The Distribution of Olefinic Linkages in Elastomers

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Synopsis

A method for determining the distribution of olefinic bonds in elastomers has been developed using dual detector GPC analysis of the polymer after derivatization with 2,4-dinitrobenzenesulfenyl chloride. The method is particularly useful for determining the distribution of olefinic bonds in hydrocarbon copolymers having small levels of unsaturation.

INTRODUCTION

Several commercially important elastomers are prepared by the copolymerization of one or more monoolefins with a small amount of a diolefin to provide active sites for subsequent sulfur vulcanization. For example, a sulfur-curable butyl rubber may be prepared by the copolymerization of isobutene with a small amount of isoprene.[1] Ethylene–propylene–diene terpolymers have been prepared utilizing a variety of diene termonomers which include ethylidenenorbornene, 1,4-hexadiene, and dicyclopentadiene.[2] One might expect that the distribution of the active sites for vulcanization could affect the curing properties of these elastomers.

Several methods are available for the determination of the amount of unsaturation in these copolymers[3-8] but due to the laborious procedures, there is a paucity of information regarding the distribution of unsaturation in those copolymers. A fractionation procedure followed by a subsequent determination of the unsaturation of each fraction could be utilized,[9] but this would be time consuming. The purpose of this investigation was to provide a rapid and convenient method for the determination of the distribution of unsaturation in such copolymers, particularly those containing only small amounts of unsaturation.

EXPERIMENTAL

A Waters Associates Model 200 gel permeation chromatograph equipped with an automatic sample injector system and a Du Pont Model 410 photometer operating at 254 nm was used for this investigation. The GPC solvent was THF. A set of four columns with permeabilities of 10^6, 10^5, 10^4, and 10^3 Å were used and operated at room temperature with a solvent flow rate of 1 ml/min. The GPC was connected to a minocomputer system

(Lockheed Mac 16 computer with 8K core) for data acquisition at 0.2 count intervals.

The GPC eluent was first directed through the UV detector and then through the refractive index detector. Due to the volume of the tubing between the two detectors, it was necessary to correct the UV response data by shifting the data to a higher elution volume or GPC count. The exact shift of the UV data was determined by injecting a polystyrene standard into the GPC. The areas of the differential index and UV peaks were normalized and plotted using a CALCOMP plotter. The UV data were shifted to progressively higher elution volumes until the two plots were identical. It was found that a shift of 0.43 counts to a higher elution volume was required. Our data acquisition system allows one to introduce this shift factor before the data are stored in the minicomputer by delaying the acquisition of the UV data by a predetermined count interval. All data were sampled at 0.2 count intervals and punched on IBM cards for subsequent calculations.

The polymers were derivatized by dissolving 24 g of the polymer in 240 ml benzene (Matheson, Coleman and Bell, purified) contained in a 28-oz beverage bottle. After addition of the polymer, the bottle was capped with a perforated crown cap having a Viton A liner covered with a Teflon film and placed in a rotation-type polymerization box until the polymer dissolved. The cap was removed from the bottle and the solution dried by venting 40 ml of the solution from the bottle by heating the contents on a sand bath while purging the solution with nitrogen. The bottles were removed from the sand bath, and 2.4 g 2,4-dinitrobenzenesulfenyl chloride (Matheson, Coleman and Bell) dissolved in approximately 50 ml of dry benzene was added to the polymer solution under a nitrogen purge. The bottles were again capped and placed in a 50°C rotation-type polymerization bath for 24 to 72 hr. The polymers were coagulated in methanol (practical grade), washed with methanol, redissolved in toluene (Matheson, Coleman and Bell, reagent), and recoagulated and washed with methanol to remove excess 2,4-dinitrobenzenesulfenyl chloride. The derivatized polymers were dried overnight in a vacuum oven at 50°C.

The isobutylene–isoprene copolymer (Enjay 218) was obtained from Enjay Chemical Company and had a nominal value of 1.75 mole-% unsaturation and an ML/8/212°F of 75. The ethylene–propylene–ethylidenenorbornene terpolymer (Epsyn 55) was obtained from Copolymer Rubber and Chemical Company. The polymer had a relative unsaturation value of 2.9, contained 65 mole-% ethylene, and had a ML/1 + 8/250°F of 58.

Two high-vinyl polybutadienes differing in molecular weight were prepared in a 1-gallon stirred reactor using n-butyllithium as the catalyst (1.04mM and 0.48mM of n-butyllithium/100 butadiene) and N,N;N′,N′-tetramethylethylenediamine as a modifier.[10] The properties of these polymers are summarized in Tables I and II. The polymers were hydrogenated using a previously described[11] homogeneous nickel catalyst com-

TABLE I
Properties of Polybutadiene-1

	Before hydrogenation	After hydrogenation
% 1,2[a]	63.3	0
% 1,4[a]	31.6	14.0
% Saturation[a]	5.1	86.0
ML/4/212°F	72	93

[a] NMR analysis.

TABLE II
Properties of Polybutadiene-2

	Before hydrogenation	After hydrogenation
% 1,2[a]	69.2	44.8
% 1,4[a]	28.8	24.9
% Saturation[a]	2.0	30.3
ML/4/212°C	25	27

[a] NMR analysis.

prised of triethylaluminum (8.1mM/100 g polymer), nickel octanoate (2.7mM/100 g polymer), and cyclohexene (2.7mM/100 g polymer). The properties of these hydrogenated polymers are also shown in Tables I and II.

RESULTS AND DISCUSSION

A gel permeation chromatograph (GPC) equipped with both refractive index and ultraviolet detectors has been previously used to study the styrene distribution in butadiene–styrene copolymers.[12] The ultraviolet detector was used to monitor the amount of styrene in the copolymer, and the refractive index detector was used to determine the total amount of copolymer as a function of elution volume. Since this analysis depends upon one of the comonomers being UV active, the method is not directly applicable for the determination of the distribution of olefinic linkages in aliphatic hydrocarbon copolymers.

Kharasch and Buess[13] found that 2,4-dinitrobenzenesulfenyl chloride was a useful reagent for the characterization of olefins. For example, this reagent adds to cyclohexene to yield 2-chlorocyclohexyl 2′,4′-dinitrophenyl sulfide:
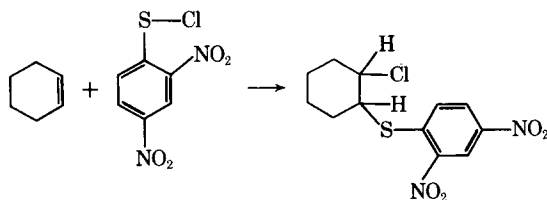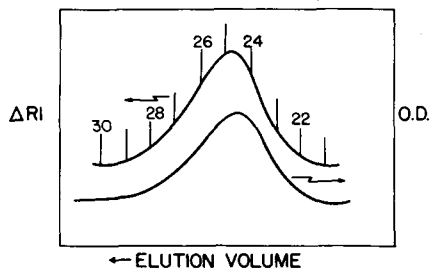
Fig. 1. Gel permeation chromatogram of an isobutylene–isoprene copolymer after derivatization with 2,4-dinitrobenzenesulfenyl chloride obtained using ultraviolet and differential refractive index detectors.

The reaction is rapid and the yields were excellent when glacial acetic acid was used as the solvent. Benzene may also be used as a solvent, but the rate of addition is much slower in this solvent.

We believed that by reacting the olefinic linkages of aliphatic hydrocarbon copolymers with 2,4-dinitrobenzenesulfenyl chloride, the addition product would have sufficient UV absorptivity for detection. This was confirmed and is illustrated in Figure 1, which is a chromatogram of butyl rubber after derivatization with 2,4-dinitrobenzenesulfenyl chloride. Although the reaction is not quantitative, particularly in the inert solvents required to dissolve the polymers, one would expect[14] the reaction to be random and independent of the molecular weight of the individual polymer chains or the location of double bonds in a particular polymer chain. By assuming that the distribution of the derivatized olefinic linkages accurately reflects the distribution of the total number of double bonds in the polymer, it should then be possible to determine the distribution of olefinic bonds in a copolymer using the dual detector GPC analysis.

Our procedure for determining the distribution of olefinic bonds in a copolymer was to first react the polymer with 2,4-dinitrobenzenesulfenyl chloride. After isolating the derivatized polymer, the sample is analyzed using the dual detector GPC technique. The weight fraction of copolymer (F_i^c) eluting at GPC count i is equal to the normalized refractive index peak height at count i:

$$F_i^c = \frac{g_i}{\sum g_i} \tag{1}$$

where g_i is the peak height at count i as measured from the GPC refractive index peak at constant count intervals and $\sum g_i$ is the summation of the peak heights.

If the underivatized copolymer has no UV absorbance at the particular wavelength used for analysis, the mole or weight fraction of the olefinic bonds, F_i^0, eluting at GPC count i is equal to the normalized UV absorbance of the derivatized polymer at count i:

$$F_i^0 = \frac{A_i}{\sum A_i} \tag{2}$$

where A_i is UV absorbance at count i obtained at constant count intervals and $\sum A_i$ is the summation of these values.

The ratio of the weight fraction of olefinic bonds to the weight fraction of copolymer should be constant with a value of unity over the entire GPC chromatogram peak for a polymer with a uniform distribution of double bonds. If the concentration of double bonds per gram of polymer is known from an independent determination, the concentration of double bonds as a function of elution volume could be calculated. However, the relative concentration of double bonds as measured by the ratio of F_i^0 to F_i^c is sufficient to establish the relative distribution as a function of elution volume.

Since our intent was to use this method to establish the distribution of carbon–carbon double bonds in copolymers such as polyisobutylene containing a small amount of isoprene as a comonomer and ethylene–propylene terpolymers, we expected and found eq. (2) to be satisfactory. If the underivatized polymer absorbed at 254 nm, the UV absorbance of the underivatized polymer would have to be subtracted from the UV absorbance of the derivatized polymer at each count interval before one could calculate the weight fraction of double bonds as a function of elution volume. This is expressed by the following equation:

$$F_i^0 = \frac{\Delta A_i}{\sum \Delta A_i} \tag{3}$$

where ΔA_i is the difference in UV absorbance between the derivatized and the underivatized polymer at GPC count i.

In order to determine the applicability of the method, it was decided that the distribution of olefinic linkages of two polymers differing in molecular weight and total unsaturation should be determined. The distribution would also be determined for a blend of the two polymers and compared to the distribution calculated from the distribution of the individual polymers. Two hydrogenated polybutadienes were prepared for this purpose which differed significantly in molecular weight and degree of unsaturation.

The per cent saturation and per cent vinyl unsaturation for the first of these hydrogenated polymers is shown in Table I. For comparison, we have also included in this table the per cent saturation and per cent vinyl unsaturation of the polymer before hydrogenation. The small observed level of saturation for the polymer before hydrogenation is believed to be due to cyclization during polymerization. It has been previously reported[15] and confirmed in this investigation (Table I) that the vinyl unsaturation of polybutadiene is hydrogenated more rapidly than the cis and trans olefinic bonds resulting from 1,4-addition of butadiene to the polymer chain. The GPC chromatogram of the derivatized polymer and the distribution of unsaturation shown as a plot of F_i^0/F_i^c, which is the ratio of the weight fraction of olefinic bonds to the weight fraction of polymer, versus GPC count are shown in Figure 2. We concluded from these data that this polymer has a relatively uniform distribution of unsaturation, but a decrease in
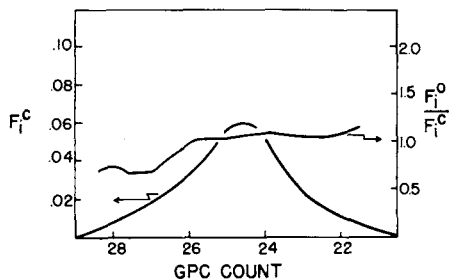
Fig. 2. The distribution of unsaturation in sample 1,
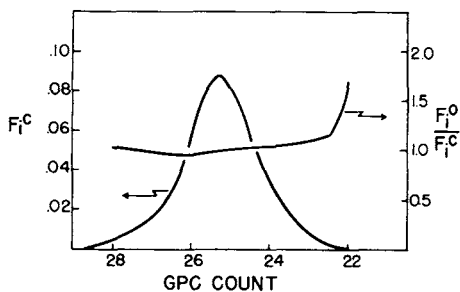a partially hydrogenated polybutadiene.

Fig. 3. The distribution of unsaturation in sample 2,
a partially hydrogenated polybutadiene.

the concentration of double bonds was observed at higher elution volumes. Variations in the distribution are frequently observed at the extremes of the chromatogram due to very small values for the UV absorbance and differential refractive index. Although the total UV area of the GPC peak for this derivatized polymer was the smallest observed for any polymer studied, the observed variation at the higher count values was reproducible.

The properties of the second hydrogenated polybutadiene studied are shown in Table II with the properties of the polymer before hydrogenation. This hydrogenated polymer has a higher vinyl content, greater unsaturation, and a lower molecular weight than the polymer previously discussed. The GPC chromatogram and the distribution of unsaturation are shown in Figure 3. Note that this polymer has a more narrow size distribution than the previous polymer. A very uniform distribution of unsaturation was observed. This was not an unexpected result since the polybutadienes were hydrogenated in solution using a homogeneous catalyst. The deviation in distribution of unsaturation at the low GPC count value is typical of the variations introduced at the molecular weight extremes due to experimental error.

A 50/50 weight-% blend of these two hydrogenated polybutadienes was prepared by dissolution in benzene followed by derivatization with the 2,4-dinitrobenzene sulfenyl chloride. The GPC chromatogram for the derivatized blend and the plot of F_i^0/F_i^c as a function of GPC count are shown in
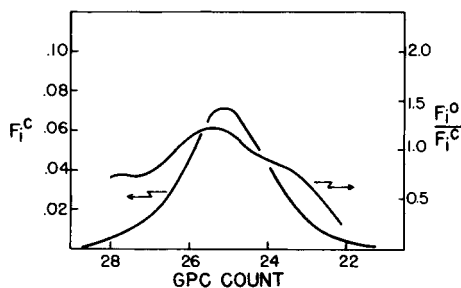
Fig. 4. Determined distribution of unsaturation in a 50/50 blend of samples 1 and 2, partially hydrogenated polybutadienes.
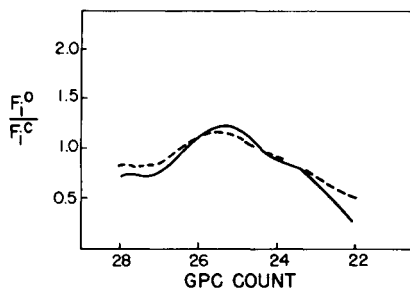
Fig. 5. Comparison of the calculated and determined distribution of unsaturation in a 50/50 blend of the partially hydrogenated polybutadienes (samples 1 and 2): (———) determined values; (- - - - - -) calculated values.

Figure 4. The observed distribution was not uniform since the low molecular weight polymer has nearly five times the unsaturation of the higher molecular weight polymer.

The distribution of unsaturation in the blend as calculated from the data for the individual polymers was not exactly that determined for the blend. The calculated distribution was obtained by multiplying the UV and normalized RI peak heights at each count interval by the weight fraction (0.5) of that polymer component in the blend and summing the products for the two components at each count interval. From these data, the distribution was calculated according to the usual procedure. Figure 5 is a plot of the calculated and determined values for the ratio F_i^0/F_i^c as a function of GPC count.

Perhaps it is unrealistic to expect a better agreement between the distribution of unsaturation calculated from chromatograms of the individual polymers which had been derivatized and the determined distribution obtained from chromatograms of the blend after derivatization. The polymers used to prepare the blend differed significantly in vinyl content. If the vinyl unsaturation reacts more rapidly than the cis and trans 1,4-units with the 2,4-dinitrobenzenesulfenyl chloride, one would expect a large difference between the observed and calculated distributions. In addition, Ouano[16] has found that nonlinear fractionation effects result in significant
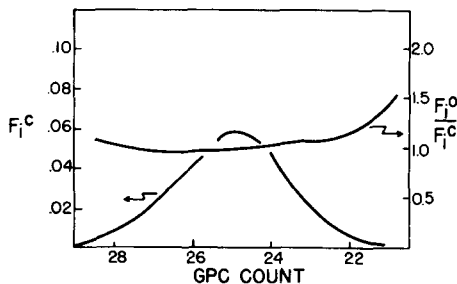
Fig. 6. Distribution of unsaturation in an isobutylene–isoprene copolymer.

differences in the GPC chromatograms of a mixture of standard polystyrenes and the computed envelopes of the individual chromatograms of the components of the mixture. The disagreement in determined and calculated chromatograms became more pronounced as the sample loading was increased and the molecular weight distribution of the sample was narrowed. The effect was also shown to be molecular weight dependent.

In view of the difficulties involved, the results for the calculated and observed distribution in the blend of partially hydrogenated polybutadienes were not too poor. We believe that these data provide sufficient evidence to conclude that the method provides valid information about the distribution of unsaturation in copolymers. It is expected a priori that if large differences exist in the reactivity of different olefinic linkages with 2,4-dinitrobenzenesulfenyl chloride, the method may not reflect the actual distribution. However, if all the double bonds which differ in reactivity have the same distribution as a function of GPC elution volume, the method would still be expected to be valid.

Further studies of copolymers of other types provide additional evidence for the validity of this technique. A sample of a commercial polyisobutylene containing a small amount of isoprene as a comonomer was analyzed, and the olefinic bonds were found to be quite uniformly distributed, as shown in Figure 6. The unsaturation incorporated by the addition of isoprene to the polymer chain has been shown to be almost solely of the 1,4-configuration. Butyl rubber has been previously shown to have a uniform distribution of unsaturation, providing additional evidence for the validity of the method.[9] Similarly, we have analyzed an ethylene–propylene–ethylidenenorbornene terpolymer. This copolymer also was shown to have a relatively uniform distribution of double bonds, as illustrated in Figure 7. It is not surprising the ethylene–propylene–ethylidenenorbornene copolymer has a uniform distribution of unsaturation since this sample was a commercial product prepared using a process likely optimized to give a uniform distribution of the unsaturation.

This method of determining the distribution of unsaturation should be useful for the optimization of processes for the preparation of similar polymers. It should now be possible to more easily investigate the effect of the distribution of olefinic linkages on the curing properties of elastomers
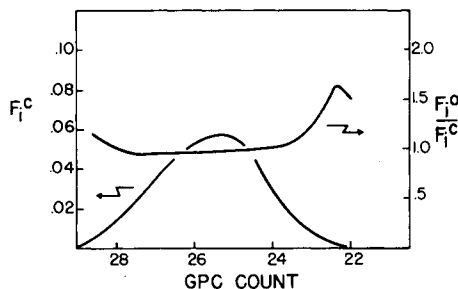
Fig. 7. Distribution of unsaturation in an ethylene–propylene–ethylidenenorbornene terpolymer.

and the physical properties of their vulcanizates. This investigation also illustrates the usefulness of derivatization to alter a functional group of a polymer to one which can be readily and selectively detected. A UV photometer or another type of detector makes possible dual-detector GPC analysis. This method should have broad applications and be limited only by the selectivity of the reagent used for derivatization of a particular functional group, and the sensitivity of the second detector used in conjunction with the usual differential refractive index detector to the derivatized functional group. If the derivatization reaction is quantitative, the concentration of a particular functional group as a function of elution volume could be determined after appropriate calibration of the detector. Quantitative yields were not expected for the addition of 2,4-dinitrobenzenesulfenyl chloride to the olefinic bonds of the elastomers studied since the rate of addition is quite slow when benzene is used as a solvent.[13]

SUMMARY

A technique for determining the distribution of unsaturation in copolymers containing a small amount of olefinic bonds as a function of GPC elution volume was developed. The method utilizes a GPC equipped with UV photometer and differential refractometer detectors. The polymers are derivatized with 2,4-dinitrobenzenesulfenyl chloride, which adds to the olefinic bonds of the polymer, with the derivative having sufficient UV absorptivity for detection. Dual-detector GPC analysis enables one to calculate the ratio, F_i^0/F_i^c, which is the ratio of the weight fraction of olefinic bonds to the weight fraction of polymer.

The validity and applicability of the technique was demonstrated using a blend of hydrogenated polybutadienes differing in degree of hydrogenation and the hydrogenated polymers used to prepare the blend, and ethylene–propylene–ethylidenenorbornene terpolymer and an isobutylene–isoprene copolymer. The commercial isobutylene–isoprene copolymer and ethylene–propylene–ethylidenenorbornene terpolymer were shown to have uniform distributions of double bonds. Two partially hydrogenated polybutadienes also had relatively uniform distributions of unsaturation, but a

decrease in the relative concentration of double bonds at higher elution volumes (lower molecular weight) was observed for the polymer with the lowest total concentration of double bonds. It was suggested that this concept should be applicable for the determination of the distribution of other functional groups with the choice of suitable reagents for derivatization.

References

1. P. Meares, *Polymer: Structure and Bulk Properties*, Van Nostrand Reinhold Company, London, 1965, p. 165.

2. F. B. Baldwin and G. Ver Strate, *Rubber Chem. Technol.*, **45,** 709 (1972).

3. T. S. Lee, I. M. Kolthoff, and E. Johnson, *Anal. Chem.*, **22,** 995 (1950).

4. S. G. Gallo, H. K. Weise, and J. F. Nelson, *Ind. Eng. Chem.*, **40,** 1277 (1948).

5. I. J. Levine and R. G. Haines, *Rubber Chem. Technol.*, **43,** 445 (1970).

6. R. Hank, *Rubber Chem. Technol.*, **40,** 936 (1967).

7. P. R. Sewell and D. W. Skidmore, *J. Polym. Sci. A-1*, **6,** 2425 (1968).

8. A. G. Altenau, L. M. Headly, C. O. Jones, and H. C. Ransaw, *Anal. Chem.*, **42,** 1280 (1970).

9. J. Rehner, *Ind. Eng. Chem.*, **36,** 46 (1944).

10. T. A. Antkowiak, A. E. Oberster, and A. F. Halasa, *J. Polym. Sci. A-1*, **10,** 1319 (1972).

11. T. Yoshimoto, S. Kaneko, T. Narumiya, and H. Yoshii (to Bridgestone Tire Company, U.S. Pat. 3,531,450 (1970).

12. H. E. Adams, in *Gel Permeation Chromatography*, K. H. Altgelt and L. Segal, Eds., Marcel Dekker, New York, 1971, pp. 391–405 (1970).

13. N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, **71,** 2724 (1948).

14. P. J. Florry, *Ind. Eng. Chem.*, **38,** 417 (1946).

15. J. C. Falk, *Makromol. Chem.*, **160,** 291 (1972).

16. A. C. Ouano, *J. Polym. Sci.*, **A-1,** 2179 (1971).

17. H. Y. Chen and J. E. Field, *Rubber Chem. Technol.*, **42,** 392 (1969).