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Quantitative Analysis of Sequence Length Distribution of 1,2 Units in Polybutadienes by Ozonolysis−GPC Method

Keiko Kakuta,[†] Hironori Tamai,[†] Peng- Huwen Wong,[†] Seiichi Kawahara,*,[‡] and Yasuyuki Tanaka[†]

Division of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan, and Department of Chemistry, Faculty of Engineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan

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ABSTRACT: The sequence distribution of 1,2 units in commercial and laboratory produced polybutadienes, containing 1,2 units from 0.5 to 87%, was analyzed by an ozonolysis−GPC method. Ozonides from polybutadiene were converted to trifluoroacetates by reduction with $LiAlH_4$, followed by esterification with trifluoroacetic anhydride. The trifluoroacetates derived from 1,4−1,4 and 1,4−$(1,2)_n$−1,4 sequences, from $n = 1$ to 7, were observed as respective GPC peaks using an refractive index detector. The relative intensities of these peaks were converted to the concentration of each sequence by using correction factors determined with model compounds and by direct weighing of each peak. Polybutadienes prepared by anionic polymerization showed a sequence distribution of 1,2 and 1,4 units corresponding to Bernoulian statistics, whereas the 1,4−$(1,2)_2$−1,4 sequence was significantly higher than the theoretical value for 1,2 units in *cis*-1,4 polybutadiene.

Introduction

The sequence distribution of isomeric units in polybutadiene has been anticipated to be an important factor in governing physical properties. For example, the melting temperature (T_m) of cis-1,4 polybutadienes prepared by Co−AlR_2Cl catalyst was independent of the content of *cis*-1,4 units, whereas the T_m of cis−trans isomerized polybutadiene was proportional to the cis-1,4 content.[1] Several approaches have been developed for the determination of the sequence distribution of the isomeric units. ^{13}C NMR spectroscopy provides quantitative information on the distribution of diad to triad sequences. The diad sequence distribution of cis-1,4, trans-1,4 and 1,2 units determined by ^{13}C NMR showed a good agreement with those assumed on the basis of Bernoulian statistics for polybutadienes from anionic and radical initiators as well as those from Co−Al catalysts.[2] ^{13}C NMR studies on hydrogenated polybutadienes also have shown that racemic sequences of 1,2 units longer than 3.7 are necessary to crystallize syndiotactic 1,2 polybutadiene.[3,4] Gas chromatographic analysis of ozonolysis or metathesis products from polybutadiene also give information on the diad sequence of 1,2 and 1,4 units.[5−8] However, these methods provide only information on diad or triad sequences, and the limit of detection is not low enough to analyze small differences in the sequence distribution.

We have established a novel method for the analysis of the sequence distribution of styrene and styrene−1,2 units in styrene−butadiene copolymers (SBR) by the GPC analysis of ozonolysis products.[9−11] This ozonolysis−GPC method has proven to be a powerful tool for analysis of the entire sequence distribution from short to long sequences in commercial SBRs.[12,13] The method was applied to the analysis of the sequence distribution of 1,2 units in polybutadiene by GPC measurement of ozonolysis products, which were transformed into trifluoroacetates after reductive degradation of the ozonide with $LiAlH_4$.[14] A commercial polybutadiene showed GPC peaks corresponding to 1,4−1,4 and 1,4−$(1,2)_n$−1,4 sequences from $n = 1$ to 9 using a refractive index (RI) detector. However, the quantitative measurement of sequence distribution was not made due to the lack of information on the relative RI for each GPC peak. In this paper, we report the sequence distribution of various polybutadienes polymerized with a lithium initiator and coordination catalysts, using correction factors for each GPC peak.

Experimental Section

The samples used were commercially available polybutadienes and laboratory products. The 1,2 unit content of the polybutadienes was determined by ^1H NMR spectroscopy as shown in Table 1. The polybutadienes were purified in the usual way by reprecipitation from toluene solution into methanol. As a model of 1,4−1,2−1,4 sequence, 4-vinyl-1-cyclohexene, purchased from Tokyo Chemical Industry Co., was used after purification by washing with 10% w/v NaOH and ion-exchange water. Ozonization was carried out by blowing an equimolar amount of ozone in ozonated oxygen (1.3%) to carbon−carbon double bonds in 0.4% w/v methylene chloride solution of polybutadiene at −30 °C. Reductive degradation of the resulting ozonides was performed by reaction with 4 mol of lithium aluminum hydride in ethyl ether, followed by the addition of a small amount of water. After reductive degradation, neutralization of the resulting LiOH and $Al(OH)_3$ was carried out by adding 1.5 mol of trifluoroacetic acid. The solvents were distilled at 70 °C, followed by distillation at reduced pressure (30−40 mmHg). The resulting reductively degraded products were suspended in dry chloroform and reacted 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, (on the basis of hydroxyl

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* To whom correspondence should be addressed.

[†] Tokyo University of Agriculture and Technology.

[‡] Nagaoka University of Technology.

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Table 1. 1,2 Unit Content and Catalyst System of Polybutadiene

specimen	1,2 unit content (%)	catalyst	supplier
Lab-A	0.5	rare earth element	Asahi Chemical Industry
Ubepol-BR	1.5	Co	Ubekosan
BR-01	1.7	Ni	JSR
Buna CB 11	3.7	Ti	Bayer AG.
Asadene 55	11.1	Li	Asahi Chemical Industry
Solprene 255	12.9	Li	Japan Elastomer
BR-4	19.4	Li	Yokohama Rubber
Lab-B	38.5	Li	Asahi Chemical Industry
BR-5	40.2	Li	Yokohama Rubber
BR-6	45.7	Li	Yokohama Rubber
BP1949	57.2	Li	Bunawerke Hules GmbH
Nipole1240	72.8	Li	Nippon Zeon
84%	86.5	Li	Goodyear Tire & Rubber
90%	85.2	Li	Goodyear Tire & Rubber

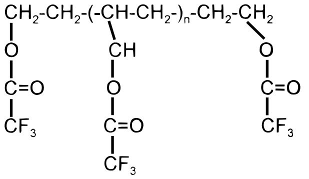
groups) at 40 °C for 6 h. Upon completion of the reaction, the precipitate was filtered. The trifluoroacetates were obtained after the solvent was distilled off.

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.

Results and Discussion

Correction Factors. In our previous paper,[14] we reported that almost all of the polyols obtained from ozonolysis products of polybutadiene were converted to trifluoroacetates, which were soluble in chloroform, facilitating the GPC measurement. The trifluoroacetates were detected by both RI and UV detectors and were evidently separated in each sequence of 1,2 units due to the significant difference in molecular weight of the trifluoroacetyl groups.

Figure 1 shows a GPC curve for trifluoroacetates of ozonolysis products from polybutadiene prepared by anionic polymerization with a lithium initiator, such as Nipole 1240. A series of short−long sequences of 1,2 units was detected by GPC as isolated peaks. The peak at the greatest elution volume on GPC curve was attributed to the 1,4−1,4 sequence derived from the 1,4−1,4 linkages corresponding to $n = 0$ in eq 1. This assignment was confirmed by a comparison with the corresponding compound derived from 1,4-butandiol. The other peaks were assigned to $1,4-(1,2)_n-1,4$ sequences as reported in our previous paper,[14] where n represents the number of 1,2 units, i.e., 1−4 and so on.



(1)

Because polyols from the ozonolysis products were soluble in chloroform after esterification with trifluoroacetic anhydride, the intensity of GPC peaks was expected to approximately be proportional to the amount of ozonolysis products. This implies that mole fractions of 1,2 unit sequences can, in principle, quantitatively be determined from the ratio of areas under the peaks. However, it is necessary to know the refractive index for each trifluoroacetate.

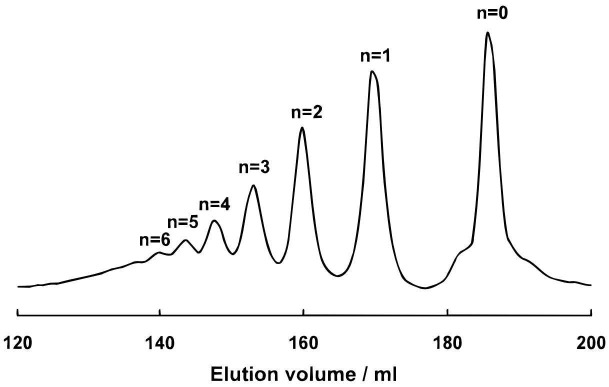


Figure 1. High-resolution GPC curve for trifluoroacetates of ozonolysis product from polybutadiene prepared with lithium catalyst, Nipole 1240. Peak n indicates the number of 1,2 units in $1,4-(1,2)_n-1,4$ sequences.

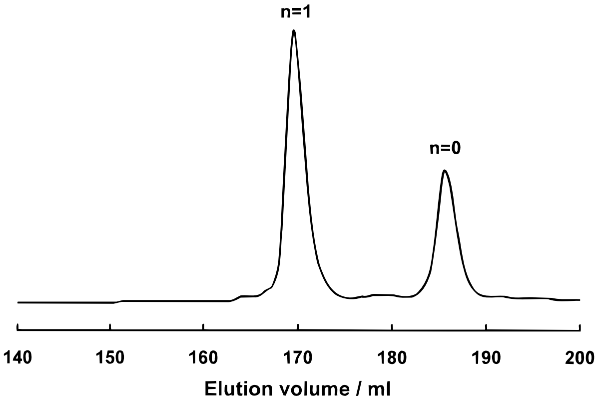


Figure 2. High-resolution GPC curve for trifluoroacetates of ozonolysis product from 1:2 mixture of Lab-A and 4-vinyl-1-cycrohexene.

The correction factor, K_1 for the 1,4−1,2−1,4 sequence was obtained to compensate for the difference in the refractive index between 1,4−1,4 and 1,4−1,2−1,4 sequences:

$$S_1/S_0K_1 = [1,4-1,2-1,4]/[1,4-1,4] \qquad (2)$$

where S_0 and S_1 are peak areas of 1,4−1,4 and 1,4−1,2−1,4 sequences, respectively, and [1,4−1,2−1,4]/[1,4−1,4] is the molar ratio of 1,4−1,4 to 1,4−1,2−1,4 sequences estimated from weights of fractionated sequences. To determine the K_1 value experimentally, the ozonolysis products from *cis*-1,4 polybutadiene (Lab A) and 4-vinyl-1-cyclohexene were used as model compounds for 1,4−1,4 and 1,4−1,2−1,4 sequences, respectively. The GPC curve of ozonolysis products from a mixture of Lab-A and 4-vinyl-1-cyclohexene in a ratio of 1.000:2.000 by mole is shown in Figure 2. Only two peaks, corresponding to 1,4−1,4 and 1,4−1,2−1,4 sequences, were observed in the chromatogram. In Table 2, the estimated K_1 value for mixtures of Lab A and 4-vinyl-1-cyclohexene is shown to be approximately independent of the molar ratio of Lab-A to 4-vinyl-1-cyclohexene within the error. Thus, K_1 was determined to be 0.96 by averaging the values shown in Table 2.

Each of the refractive indexes for the peaks for $1,4-(1,2)_n-1,4$ sequences of n > 2 were corrected by using

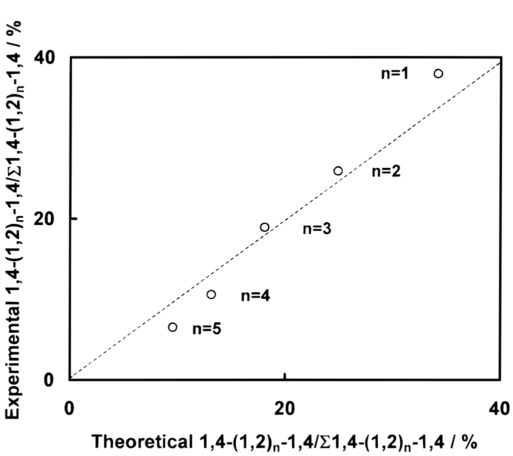


Figure 3. Experimental mole fraction of 1,4−(1,2)$_n$−1,4 sequences for Nipole 1240 determined by ozonolysis−GPC vs theoretical mole fraction estimated in terms of the random distribution of Bernoullian statistics from 1,2 unit contents.

Table 2. Correction Factor for 1,4−1,2−1,4 Sequence, K_1, of the Mixture of Lab-A and 4-Vinyl-1-cyclohexene

molar ratio Lab-A:4-vinyl-1-cyclohexene	K_1
1:0.5	0.93
1:1	0.99
1:2	0.99
1:3	0.97
average	0.96

Table 3. Correction Factor for 1,4−(1,2)$_n$−1,4 Sequences, K_n, Determined with Nipole 1240

	n^a				
	1	2	3	4	5
K_n	0.96	1.09	1.15	1.23	1.42

[a] n = number of repeating 1,2 units in 1,4−(1,2)$_n$−1,4 sequences.

Nipole 1240 as a standard. Mole fractions of 1,4−(1,2)$_n$−1,4 sequences were estimated from the peak area of the respective 1,4−(1,2)$_n$−1,4 sequences divided by the sum of peak areas of 1,4−(1,2)$_n$−1,4 sequences (n = 0−5), because peaks corresponding to 1,4−(1,2)$_n$−1,4 sequences (n = 0−5) appeared separately, as shown in Figure 1. The estimated mole fraction of 1,4−(1,2)$_n$−1,4 sequences is shown in a plot of experimental versus theoretical value in Figure 3. Here, the theoretical value was estimated in terms of the random distribution from Bernoullian statistics for the fraction of 1,2 units, x, of polybutadiene:

$$\text{Theoretical mole fraction} = (1-x)^2x^n/\Sigma(1-x)^2x^n \quad (n = 0-5)$$

As shown in Figure 3, the theoretical mole fraction of the 1,4−(1,2)$_n$−1,4 sequences was approximately to be proportional to the experimental value of 1,4−(1,2)$_n$−1,4/Σ1,4−(1,2)$_n$−1,4. The deviation from the linearity may be due to the overlapping peaks for $n > 5$.This demonstrates that the 1,2 unit sequence distribution of Nipole 1240 is statistically random. Therefore, the correction factors for longer 1,2 unit sequences, K_n, were estimated from the theoretical and experimental mole fractions of 1,4−(1,2)$_n$−1,4 sequences. The estimated values of K_n are shown in Table 3. The values of K_n increased as sequence length of 1,2 units increased, suggesting the dependence of the refractive index on n.

Table 4. Sequence Distribution of 1,2 Units of Various Polybutadienes Prepared with Lithium Initiator and Theoretical Distribution Estimated in Terms of Bernoullian Model

specimen	1,2 unit (%)	fraction of 1,4−(1,2)$_n$−1,4					
		n =	0	1	2	3	4
Diene 55	11.1	experimental	94.1	5.8	0.1	none	none
		theoretical	89.0	9.9	1.1		
Solprene 255	12.9	experimental	81.3	16.3	2.1	0.3	none
		theoretical	87.1	11.2	1.4	0.2	
BR-4	19.4	experimental	81.1	16.3	2.3	0.3	none
		theoretical	80.7	15.7	3.0	0.6	
Lab-B	38.5	experimental	62.9	29.3	6.4	1.3	0.1
		theoretical	62.0	23.9	9.2	3.5	1.3
BR-5	40.2	experimental	62.6	26.4	8.5	2.2	0.3
		theoretical	60.4	24.3	9.8	3.9	1.6
BR-6	45.7	experimental	62.6	25.8	8.7	2.3	0.6
		theoretical	55.4	25.3	11.6	5.3	0.2
BP-1949	57.2	experimental	53.4	27.7	11.8	5.0	2.1
		theoretical	45.6	26.1	14.9	8.5	4.9
Nipole 1240	72.8	experimental	37.8	30.3	18.5	9.5	3.9
		theoretical	34.2	24.9	18.1	13.2	9.6
84%	86.5	experimental	36.1	24.1	20.2	11.6	8.0
		theoretical	26.2	22.6	19.6	16.9	14.7
90%	85.2	experimental	28.3	28.5	22.1	13.7	7.4
		theoretical	26.9	22.9	19.5	16.6	14.2

Sequence Distribution of Polybutadiene. The quantitative analysis of the sequence distribution of 1,2 units in polybutadiene prepared with a lithium initiator was carried out by using the correction factors K_n. The fraction of 1,2 unit sequences (mol %) estimated from the GPC peak area of the ozonolysis products is shown for 10 different polybutadienes in Table 4, together with the theoretical mole fractions of 1,4−(1,2)$_n$−1,4 sequences to compare with the experimental values. The experimental values were almost identical to the theoretical values for shorter sequences. However, differences between experimental and theoretical mole fractions were clearly observed at sequences longer than n = 4, which may be due to the overlap of peaks in the chromatogram. Thus, the four fractions, i.e., 1,4−(1,2)$_n$−1,4 sequences of n = 0−3, were used for more precise quantitative analysis.

It is convenient to note the relationship between the sequence distribution of 1,2 units and fraction of 1,2 units, as follows:

$$f[1,2] + f[1,4] = 1$$

$$f[1,4-1,2] = f[1,2-1,4] = X$$

$$f[1,4-(1,2)_n-1,4] = (1-x)^2X^n$$

$$f[1,4-(1,2)_{n-1}-1,4] = (1-x)^2X^{n-1}$$

$$f[1,4-(1,2)_n-1,4]/f[1,4-(1,2)_{n-1}-1,4] = X \quad (n = 1-3, \cdots) \quad (3)$$

where $f[1,4-(1,2)_n-1,4]$ represents an existing probability of 1,4−(1,2)$_n$−1,4 sequence and X is thefraction of 1,2 units of polybutadiene determined by ^{1}H NMR spectroscopy. The theoretical and experimental molar ratios of 1,4−(1,2)$_n$−1,4 to 1,4−(1,2)$_{n-1}$−1,4 versus X is shown in Figure 4, where theoretical values were directly proportional to X, as is evident from eq 3. The experimental values are in fairly good agreement with the theoretical values for all the samples, despite the wide variety of the content of 1,2 units. This demonstrates that the sequence distribution of 1,2 and 1,4

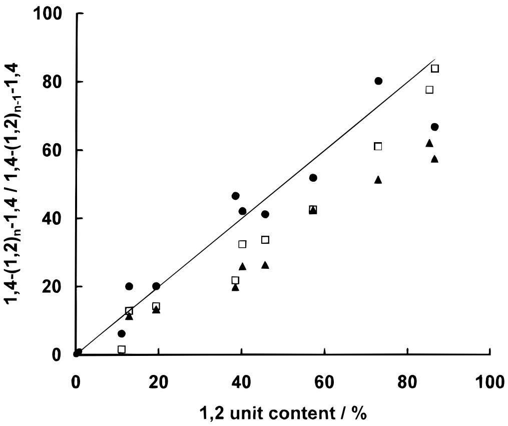


Figure 4. Molar ratio of 1,4−(−1,2-)$_n$−1,4 to 1,4-(−1,2−)$_{n-1}$−1,2 ($n = 0-3$) in theoretical and experimental distribution for polybutadienes prepared with lithium catalyst; ●, 1,4−1,2−1,4/1,4−1,4; □, 1,4−(1,2)$_2$−1,4/1,4−1,2−1,4; ▲, 1,4−(1,2)$_3$−1,4/1,4−(1,2)$_2$−1,4.

Table 5. Sequence Distribution of 1,2 Units of Polybutadienes Prepared with Coordination Catalyst and Theoretical Distribution Estimated in Terms of Bernoullian Model

		fraction of 1,4−(1,2)$_n$−1,4			
specimen	1,2 unit (%)	n =	0	1	2
Lab-A	0.5	experimental	95.50	0.50	none
		theoretical	95.50	0.50	
Ubepol-BR 150	1.5	experimental	97.92	1.94	0.14
		theoretical	98.50	1.48	0.02
BR-01	1.7	experimental	97.05	2.77	0.18
		theoretical	98.3	1.67	0.03
Buna CB 11	3.7	experimental	94.13	5.22	0.65
		theoretical	96.31	3.56	0.13

units in polybutadiene prepared with lithium catalyst is statistically random. It is, consequently, clear that the 1,2 and 1,4 additions of 1,3-butadiene monomer occur randomly in anionic polymerization.

The ozonolysis−GPC method was also applied to *cis*-1,4 polybutadiene to detect the diad sequence of 1,2 units which was not found by ^{13}C NMR measurement due to the low relative intensity and overlapping with other signals. Table 5 shows theoretical and experimental mole fractions of 1,4−(1,2)$_n$−1,4 sequences for cis-1,4 polybutadienes prepared with a coordination catalyst. Three peaks associated with 1,4−1,4, 1,4−1,2−1,4 and 1,4−(1,2)$_2$−1,4 sequences were detected easily by GPC for Ubepol-BR150, BR-01, and Buna CB11. Conversely, only two peaks associated with 1,4−1,4 and 1,4−1,2−1,4 sequences appeared in the GPC curve for Lab-A, suggesting the absence of diad sequence of 1,2 units in this polymer. As shown in Table 5, the experimental value of 1,4−1,4 and 1,4−1,2−1,4 sequences was quite similar to the theoretical one. However, the experimental value of the 1,4−(1,2)$_2$−1,4 sequence was higher by a factor of approximately 5 than the theoretical value, showing that the fraction of 1,4−(1,2)$_2$−1,4 sequence did not follow the random distribution. This may suggest the presence of a short blocky sequence of 1,2 units. In the previous work,[15] the stereospecific polymerization to form cis-1,4 units was reported to be influenced by electronic, steric, and geometric factors of coordination catalysts. For example, the formation of 1,2 and cis-1,4 units has been suggested to derive from a coordination intermediate with an antistructure of the butenyl group and a cis-η^4 coordination of the monomer, respectively.[16,17] On the other hand, no steric factor affects the anionic polymerization with a lithium initiator. This implies that the sequence distribution of polybutadiene prepared with a coordination catalyst can be distinguished from the statistical random distribution for anionic polymerization.

Conclusion

The ozonolysis products corresponding to 1,4−(1,2)$_n$−1,4 sequences, $n = 0-4$ and so on, obtained by reductive degradation of polybutadiene ozonide with $LiAlH_4$, were converted into chloroform-soluble trifluoroacetates. Each sequence up to $n = 4$ was detected as an isolated peak in high-resolution GPC. The correction factors for the refractive index of each peak was determined to be $K_1 = 0.96$, $K_2 = 1.09$, $K_3 = 1.15$, $K_4 = 1.23$, and $K_5 = 1.42$, where subscript figures represent the number of repeating 1,2 units, n, in 1,4−(1,2)$_n$−1,4. The determined mole fractions of 1,4−(1,2)$_n$−1,4 sequences for polybutadienes prepared with lithium initiator were in good agreement with those estimated in terms of a Bernoullian model, suggesting the random distribution of 1,2 units in these polymers. The sequence of 1,2 units in *cis*-1,4 polybutadiene from a coordination catalyst deviated from the random distribution. The experimental mole fraction of 1,4−(1,2)$_2$−1,4 sequence of cis-1,4 polybutadienes was significantly higher than the theoretical value, providing a short blocky distribution in these polymers. The ozonolysis−GPC method was shown to be a powerful technique for detecting a sequence that is a minor component, such as the diad sequence of 1,2 units in *cis*-1,4 polybutadiene that was not detected by ^{13}C NMR measurement.

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