Notes

Analysis of the Sequence Distribution of 1,2 Units in Polybutadiene by an Ozonolysis–GPC Method

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Introduction

Polybutadiene is regarded as a copolymer consisting of three isomeric units, cis-1,4, trans-1,4, and 1,2. The variety of sequence distributions of these isomeric units and the tacticities of 1,2 units are governed by the initiator and solvent of polymerization. The control of these structural factors is significantly important for getting a good performance of rubber properties. Several approaches have been used for the determination of the average sequence length and tacticity of 1,2 units by using either a spectroscopic or chromatographic method. ^{13}C-NMR studies on hydrogenated polybutadiene provided the information that syndiotactic 1,2 sequences were allowed to crystallize with longer than 3.7 racemic succession of 1,2 units.[1,2] The gas chromatographic measurements of ozonolysis products or metathesis products from polybutadiene were applied to the analysis of some diad and triad sequences of 1,2 units.[3,4] However, the structural information thus far obtained was restricted in principle only to short sequences, i.e., diad, triad, and so on. If the alignment of 1,2 units is characterized as a distribution from short to long sequences including the tacticity, it will provide definitive evidence on the relationship between the microstructure and physical properties, as well as that of the polymerization conditions and microstructure.

We have proposed a new method for the characterization of the sequence distribution of styrene units in styrene–butadiene copolymers by a combination of selective ozonolysis of the double bonds in butadiene units and gel permeation chromatography (GPC) measurements of the resulting products. This method is based upon high-resolution GPC analysis of the alcohols corresponding to styrene sequences obtained by the scission of all the carbon–carbon double bonds of butadiene units. The ozonolysis–GPC method has been proven to be a very powerful tool to characterize the sequence distribution of styrene units and the tacticity in random, partially blocked, and triblock styrene–butadiene copolymers.[5–10] In this study, a new analytical method of the sequence distribution of 1,2 units in polybutadiene was investigated on the basis of the ozonolysis–GPC method.

Experimental Section

Commercially available polybutadiene (BP-1949; Bunawerke Huels GmbH; containing 57.2% of 1,2 units determined by ^{1}H-NMR) was purified in a chloroform–methanol reprecipitation way. Ozonization was carried out by blowing an equimolar amount of ozonated oxygen (1.3%) to carbon–carbon double bonds in a 0.4% w/v chloroform solution of the polybutadiene at −30 °C. Reductive degradation of the resulting ozonide was performed by the addition of a small amount of water, after the ozonide had reacted with 4 mol of lithium aluminum hydride in ethyl ether. After reductive degradation, neutralization was carried out by adding 1.5 mol of trifluoroacetic acid (TFA) into the resulting LiOH and $Al(OH)_3$. The resulting product was distilled off at atmospheric pressure followed by distillation at reduced pressure. Trifluoroacetates were prepared by allowing the reductive degraded products suspended in dry chloroform to react with 5 mol of trifluoroacetic anhydride (TFAA) in the presence of a catalyst mixture consisting of 1 mol % 4-(dimethylamino)pyridine and an equimolar amount of triethylamine based on hydroxyl groups at 38 °C for 14 h. Upon the completion of the reaction, precipitate was filtered. Trifluoroacetates were obtained after chloroform had been removed at atmospheric pressure.

GPC measurements were made with a Jasco 880-PU high-pressure pump and a Jasco 830-RI detector. The high-resolution GPC curve was obtained by two columns (21.2 mm i.d. × 600 mm) packed with polystyrene gel connected in series having an exclusion limit of 3000. The theoretical plate number of the columns was 45 000. The measurements were performed using chloroform as eluent at a flow rate of 4.0 mL/min. The measurement of the maximum absorption of the ultraviolet wavelength was made with a Jasco Multi-330 multichannel detector. The ^{13}C-NMR spectra were obtained by a JEOL GX-270 FT-NMR spectrometer at 67.8 MHz. The measurements were carried out in a $CDCl_3$ solution (1.8% w/v) with tetramethylsilane as an internal standard. The spectra were obtained at room temperature, a pulse angle of 45°, a pulse delay time of 4.0 s, and accumulating 18 000 scans.

Result and Discussion

Polyols corresponding to 1,4–$(1,2)_n$–1,4, $n = 0$–3 and so on, sequences are the products obtained by reductive degradation of polybutadiene ozonide with $LiAlH_4$. Direct measurements of the polyol fractions by GPC or HPLC were found to be difficult because the long-chain polyols were insoluble in most organic solvents or water. Therefore, the polyols were converted into chloroform-soluble trifluoroacetates via esterification with TFAA. Figure 1 shows a high-resolution GPC curve of the trifluoroacetates obtained from the ozonolysis products of polybutadiene.

Accordingly, a model compound corresponding to the 1,4–1,2–1,4 sequence was prepared by ozonolysis of 4-vinyl-1-cyclohexene, followed by esterification with TFAA. The GPC elution volume of this model compound was found to be 171 mL. Therefore, the corresponding peak observed in Figure 1 is assignable to the 1,4–1,2–1,4 sequence. The peak appearing at the elution volume 187 mL is assigned to the 1,4–1,4 sequence because it has the same elution volume as trifluoroacetate derived from 1,4-butanediol as a model compound corresponding to the 1,4–1,4 sequence. The other peaks that appeared in the order of decreasing elution volume in Figure 1 are presumed to be $n = 2$–9, respectively, as shown in 1. A plot of log M_w of $n = 0$–9 in 1 versus elution volume gave a straight line as shown in Figure 2. This shows that the structural assignment is valid.

Parts a and b of Figure 3 show the ^{13}C-NMR spectra of the compounds corresponding to $n = 1$ and 2, respectively. The former was prepared by the ozonolysis of 4-vinyl-1-cyclohexene, and the latter was obtained by GPC frac-

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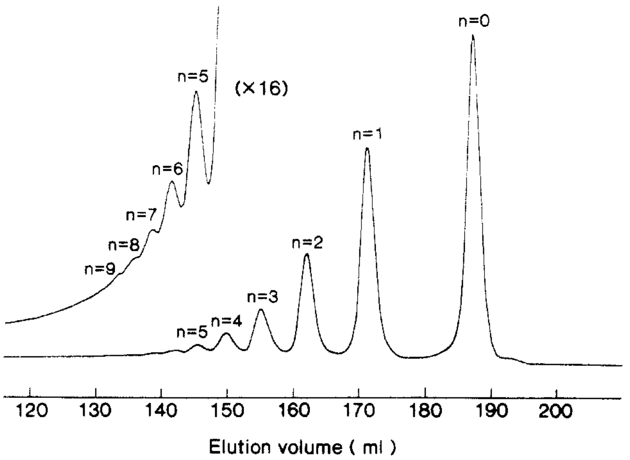


Figure 1. High-resolution GPC curve for the trifluoroacetates of ozonolysis products from polybutadiene. Peak n indicates the number of 1,2 units in 1,4–(1,2)$_n$–1,4 sequences.

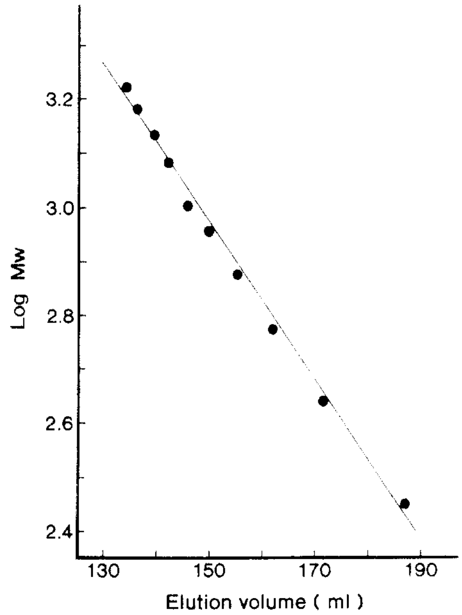
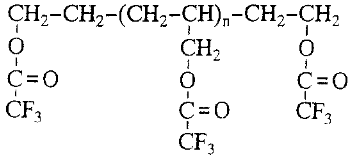


Figure 2. Relationship between the elution volume of the GPC peaks and the molecular weight of trifluoroacetates.



$$\begin{array}{ccc} \mathrm{CH_2{-}CH_2{-}(CH_2{-}} & \mathrm{CH)_n{-}CH_2{-}} & \mathrm{CH_2} \\ | & | & | \\ \mathrm{O} & \mathrm{CH_2} & \mathrm{O} \\ | & | & | \\ \mathrm{C{=}O} & \mathrm{O} & \mathrm{C{=}O} \\ | & | & | \\ \mathrm{CF_3} & \mathrm{C{=}O} & \mathrm{CF_3} \\ & | & \\ & \mathrm{CF_3} & \end{array}$$

(1)

tionation of the ozonolysis product of polybutadiene. It is clear that all the hydroxyl groups have been esterified with TFAA.

The trifluoroacetates in a chloroform solution were found to have a maximum absorption wavelength of 270 nm as measured by a multichannel UV–vis detector. Therefore, the above GPC measurements can also be performed with a UV detector.

Acetate derivatives prepared with acetic anhydride were also found to be soluble in chloroform. Figure 4 shows the GPC curve of acetate derivatives obtained from the ozonolysis product of polybutadiene in a way similar to the case of TFAA. In this chromatogram, the peak of the 1,4–1,2–1,4 sequence appeared at an elution volume of 164 mL. Other peaks corresponding to the products of the 1,4–(1,2)$_n$–1,4 sequence of n = 2–9 were also observed. However, the peak of the 1,4–1,4 sequence was not detected because it overlapped with an intense impurity peak. A small shoulder observed at the peak of 164 mL is presumed to arise from unreacted hydroxyl groups that partially remained in the acetate derivatives. Therefore, the reactivity of acetic anhydride toward polyols is lower than that of TFAA. The GPC chromatogram of acetate derivatives of the ozonolysis products from polybutadiene showed a poorer separation than that of TFAA derivatives due to the smaller molecular weight of acetate groups. In contrast with trifluoroacetates, acetate derivatives in a chloroform solution were found to have no maximum absorption in the UV region as shown by a multichannel detector.

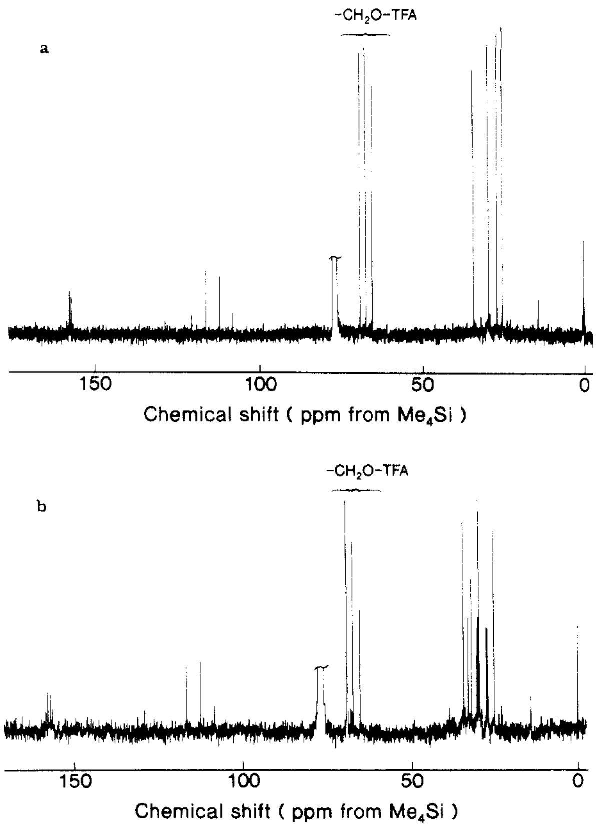


Figure 3. ^{13}C-NMR spectra of trifluoroacetates corresponding to the 1,4–1,2–1,4 sequence from the ozonolysis product of 4-vinyl-1-cyclohexene (a) and the GPC fraction corresponding to the 1,4–(1,2)$_2$–1,4 sequence (b).

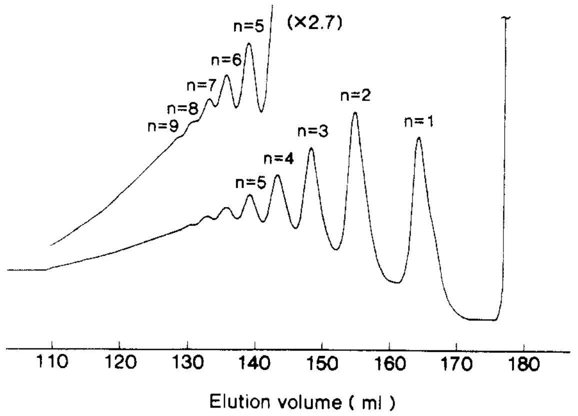


Figure 4. High-resolution GPC curve for the acetate derivatives of the ozonolysis products from polybutadiene. Peak n shows the number of 1,2 units in 1,4–(1,2)$_n$–1,4 sequences.

The findings clearly indicate that the ozonolysis–GPC method can also be applied to the analysis of the sequence distribution of 1,2 units in polybutadiene by successive derivation of polyols to trifluoroacetates. It is remarkable that the peak corresponding to the 1,4–1,4 sequence is clearly observed in this measurement in addition to 1,4–$(1,2)_n$–1,4 sequences. On the basis of the relative intensity of each peak, the quantitative measurement of the sequence distribution can be made by compensation with an appropriate correction factor for the refractive index or UV absorptivity of each fraction. The details on these corrections and the quantitative determination of the sequence distribution of polybutadiene samples will be presented in a subsequent paper.

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