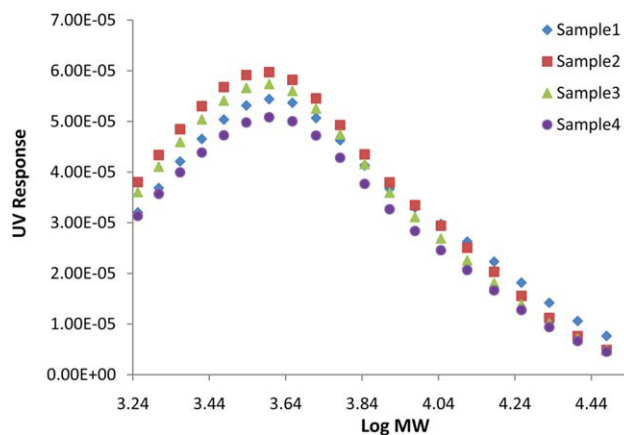
$$\text{Log(MW)} = 24.3 - 1.821\text{RT} + 0.0535\text{RT}^2 - 0.000590\text{RT}^3 \quad (1)$$

**TABLE II**  
Theoretical Relative wt % Carboxyl Content (Functionality = 2) of Polymer 4

Retention time (min)	LogMW <sup>a</sup>	MW (daltons)	wt % carboxyl <sup>b</sup>
20.0	4.56	36308	0.24
21.0	4.19	15435	0.57
22.0	3.85	7074	1.26
23.0	3.54	3467	2.60
24.0	3.26	1802	5.13

<sup>a</sup> From eq. (1).

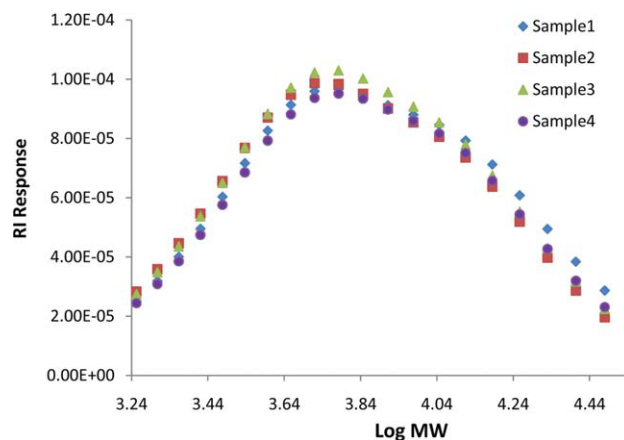
<sup>b</sup> Calculated:  $88 / (\text{MW} - 88) \times 100$ , where 88 amu = carboxyl ( $-\text{CO}_2^-$ ).



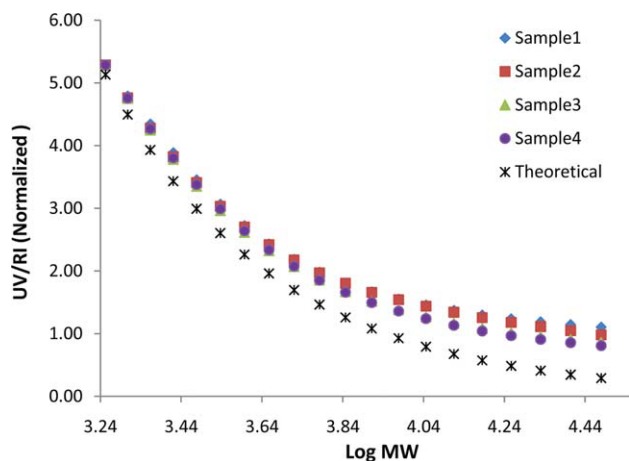
**Figure 4** Profiles of the UV response (270 nm) versus molecular weight (LogMW) of four separate samples of polymer 4 separated by GPC (RT = 20–24 min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Equation 1 was obtained using Agilent Technologies Chemstation GPC Data Analysis software (Revision B.01.01). The theoretical wt % carboxyl content was calculated for the molecular weights corresponding to RT = 20 to 24 min (Table II).

Four different samples (1–4) of polymer 4 (two samples derived from Noveon CTPB, two samples derived from Rohm and Haas CTPB) were separated by GPC (RT = 20 to 24 min) and their UV (Fig. 4) and RI (Fig. 5) responses were plotted as a function of molecular weight. The relative functionality distribution throughout the polymer can be seen by combining the data into a point-by-point plot of the UV/RI ratio for the GPC separation between 20 and 24 min (Fig. 6) where shorter retention times correspond to higher molecular weights. Using the data



**Figure 5** Profiles of the RI response versus molecular weight (LogMW) of four separate samples of polymer 4 separated by GPC (RT = 20 to 24 min). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6** Profiles of the UV/RI data versus molecular weight (LogMW) of four separate samples of polymer 4 separated by GPC (RT = 20–24 min). Data are compared to a theoretical sample of CTPB with absolute carboxyl functionality = 2 over all molecular weights. The profiles of samples 1–4 are normalized to the first (lowest MW) data point on the theoretical profile. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

from Table II, a profile of a theoretical sample of polymer 4 with absolute carboxyl concentration = 2 was drawn for comparison to the experimental samples. Since the potential for branching decreases as the polymer molecular weight gets smaller, the overlaid profiles in Figure 6 for samples 1–4 were normalized to the lowest molecular weight data point

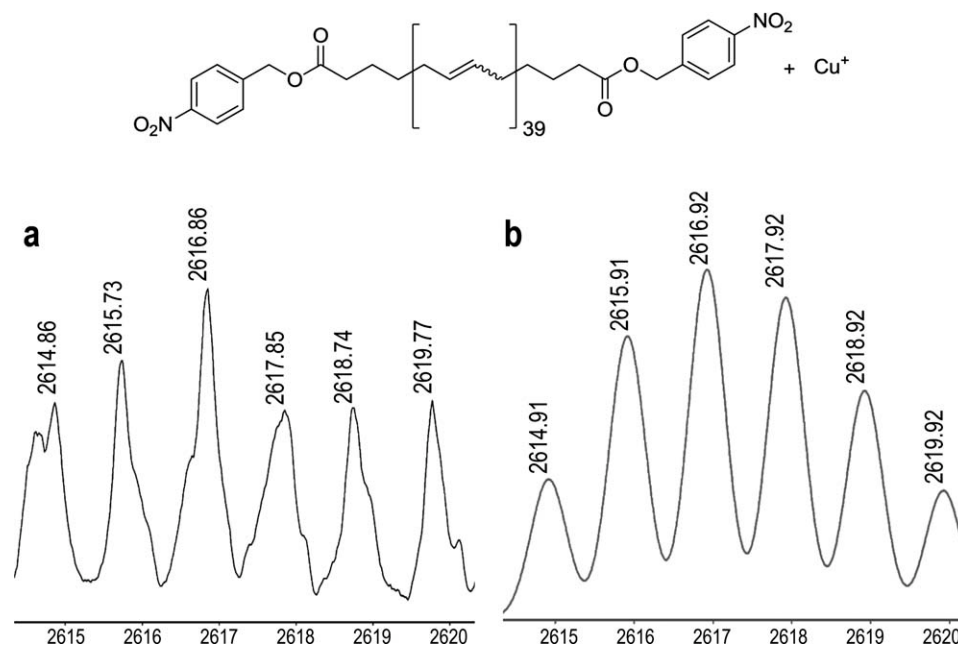
on the theoretical profile. It is worthwhile to note that the accuracy of this analysis is only as accurate as the assumption that functionality = 2 for the lowest molecular weight fraction. In this case, the GPC data reported later supports this assumption.

Comparison of the theoretical profile with the experimental profiles (Fig. 6) demonstrates that there is consistency between samples, and that they all have carboxyl concentrations slightly  $\geq 2$ . It is interesting to see that as the molecular weight increases the experimental UV/RI plots show the functionality continues to increase above 2. Thus, as the molecular weight increases there is more branching (i.e., side-chain propylene carboxyl groups) along the polymer backbone.

#### MALDI-TOF/MS characterization of polymer 4

MALDI is considered a “soft” ionization technique, where large molecules can be ionized without fragmentation. It is particularly useful for characterization of high mass species. Polymer ionization yield is dependent on the MALDI matrix compound. Use of the popular matrix 2,5-dihydroxybenzoic acid for analysis of polymer 4 yielded only lower mass signals. Improved results were obtained using retinoic acid as the matrix, such as that previously employed by Yalcin et al.<sup>18</sup>

The experimentally observed peak set in the MALDI-TOF/MS of polymer 4 [Fig. 7(a)] matches the isotopic model of the bi-derivatized 4-nitrobenzyl



**Figure 7** (a) Low molecular weight region of the experimental positive MALDI mass spectrum of polymer 4 ( $n = 39$ ) and (b) simulated isotopic pattern for  $[C_{178}H_{258}N_2O_8 + Cu]^+$  (a 4-nitrobenzyl ester-terminated polybutadiene compound where  $n = 39$ ; Cu is added to facilitate ionization). The six methylene groups adjacent to the carboxyl functions originate from glutaric acid peroxide initiator/terminator and account for 84 amu.

target compound [Fig. 7(b)]. This data confirms successful conversion of polymer 1 to polymer 4. The isotopic model in Figure 7(b) shows the  $[M + Cu]^+$  of the target compound with 39 butadiene monomer units. The low molecular weight fraction of polymer 4 was used for identification because it is statistically least likely to experience branching and, therefore, has a predictable molecular weight. Dominant peak sets in the total mass spectrum were separated by 54 amu, consistent with a single butadiene repeat unit. Samples of polymer 4, water-rinsed and non-water-rinsed, were analyzed by MALDI-TOF/MS. No hydrolysis peak shift was observed in the spectra of the two samples indicating that de-esterification of the polymer did not occur.

### CONCLUSIONS

A new method for determining relative carboxyl group concentration of CTPB by way of a mild stepwise chemical derivatization sequence involving oxalyl chloride and 4-nitrobenzyl alcohol has been developed. Complete conversion of the carboxyl groups to esters was confirmed with FTIR and NMR spectroscopy. A correlation was made between polymer molecular weight and functional group concentration using GPC-UV/RI analysis. The data can be compared to a theoretical plot of ideal CTPB or to a "known" CTPB reference standard to determine the relative functionality of the samples. The new analytical method is robust, efficient, and practical for rapid lot-to-lot functionality comparisons. Future research efforts will focus on developing an analytical standard and calibration curve for determining absolute functionality of CTPB by this derivatization method.

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