# Analysis of Polybutadienes and Butadiene-Styrene Copolymers by Infrared Spectroscopy

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**An accurate method for determining the microstructures of polybutadienes and butadiene-styrene copolymers was desired to study the effects of polymerization variables. The amounts of *cis*-1,4, *trans*-1,4, and 1,2 additions in polybutadienes, as well as styrene in butadiene-styrene copolymers, can be determined directly by measuring the intensities of bands at 14.70, 10.34, 10.98, and 14.29 microns, respectively. The total unsaturation of emulsion polymers may also be determined. Alkali metal–catalyzed polymers differ from emulsion polymers in other respects than the various types of double bonds. It is possible to obtain quantitative information about the effect of polymerization variables on the micro structures of polybutadienes and butadiene-styrene copolymers. This method may be extended to other diene copolymers.**

INCE the advent of the emulsion polymerization of synthetic rubber, particularly polybutadiene or butadiene-styrene olymer, attempts have been made in many directions to make imilar to natural rubber in physical properties. Heretofore vea has been generally recognized to be an all cis polymer of rene. Consequently it has been thought that an all *cis*-butadiene might have many of the properties of Hevea. ny attempts have been made to make such a polymer. How- r, butadiene can polymerize by both 1,4 and 1,2 additions, ling to *trans*-$RCH{=}CHR_1$, *cis*-$RCH{=}CHR_2$, and $RCH{=}CH_2$ yl) structures, where the R's are polymer chains. No chem- method was available to distinguish between these structures, hat the effects of changes in the polymerization processes e judged mostly by physical tests made on the polymer.

ith the development of infrared spectroscopy, correlations veen the *trans*-$RCH{=}CHR_1$ and $RCH{=}CH_2$ structures and ds at 10.34 and 10.98 microns were established. The band to the *cis*-$RCH{=}CHR_1$ structure is much more variable in tral position. Attempts (*2*, *5*) were made to determine the unt of *trans*-1,4 and 1,2 additions in polybutadienes by meas- g the intensities of the 10.34- and 10.98-micron bands. npton (*7*) improved the methods used by obtaining absorp- ties from polymers and by determining the amount of *cis*-1,4 ition directly. He also determined the amount of styrene utadiene-styrene copolymers.

n applying Hampton's method to the analyses of polybuta- ies and butadiene-styrene copolymers in these laboratories y variable results were obtained. The amount of polymer in lution, determined by the analysis, was very often greater n the amount known to be present by determining the total ds. The criterion of a satisfactory analysis was taken to be t the "total found" should be the known or expected unsatura- n of the polymer and certainly not more than 100%. It was found that alkali metal–catalyzed polybutadienes have dif- nt infrared spectra than the usual emulsion polymer.

hen it was observed that the spectra of many polymers had band at 13.8 microns, while the *trans*-1,4 and 1,2 determina- s showed that some *cis*-1,4 addition must be present, attempts e found to find a more suitable band for determining the 1,4 addition. One was found at 14.7 microns, after the 6.1- ron band had been tried and discarded, which has led to de- minations of the amounts of *cis*-1,4, *trans*-1,4, and 1,2 additions in more than 200 polybutadienes and butadiene-styrene copolymers with generally acceptable results when judged by the total found criterion. In addition, the determination of the amounts of styrene in copolymers has been refined so that the results generally agree with refractive index measurements over a wide range of styrene concentrations.

## EXPERIMENTAL

The concentrations of the components of a mixture can be determined spectroscopically by solving equations of the type

$$D' = (e'_1c_1 + e'_2c_2 + e'_3c_3 + e'_4c_4 + \ldots)l \qquad (1)$$

where $D$ is the measured absorbance, $e$ the absorptivity, $c$ the concentration, and $l$ the length of light path in centimeters. The subscripts refer to the components and the superscripts to the wave length. If the concentrations are in moles per liter the $e$'s will be molar absorptivities. The absorptivities are derived from calibration curves obtained by measuring the absorbances of solutions of known concentration of each of the pure components. Thus, for a four-component mixture it is necessary to make absorbance measurements at four suitable wave lengths and obtain 16 absorptivities; four at each of the four wave lengths. These wave lengths are chosen so that at each wave length, one of the $e$'s will be much larger than the other three if possible.

It is assumed that a polybutadiene is a mixture of three types of structures—namely, *cis*-$RCH{=}CHR_1$, *trans*-$R_3CH{=}CHR_2$, and $CH_2{=}CHR_4$—where the R's are polymer chains. Nothing is said about whether all three of these structures occur in one polymer chain or molecule or whether the polymer is composed of chains each containing only one of these types of structures. The bands used for the analyses are at 10.34 microns for *trans*-1,4 addition, 10.98 microns for 1,2 addition (side vinyl), 14.70 microns for *cis*-1,4 addition, and 14.29 microns for styrene.

The absorptivities in Equation 1 are found for polymers by the method described by Hampton (*7*) starting with absorptivities obtained in the usual manner from *cis*-4-octene at 14.05 microns for the *cis*-1,4 component, from *trans*-4-octene at 10.34 microns for the *trans*-1,4 component, and from 1-octene at 10.98 microns for the 1,2(side vinyl) component. Figure 1 shows typical calibration curves. All measurements reported here were made with a Beckman IR2 spectrophotometer, and the narrowest slit widths consistent with good photometric reproducibility were used. Corrections were made for the mismatch of the sample and standard cells and for the scattered light which amounted to 1.5% at 15 microns. Since the absorption due to the $-CH=CH-$ structure in *cis*-4-octene at 14.05 microns is much less than that of the *trans* absorption at 10.34 microns in *trans*-4-octene or the vinyl absorption at 10.98 microns in octene-1, a 1.0-mm. cell was used for the *cis* measurements and a 0.1-mm. cell for the *trans* and 1,2 measurements.

Polymers are prepared for analysis by dissolving in carbon disulfide (4 grams per 100 ml.), filtering through filter paper to remove gel, and precipitating with methanol. The methanol may be removed either by drying under high vacuum or by swelling in carbon disulfide and drying under vacuum. About 2 grams of the purified polymer are dissolved in 50 ml. of carbon disulfide and 0.02 part per hundred of rubber of phenyl-2-naphthylamine (PBNA) added as antioxidation inhibitor.

In using Hampton's method for determining the polymer absorptivities it is necessary to have polymers containing only either a large amount of *trans*-1,4 component, or *cis*-1,4 component, or 1,2 component and which differ in only this respect—i.e., the infrared spectra should be similar. Low temperature (<0° C.) emulsion polybutadienes generally contain a large amount of *trans*-1,4 addition as may be seen by the intensity of the 10.34-micron band. High temperature (~100° C.) emulsion polybutadienes contain more *cis*-1,4 addition than low temperature polymers, but unfortunately polybutadienes containing larger amounts of *cis*-1,4 addition than *trans*-1,4 or 1,2 additions cannot be prepared in the usual emulsion system and this introduces some uncertainty in the *cis*-1,4 absorptivities which can only be reduced by averaging many results. Polybutadienes containing large amounts of 1,2 addition can be made using sodium catalysts, but the spectra of these polymers always contain additional bands in the long-wave (13 to 15 microns) region which are not found in the usual emulsion polymer.

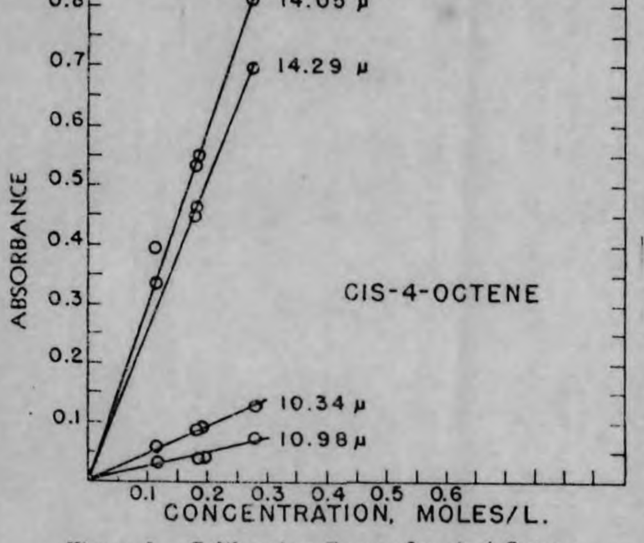

Figure 1. Calibration Curves for *cis*-4-Octene

If measurements, made with the same slit widths and cell lengths as for the pure hydrocarbons at 10.34, 10.98, and 14.70 microns, of such polymers are used to determine the polymer absorptivities by Hampton's method it will be found that the absorptivities never become constant and that the 1,2 (side vinyl) absorptivity continually increases. The absorptivities can be found using sodium and emulsion polybutadienes in the following manner. Sodium polybutadienes are chosen, the infrared spectra of which contain only one additional band near 13.8 to 13.9 microns. The *cis*-1,4 measurements at 14.70 microns for these polymers are corrected for the additional absorption due to the 13.9-micron band by subtracting from the absorbance at 14.70 microns the absorbance at the trough in the spectrum between 13.9 and 14.7 microns multiplied by the factor 0.83. How the factor is obtained is described under the analysis of alkali metal-catalyzed polymers. It may be different for different instruments. With such corrections to the *cis*-1,4 absorbances of sodium polybutadienes the absorptivities will become constant upon iteration. The polymer absorptivities derived from several of each type of polybutadiene in the manner described above are given in Table I in which Equations 2 are the corresponding absorbance equations, similar to Equation 1, and Equations 2a are the inversion of them to make machine calculations easier. Here again these absorptivities will vary somewhat with different instruments.

In deriving the absorptivities in this manner a distinction, based on the spectra of the polybutadienes, is made between ordinary emulsion polybutadienes and sodium catalyzed pol butadienes. This distinction applies to all alkali metal-catalyze polybutadienes so far studied and makes it necessary to consid the analyses of these various types separately.

**Emulsion Polybutadienes.** The infrared spectra of emulsio polybutadienes are ordinarily comparatively simple, and if an additional bands are observed in the 14- to 15-micron regio the spectrum, they are generally quite weak. The amounts *cis*-1,4, *trans*-1,4, and 1,2 additions in such polymers can determined by making absorbance measurements at 14.7 10.34, and 10.98 microns, under the same conditions as used f finding the absorptivities, and using the coefficients of Table Table II gives the results of the analyses of a number of pol butadienes. These are typical of several hundred such analyse In this table the total found value is the amount of polym in solution found by the analysis, assuming one double bond p $C_4H_6$ unit, divided by the amount of polymer in the soluti found by determining the total solids. For the most part the values correspond to the expected unsaturations of such polyme (*10*), and the results should be reliable to one unit. If th total found value is over 100% the results for the compositio are open to question and if it approaches 120% they are probab worthless.

**Analysis of Alkali Metal–Catalyzed Polybutadienes.** As ind cated above, alkali metal polybutadienes differ from the usu emulsion polybutadiene in that additional bands are gener found in the 13.6- to 15.0-micron region of their spectra. The bands may be considered as being due to additional structure Since, in the analysis of emulsion polybutadienes, only th structures are considered the method used for the analysis m be modified for alkali metal polybutadienes.

The modifications used here are of two kinds, depending up the polymer spectrum. In analyzing alkali metal-polybuta enes, measurements are made at 10.34, 10.98, and 14.70 micro (or at the peaks of these bands) in the usual manner and the r sults calculated using Equations 2 (Table I). If the total foun is over 100% the spectrum in the 13.5- to 15.0-micron region examined. When only one additional strong band is found this region at about 13.9 microns the factor method is used several additional bands are found, particularly a shoulder the 14.7-micron band at about 14.3 microns, the band envelo method is used. The validity of either of these methods is th

Table I. Polybutadiene Molar Absorptivities

| Component | 10.34 μ | 10.98 μ | 14.70 μ |
|---|---|---|---|
| *cis*-1,4 | 9.5 | 4.4 | 23 |
| *trans*-1,4 | 109 | 3.0 | 2.4 |
| Terminal vinyl (1, 2) | 7.4 | 145 | 1.2 |

$$
\begin{aligned}
d_{14.70} &= (23c_1 + 2.4c_2 + 1.2c_3)\,0.1 \\
d_{10.34} &= (9.5c_1 + 109c_2 + 7.4c_3)\,0.01 \\
d_{10.98} &= (4.4c_1 + 3c_2 + 145c_3)\,0.01
\end{aligned}
\tag{2}
$$

$$
\begin{aligned}
c_1 &= 0.04393D_1 - 9.58 \times 10^{-4}D_2 - 3.15 \times 10^{-4}D_3 \\
c_2 &= -3.744 \times 10^{-3}D_1 + 9.269 \times 10^{-3}D_2 - 4.43 \times 10^{-4}D_3 \\
c_3 &= -1.256 \times 10^{-3}D_1 - 1.63 \times 10^{-4}D_2 + 6.915 \times 10^{-3}D_3 \\
D_1 &= d_{14.70}/0.1,\ D_2 = d_{10.34}/0.01,\ D_3 = d_{10.98}/0.01
\end{aligned}
\tag{2a}
$$

Table II. Analyses of Emulsion Polybutadienes

| Polymer No. | Temp., ° C. | Feature | *cis*-1,4 | *trans*-1,4 | 1,2 | Tot Fou |
|---|---|---|---|---|---|---|
| 1164 | 170 | 27% conv. 5 min. | 0.207 | 0.576 | 0.217 | 1.0 |
| 988 | 70 | Armeen 120 | 0.203 | 0.597 | 0.201 | 0.9 |
| 2FR89-1 | 70 | Nitrazole | 0.205 | 0.597 | 0.198 | 0.9 |
| 796 | 50 | Nitrazole | 0.192 | 0.628 | 0.189 | 0.9 |
| 1049 | 50 | Carbon black latex | 0.188 | 0.625 | 0.188 | 0.9 |
| 1112 | 5 | 8.8% K-oleate | 0.147 | 0.686 | 0.167 | 0.9 |
| 1088 | 5 | 16% K-oleate | 0.114 | 0.715 | 0.171 | 0.9 |
| 1074 | −33 | 0.15 Sulfole B8 | 0.059 | 0.794 | 0.147 | 1.0 |
| 401-71 | −35 |  | 0.042 | 0.773 | 0.185 | 0.9 |
| 1D[a] | 50 |  | 0.192 | 0.647 | 0.161 | 0 |
| 3D[a] | 50 |  | 0.196 | 0.634 | 0.170 | 0 |
| 3D1[a] | 50 |  | 0.190 | 0.637 | 0.174 | 0 |

[a] 1D and 3D are same preparations in different bottles. 3D and 3D are two samples from same polymer.

**Table III. Compositions of Alkali Metal–Catalyzed Polybutadienes**

| Polymer No. | Temp., ° C. | Catalyst | *cis*-1,4, % Un-corr. | *cis*-1,4, % Corr. 1[a] | *cis*-1,4, % Corr. 2[b] | *trans*-1,4, % Un-corr. | *trans*-1,4, % Corr. 1[a] | *trans*-1,4, % Corr. 2[b] | 1,2, % Un-corr. | 1,2, % Corr. 1[a] | 1,2, % Corr. 2[b] | Total Found, % Un-corr. | Total Found, % Corr. 1[a] | Total Found, % Corr. 2[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 81PD1 | 60 | Na | 31.8 | 11.6 | 9.2 | 14.3 | 20.3 | 21.0 | 53.9 | 68.1 | 69.8 | 119 | 94.9 | 92.7 |
| 81PC5 | 50 | Na | 32.9 | 5.6 | 7.4 | 12.7 | 20.3 | 19.4 | 54.3 | 74.0 | 72.9 | 134 | 99.7 | 101 |
| 81PA9 | 30 | Na | 33.0 | 11.2 | 8.8 | 12.7 | 18.8 | 19.5 | 54.3 | 70.0 | 71.9 | 122 | 95.8 | 93.5 |
| 739-28 | 45 | Na-K (50:50) | 36.0 | ... | 9.6 | 29.1 | ... | 42.4 | 34.9 | ... | 48.0 | 135 | ... | 100.3 |
| 739-26 | 45 | K | 27.8 | 14.0 | 4.8 | 33.7 | 40.7 | 45.4 | 38.5 | 45.3 | 49.9 | 111 | 95.8 | 87.5 |
| 739-23 | 45 | Na | 31.0 | 13.1 | 6.3 | 20.2 | 26.7 | 29.1 | 48.7 | 60.2 | 64.4 | 117 | 95.6 | 99.8 |
| 739-11 | 30 | Na | 33.1 | 8.3 | 9.6 | 16.5 | 24.7 | 20.6 | 50.4 | 67.0 | 66.2 | 120 | 91.7 | 92.9 |
| 78PC17A10 | 77 | Na-K (90:10) | 34.5 | ... | ... | 19.9 | ... | ... | 45.6 | ... | ... | 100.0 | ... | ... |
| 78PC17A42 | 93 | Na-K (90:10) | 34.4 | ... | ... | 19.1 | ... | ... | 46.7 | ... | ... | 100.1 | ... | ... |
| 78PC18A43 | 88 | Na-K (90:10) | 34.6 | ... | ... | 18.8 | ... | ... | 46.6 | ... | ... | 103.3 | ... | ... |
| 78PC28 | .. | Na | 29.0 | ... | 8.2 | 22.8 | ... | 20.9 | 48.2 | ... | 60.9 | 115 | ... | 92.1 |

[a] Correction 1. $D_{cis}$ *vs.* $D_{14.3}$ curve.
[b] Correction 2. $D_1 = (d_{14.7} - 0.83d_{14.3})/0.1$.

the total found should be about 92% for sodium polybutadienes (*10*).

The factor method consists of subtracting from the measured absorbance at 14.70 microns the absorbance at the trough in the absorbance spectrum between the 13.9- and 14.7-micron bands multiplied by 0.83. The factor 0.83 will vary with the instrument used and is found as follows: A number of sodium polybutadienes are analyzed in the same manner as emulsion polybutadienes. The total found values will generally exceed 92%, and the amounts by which the *cis*-1,4 absorbances at 14.70 microns must be reduced to make the "total found" values about 92% can be calculated. These amounts are plotted against the absorbance at the trough in the spectrum between 13.6 and 15.0 microns. A straight line can be drawn through the points. Either this curve can be used for correcting the *cis*-1,4 absorbance at 14.70 microns in subsequent analyses or the slope of it can be used as a multiplying factor. In these experiments this slope was 0.83.

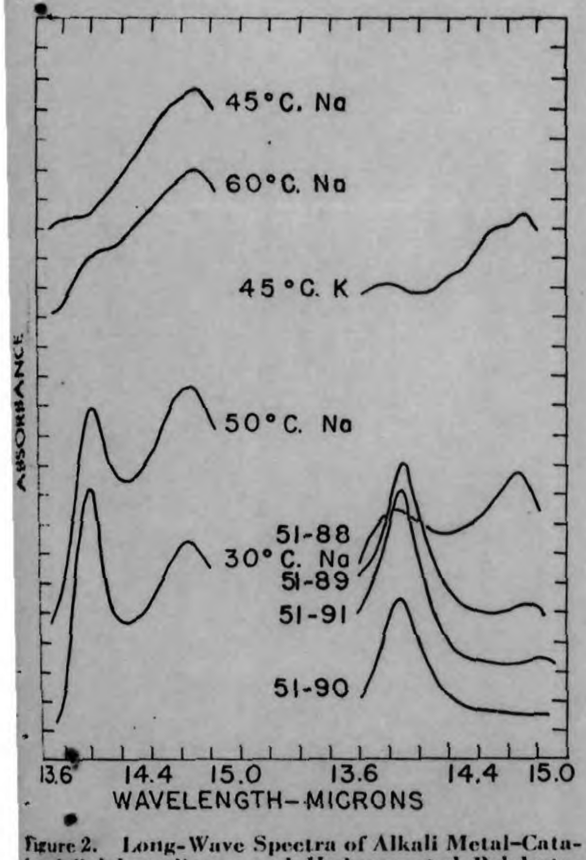

Figure 2. Long-Wave Spectra of Alkali Metal–Catalyzed Polybutadienes and Hydrogenated Polybutadienes

If the long-wave spectrum of the alkali metal–catalyzed polymer is more complicated, as is generally the case with potassium polymers and some sodium polymers, the factor method cannot be used since the additional bands probably represent other structures. In these cases successful analyses can sometimes be made by drawing in band envelopes of the absorbance or absorptivity curve of the spectrum. The overlap of the additional bands on the 14.70-micron band is subtracted from the absorbance at 14.70 microns and the remainder used for the *cis*-1,4 absorbance in Equations 2. The band envelopes may be obtained as described by Wulf and Deming (*12*). Reasonable total found values (about 92%) cannot always be obtained by this method, and in these cases it seems likely that there are other bands in the spectra which make accurate analyses impossible.

**Table IV. Composition of Hydrogenated and Alfin Polybutadienes**

| Polymer No. | *cis*-1,4, % | *trans*-1,4, % | 1,2, % | Total Found, % | Reported Unsatd., %[a] |
|---|---|---|---|---|---|
| SX51-88 | 12.9 | 70.6 | 16.6 | 97.4 | 97.7 |
| SX51-89 | 4.8 | 79.4 | 15.8 | 60.9 | 60.8 |
| SX51-90 | 0 | 85.4 | 14.6 | 32.2 | 33.5 |
| SX51-91 | 0 | 80.5 | 19.5 | 15.9 | 14.7 |
| 3-130S Alfin | 9.8 | 68.9 | 21.4 | 96.0 | |
| MX1612 Alfin | 11.7 | 63.2 | 25.1 | 104.1 | |
| MS1614 Alfin | 11.3 | 64.2 | 24.4 | 101.7 | |
| MIT Alfin | 11.0 | 70.6 | 18.4 | 96.0 | |

[a] By Phillips Petroleum Co

**Table V. Butadiene-Styrene Copolymer Absorptivities**

| Component | 10.34μ | 10.98μ | 14.29μ | 14.70μ |
|---|---|---|---|---|
| *cis*-1,4 | 9.5 | 4.4 | 25 | 23 |
| *trans*-1,4 | 109 | 3.0 | 2.3 | 2.4 |
| 1,2 | 7.4 | 145 | 1.4 | 1.2 |
| Styrene | 3.1 | 7.2 | 154 | 1.1 |

The analyses of a number of sodium, sodium-potassium, and potassium catalyzed polybutadienes are given in Table III. The effect of the corrections on the analyses is also shown. No corrections were employed in the analyses of the three 90 to 10 sodium-potassium polybutadienes because the spectra contained only weak additional bands.

**Analysis of Hydrogenated and Alfin Polybutadienes.** Figure 2 shows the long-wave spectra of a polybutadiene which has been hydrogenated to various degrees of unsaturation. As the polymer is hydrogenated the intensity of the band at 14.0 microns increases while that of the 14.70-micron band decreases and finally disappears. At the lowest unsaturation a new weak band appears at about 14.8 micron. As might be expected, these polymers can be analyzed by the factor method as used for sodium polybutadienes. The results of the analyses of several hydrogenated polybutadienes are given in Table IV, using the correction 2 of Table III.

**Table VI. Compositions of Butadiene-Styrene Polymer Solutions**

| Solution | *cis*-1,4, Grams/Liter |  |  | *trans*-1,4, Grams/Liter |  |  | 1,2, Grams/Liter |  |  | Styrene, Grams/Liter |  |  |  | Styrene, Grams/Liter |  |  | Total Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  | Found |  |  |  |  |  |  |  |
|  | Uncorr.[a] | Corr. 1[b] | Corr. 2[c] | Uncorr.[a] | Corr. 1[b] | Corr. 2[c] | Uncorr.[a] | Corr. 1[b] | Corr. 2[c] | Uncorr.[a] | Corr. 1[b] | Corr. 2[c] | Added | Uncorr.[a] | Corr. 1[b] | Corr. 2[c] | Corr. 2[c] |
| X-599 | 2.422 | 2.324 | 2.470 | 13.032 | 13.111 | 13.112 | 2.491 | 2.565 | 2.594 | 6.4241 | 6.445 | 5.257 | 0.000 | ... | ... | ... | 0.9449 |
| X-599-1 | 2.459 | 2.184 | 2.449 | 13.100 | 13.215 | 13.215 | 2.259 | 2.452 | 2.506 | 15.6718 | 15.687 | 13.521 | 8.265 | +0.983 | +0.977 | −0.001 | 0.9622 |
| X-599-2 | 2.506 | 2.140 | 2.440 | 13.064 | 13.202 | 13.202 | 2.284 | 2.537 | 2.598 | 20.5566 | 20.575 | 18.129 | 12.584 | +1.549 | +1.546 | +0.288 | 0.9763 |
| X-599-3 | ... | 2.365 | 2.664 | ... | 12.988 | 12.988 | ... | 2.455 | 2.500 | 24.656 | 24.656 | 22.210 | 17.154 | ... | +1.057 | −0.201 | 0.9651 |
| C-361 | 3.615 | 3.590 | 3.720 | 9.347 | 9.414 | 9.414 | 2.398 | 2.456 | 2.493 | 5.0638 | 5.098 | 3.630 | 0.000 | ... | ... | ... | 0.9491 |
| C-361-4 | 3.858 | 3.403 | 3.711 | 9.309 | 9.454 | 9.454 | 1.766 | 2.079 | 2.142 | 24.8799 | 24.911 | 22.395 | 18.527 | +1.289 | +1.286 | +0.138 | 0.9624 |
| C-361-5 | 4.242 | 3.699 | 3.973 | 9.096 | 9.262 | 9.262 | 1.825 | 2.200 | 2.256 | 29.6150 | 29.648 | 27.412 | 23.920 | +0.631 | +0.630 | −0.138 | 0.9626 |
| C-361-6 | 4.440 | 3.745 | 3.771 | 7.350 | 8.919 | 8.919 | 1.615 | 2.091 | 2.096 | 37.5378 | 37.571 | 36.660 | 32.559 | −0.085 | −0.086 | +0.683 | 0.9801 |

[a] Uncorr. No correction.
[b] Corr. 1. Corrected absorptivities.
[c] Corr. 2. Corrected absorptivities and Beer's law correction.

It is difficult to obtain solutions which are sufficiently concentrated (35 grams per liter) with most Alfin-catalyzed polybutadienes. However, solutions containing about 20 grams per liter of polymer which can be filtered through filter paper may be prepared by stirring with a Waring Blendor. The final solution can be made as concentrated as may be handled without blocking the absorption cells. The analysis is performed in the same manner as for emulsion polybutadienes. The analyses of some Alfin polybutadienes are also given in Table IV.

**Analyses of Butadiene-Styrene Copolymers.** It is assumed that a butadiene-styrene copolymer may be treated as a mixture of polybutadiene and polystyrene. The band at 14.29 microns in the spectra of butadiene-styrene copolymers is used to determine the styrene content and the necessary additional absorptivities are found by using carbon disulfide solutions of pure polystyrene in the same manner as for the pure hydrocarbons. Figure 3 shows the calibration curve obtained; Table V gives the absorptivities derived from them.

**Table VII. Butadiene-Styrene Copolymer Absorptivities**

| Component | 10.34μ | 10.98μ | 14.29μ | 14.70μ |
|---|---|---|---|---|
| *cis*-1,4 | 9.5 | 4.4 | 20.0 | 23.0 |
| *trans*-1,4 | 109 | 3.0 | 2.3 | 2.4 |
| 1,2 | 7.4 | 145 | 1.4 | 1.2 |
| Styrene | 2.6 | 8.0 | 154 | 5.5 |

$$\begin{aligned}
C_1 &= 0.04531D_1 - 9.56 \times 10^{-4}D_2 - 3.11 \times 10^{-4}D_3 - 1.586 \times 10^{-3}D_4\\
C_2 &= -3.744 \times 10^{-3}D_1 + 9.269 \times 10^{-3}D_2 - 4.56 \times 10^{-4}D_3 - 0\\
C_3 &= -9.77 \times 10^{-4}D_1 - 1.62 \times 10^{-4}D_2 + 6.916 \times 10^{-3}D_3 - 3.22 \times 10^{-4}D_4\\
C_4 &= -5.820 \times 10^{-3}D_1 - 1.28 \times 10^{-5}D_2 - 1.59 \times 10^{-5}D_3 + 6.720 \times 10^{-3}D_4
\end{aligned} \tag{3}$$

$C_1$, $C_2$, $C_3$, $C_4$ are the concentrations in moles per liter of the *cis*-1,4, *trans*-1,4, 1,2, and styrene components respectively. $D_1 = d_{14.70}/0.1$, $D_2 = d_{10.34}/0.01$, $D_3 = d_{10.98}/0.01$, $D_4 = d_{14.29}/0.01$. The $d$'s are absorbances of solutions at indicated wave lengths.

Analyses of several butadiene-styrene copolymers using these absorptivities always resulted in total found values of more than 100% and values for the styrene concentrations which apparently were sometimes too large or too small, judging by the loading and refractive index values for the styrene. To determine the source of error, known amounts of polystyrene in carbon disulfide solutions were added to solutions of four different polymers and the mixtures analyzed using the above absorptivities. Table VI gives the results for some solutions of two of the polymers used. The difference in the styrene found by analysis and the amount added varies and the amount of *cis*-1,4 addition increases with increasing styrene. By trial and error the amount by which the styrene absorptivity at 14.70 microns must be changed so that the amount of *cis*-1,4 addition did not increase with increasing styrene was found. The corrected absorptivities thus obtained are given in Table VII and the effect of these changes in Table VI under correction 1. The results for the other two polymers used were similar to those of polymer X-599.

With these corrected absorptivities the amounts of *cis*-1,4, *trans*-1,4, and 1,2 additions found decreased, in general, as they should with increasing styrene concentration, but the agreement between the styrene added and the styrene found was not improved as Table VI shows (correction 1). The error was found to arise from the fact that the styrene calibration curve is not actually linear as Figure 3 shows. In the analyses it is assumed that it is. This situation is similar to that described by Brattain, Rasmussen, and Cravath (*4*) for $C_4$ analyses and was treated in

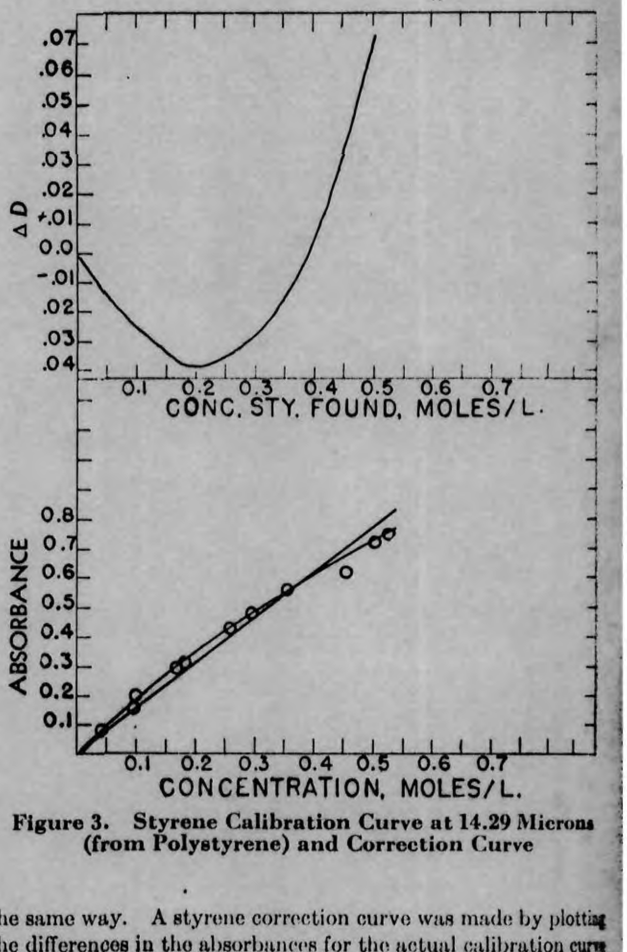

**Figure 3. Styrene Calibration Curve at 14.29 Microns (from Polystyrene) and Correction Curve**

the same way. A styrene correction curve was made by plotting the differences in the absorbances for the actual calibration curve and for the straight line given by the absorptivity at various concentrations of styrene. This correction curve is shown in the upper part of Figure 3. In use the styrene concentration is determined from the measurements using Equations 3 (Table VII). The correction to the absorbance at 14.29 microns is then found from the correction curve and the styrene concentration calculated using this new $D_4$. A second value for the

**Table VIII. Analyses of Emulsion Butadiene-Styrene Copolymers**

| Temp., ° C. | Load | *cis*-1,4, % |  | *trans*-1,4, % |  | 1,2, % |  | Styrene, % | Total Found, % |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Polymer | Butadiene | Polymer | Butadiene | Polymer | Butadiene |  |  |
| −29 | 70/30 | 5.1 | 6.9 | 59.3 | 79.6 | 10.2 | 13.7 | 25.5 | 101.8 |
| −18 | 70/30 | 8.0 | 10.6 | 57.6 | 76.1 | 10.0 | 13.2 | 24.3 | 98.9 |
| 5 | 75/25 | 8.5 | 11.0 | 57.3 | 73.9 | 11.7 | 15.1 | 22.5 | 97.0 |
| 5 | 70/30 | 10.3 | 13.5 | 53.7 | 70.4 | 12.2 | 16.0 | 23.8 | 98.8 |
| 50 | 70/30 | 13.4 | 17.9 | 48.7 | 64.9 | 12.9 | 17.2 | 25.0 | 101.2 |
| 50 | 75/25 | 14.1 | 17.9 | 51.2 | 64.9 | 13.6 | 17.2 | 21.1 | 99.1 |
| 100 | 70/30 | 15.0 | 22.7 | 39.3 | 59.4 | 11.9 | 18.0 | 33.8 | 97.1 |
| 100 | 76/24 | 19.9 | 24.5 | 47.6 | 58.7 | 13.6 | 16.8 | 18.9 | 91.0 |
| 150 | 76/24 | 17.1 | 21.5 | 48.1 | 60.4 | 14.5 | 18.2 | 20.3 | 96.4 |

ncentration of styrene is obained which is then used to dermine a new $D_4$. This process is repeated until there are o significant changes in the rrected absorbance. This rrected value for $D_4$ is then ed in determining the conntrations of the other comnents.

The effects of both of these rrections are shown under rrection 2 of Table VI. Not ly is the agreement between the styrene added and styrene nd very satisfactory but the total found values are in the ge to be expected based on the unsaturation of the samples. ble VIII gives additional analyses of butadiene-styrene coymers.

No satisfactory method of analyzing alkali metal–catalyzed adiene-styrene copolymers has been developed because of complications introduced by the 13.9- and 14.3-micron bands. method used for such polybutadienes cannot be used since styrene band appears at about the trough in the spectrum of butadienes and, of course, these bands would make the ap- nt styrene absorption at 14.29 microns too large. If the ene were determined independently, by refractive index for nple, the butadiene part of the copolymer could probably be lyzed for the *cis*-1,4, *trans*-1,4, and 1,2 additions. It is not ain, however, that the same refractive index *vs.* loading es which are used in the refractive index method for emulsion mers can be used for alkali metal–catalyzed polymers.

## DISCUSSION

**-1,4 Determinations.** Two questions arise regarding the use h 14.7-micron band for the *cis*-1,4 determinations. The is whether it is characteristic of cis-1,4 addition in polydiene since this is essential for a successful analytical prore. It is not absolutely necessary that the band correlate the *cis* $RCH{=}CHR_1$ structure because, as an examination e spectra of *cis* and *trans* olefins will show, there are differ- in the spectra in addition to the bands due to *cis* and *trans* $={CHR_1}$ structures. If the 14.70-micron band were not cteristic of *cis*-1,4 addition in polybutadiene, it seems un- that the total found values obtained in the analyses reported or in the analyses of a wide variety of polybutadienes and diene-styrene copolymers reported by Binder (*3*) would agree ll with the known or expected unsaturations. Moreover esults reported by Foster and Binder (*6*) for the analyses variety of diene copolymers would not have been obtained ould the results with the hydrogenated polybutadienes.

e other question is whether the 14.70-micron band may be ated with the *cis* $>CH{=}CH<$ structure in polybutadienes. pears probable that such an assignment is valid for several s. It would be expected in hydrogenating an unsaturated carbon containing both cis and trans isomers that the cis r would hydrogenate first. The spectra of the hydrogen- polybutadienes (Figure 2) show that the intensity of the micron band decreases to zero as the hydrogenation pro-

Complete spectra of similar polybutadienes have been ed by Jones, Moberly, and Reynolds (*9*) which are similar, long-wave region, to those reported here. The differ- due to some being spectra of solutions and the others of st be considered especially in the 13.9-micron region for substances. Ahlers, Brett, and McTaggart (*1*) have re- reported the spectra of a series of cis and trans isomers of hain fatty acids and conclude that the *cis* $>CH{=}CH<$ in the spectra of these compounds appears at 14.8 microns. ng the 14.7-micron band for the determination of *cis*-1,4 addition in polybutadienes or butadiene-styrene copolymers makes it possible to determine the three types of addition, the sum of which, in suitable units, should equal the unsaturation of the polymer. Since polybutadienes differ in structure in other respects than the amounts of the three types of double bond structures, the total found value is the only criterion of the validity of an analysis. The unsaturation of the polymer may not be as large as 98%, so that if the total found value is over 100%, additional bands, particularly in the long-wave region, will undoubtedly be found in the spectrum. These bands will be found only when the sample thickness and other conditions are such that the 14.7-micron band appears. A consequence of the varying unsaturation is that normalizing the results to 100% is never justified. A further consequence of the varying unsaturation is that analyses of polybutadienes made by finding the *cis*-1,4 addition by difference may be erroneous. When this is done it is assumed that the unsaturation, total found, is 100% which it never is. The effect of the *cis*-1,4 absorption on the *trans*-1,4 and 1,2 absorptions at 10.34 and 10.98 microns, respectively, must be neglected. If the amount of *cis*-1,4 addition is large this effect is appreciable.

**Alkali Metal–Catalyzed Polybutadienes.** As the spectra of Figure 2 show, the structures of alkali metal–catalyzed polybutadienes must differ in more respects than the amounts of *cis*-1,4, *trans*-1,4, and 1,2 additions. In developing this method, using the 14.7-micron band for the *cis*-1,4 determinations, it was soon found that the sodium polybutadienes were the cause of the *cis*-1,4 absorptivities continually decreasing and the 1,2 absorptivities increasing in the iteration process. It was found, empirically, that if the 1,2 absorptivity at 14.7 microns were increased to 10, constant values of the major *cis*-1,4 and 1,2 absorptivities were obtained and that the total found values of analyses of sodium polymers amounted to about 92% and of emulsion polybutadienes to about 98%. These results with about a dozen polymers may have been fortuitous. It was desirable to eliminate the empirical approach.

The new bands in the spectra of sodium or potassium polybutadienes arise from new structures which apparently are not present in the usual emulsion polybutadienes. If these structures are regarded as impurities or additional components and if they remained the same in kind and could be identified, it would be feasible to take account of their effect by a method similar to that described by Tunnicliff, Rasmussen, and Morse (*11*) for ultraviolet analyses. These conditions do not prevail and some method of taking account of the effects of these additional bands, based on the spectrum of the polymer, was sought.

The spectra of the sodium polybutadienes used in obtaining the absorptivities had only one additional band at 13.9 microns. It was found that if the absorbance at 14.0 microns was subtracted from the absorbance at 14.7 microns and the difference (on unit cell length) used as $D_1$ in the absorptivity equations, constant values of the absorptivities were obtained and satisfactory total found values in analyses. It was then found, in analyses of other sodium polymers, that the amount by which the total found exceeded 92% varied with the intensity of the 13.9-micron band; the more intense this band was the greater the difference. This variation was not linear with respect to the peak intensity of the 13.9-micron band but it was with respect to the absorbance at the trough in the absorbance curve of the spectrum. This led to the factor method described. Thus the correction to the *cis*-1,4 absorption is related to the spectrum of the polymer.

Probably the actual absorbance subtracted from the 14.7-micron absorbance of sodium polybutadienes would not matter as long as it was related to the intensity of the 13.9-micron band and provided the polymer absorptivities became constant. A different value of the multiplying factor would be obtained on analyzing sodium polybutadienes. This could then be used to correct the 14.7-micron absorbance, used in obtaining the polymer absorptivities and the process repeated until there was no change. On the basis of the experience of analyzing many sodium polybutadienes the method described in the experimental part should eliminate many of these steps.

When more than one additional band appears in the long-wave spectrum of the polymer, the factor method is inapplicable and other methods must be used. In some cases, particularly with potassium polybutadienes, in the spectra of which two additional bands are generally found at 13.9 and 14.2 to 14.3 microns, band envelopes can be drawn for the various bands and the overlap subtracted from the measured absorbance at 14.7 microns. This is time consuming but leads to satisfactory results, as a rule, if all of the bands can be resolved. If more bands appear in the polymer spectra, as often happens when promotors such as dimethoxytetraglycol are used, the spectra become so complicated with new bands throughout the 6- to 15-micron region that satisfactory analyses cannot be made with either of these methods.

The 13.9-micron band is probably due to

$$—CH_2.CH_2.CH_2.CH_2.CH_2—$$

groups and it seems likely that this is the origin of the 14.0-micron band in the hydrogenated polybutadiene spectra despite the fact that this represents a considerable shift. However, it is observed that the 10.34- and 10.98-micron bands shift slightly depending upon the preparation of the polymer. In butadiene-styrene copolymer spectra it has been found that particularly the 10.98-micron band shifts to longer wave lengths as the styrene content is increased. It is always necessary to measure the absorbances at the peaks of the bands.

**Butadiene-Styrene Copolymers.** It is not known why the styrene absorptivity at 14.70 microns measured with polystyrene solutions proved too small when used in the analyses of polybutadiene-polystyrene mixtures. It seems unlikely that it is due to experimental error since the same solutions were used in determining the other absorptivities. It has been found essential that, if the styrene analysis reported here is to check values obtained by refractive index, the polymer must be purified by the method described by the Bureau of Standards. With care the spectroscopic method will give results which agree with refractive index values within 1% over the range of 10 to 80% styrene contents.

The absorptivities and correction factors used here would not necessarily apply to another instrument. They should be determined for each instrument used.

Probably it would be more convenient to use more dilute solutions and 0.2-mm. and 2-mm. cells in these analyses because 0.1-mm. cells plug up very easily even with polymer solutions filtered through filter paper. When this happens nothing can generally be done except repolish the cell windows.

In view of variations observed in polymer spectra, it is thought that it would be advantageous to calibrate so that the base line method described by White *et al.* (*8*) could be used as well as that described here.

## CONCLUSIONS

The microstructures, specifically the amounts of $C_4H_6$ units containing *cis* $>CH=CH<$, *trans* $>CH=CH<$, and $CH_2=CH—$ double bonds, of a large number of emulsion polybutadienes have been determined directly by measuring the intensities of bands at 14.70, 10.34, and 10.98 microns, respectively. The unsaturations of the polymers found by the analyses agree with the unsaturations determined chemically for such polymers.

Polymerizations with alkali metal catalysts change the microstructures of polybutadienes depending upon the catalyst and method of use. If the changes in the polymer structure are related only to the appearance of a band at 13.9 microns, a in ordinary sodium polybutadienes, or two rather weak bands at 13.9 and 14.3 microns, as in sodium-potassium and potassium polybutadienes, the amounts of the *cis*-1,4, *trans*-1,4, and 1,2 additions can be determined by making suitable corrections for these bands.

The styrene content of emulsion butadiene-styrene copolymers can be determined spectroscopically over a wide range of concentrations with an accuracy approaching that of the refractive index method by measuring the intensity of the 14.29-micron band. Results by the two methods can be made to agree within 1%.

The amounts of *cis*-1,4, *trans*-1,4, and 1,2 additions in emulsion butadiene-styrene copolymers can be determined directly using the same method as for polybutadienes but taking into account the absorption due to polystyrene.

Alkali metal–catalyzed butadiene-styrene copolymers als have additional bands in their spectra which affect the styrene absorption at 14.29 microns. No method has yet been devised to take account of these effects.

Alfin polybutadienes can be analyzed for the amounts of *cis*-1,4, *trans*-1,4, and 1,2 additions by the method used for emulsion polybutadienes.

The method used for analyzing sodium polybutadienes can be applied to the analyses of polybutadienes, which have been hydrogenated to various degrees of unsaturation.

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## LITERATURE CITED

(1) Ahlers, N. H. E., Brett, R. A., and McTaggart, N. G., *J. Appl. Chem.* (*London*), 3, 433 (1953).
(2) Anderson, J. A., Jr., and Seyfried, W. D., Anal. Chem., 20, 99 (1948).
(3) Binder, J. L., private communication to Office of Synthetic Rubber, Reconstruction Finance Corp.
(4) Brattain, R. R., Rasmussen, R. S., and Cravath, A. M., *J. Appl. Phys.*, 14, 418 (1943).
(5) Field, J. E., Woodford, D. E., and Gehman, S. D., *Ibid.*, 17, 386 (1946).
(6) Foster, F. C., and Binder, J. L., *J. Am. Chem. Soc.*, 75, 21 (1953).
(7) Hampton, R. R., Anal. Chem., 21, 923 (1949).
(8) Heigl, J. J., Bell, M. F., and White, J. U., *Ibid.*, 19, 293 (1947).
(9) Jones, R. V., Moberly, C. W., and Reynolds, W. B., *Ind. Eng. Chem.*, 45, 1117 (1953).
(10) Lee, T. S., Kolthoff, I. M., and Mairs, M. A., *J. Polymer Sci.*, 3, 67 (1948).
(11) Tunnicliff, D. D., Rasmussen, R. S., and Morse, M. L., Anal. Chem., 21, 895 (1949).
(12) Wulf, O. R., and Deming, Lola S., *J. Chem. Phys.*, 6, 7 (1938).

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