Infrared Analysis of Low Temperature Polymers

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Because of the considerable interest in methods of polymer analysis by which the amount of each type of unsaturation can be determined, this paper gives a description of the method used in obtaining the data on 1,2 and trans-1,4 addition and an extension of the method that permits determination of cis-1,4 addition and combined styrene, and gives more accurate results for 1,2 and trans-1,4 addition.

MOST of the rubberlike polymers (both natural and synthetic) are diene addition polymers or copolymers. In diene polymerization, addition may take place in several ways. With butadiene, for example, cis-1,4, trans-1,4, and 1,2 addition are all possible (Figure 1). With substituted butadienes, such as isoprene, there is the additional possibility of 3,4 addition. (Resonance considerations, *5*, indicate that addition will normally be "head to tail.") Natural rubber is polyisoprene, that is all, or nearly all, in the cis-1,4 configuration. Balata is *trans*-1,4-polyisoprene. Synthetic polyisoprene, on the other hand, is a random mixture of at least three of the possible configurations and does not have the desirable physical properties of either rubber or balata. Ordinary GR-S contains a random mixture of styrene units and the three possible types of butadiene units. Recently Hart and Meyer have shown (*6*) that, when butadiene polymers are prepared at low temperatures, the addition of the butadiene units is preponderantly trans-1,4. Low temperature butadiene polymers have also been shown to have significantly improved (*15*, *19*) physical properties.

Accordingly, there has been considerable interest in methods of polymer analysis by which the amount of each type of unsaturation can be determined. The present paper describes the method used to obtain the data for 1,2 and trans-1,4 addition, as previously reported (*6*), and an extension of that method which permits the determination of cis-1,4 addition and combined styrene and gives more accurate results for 1,2 and trans-1,4 addition.

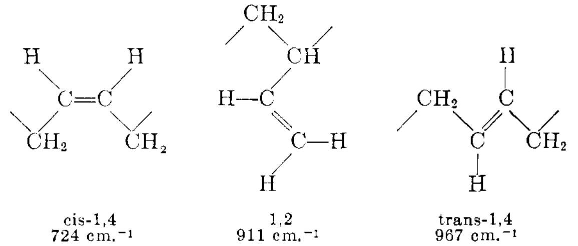


Figure 1. Polybutadiene Structures

Table I. Characteristic Absorption for National Bureau of Standards Olefins

Sample	N.B.S. No.	Absorption Maximum, Cm.$^{-1}$	$\epsilon = \frac{\text{Log } I_0/I \times \text{Molecular Weight}}{(\text{G./Liter}) \times (\text{Cm. Cell Depth})}$
cis-2-Pentene	282-5S	698	45
4-Methyl-*cis*-2-pentene	537-5S[a]	719	126
Average for *cis*-R—CH=CH—R		ca. 700	85
trans-2-Pentene	283-5S	965	141
4-Methyl-*trans*-2-pentene	536-5S[a]	966	138
trans-2-Hexene	527-5S	966	153
trans-3-Hexene	529-5S	966	133
trans-4-Octene	548-5S	968	132
Average for *trans*-R—CH=CH—R		967	139
3-Methyl-1-pentene	531-5S	910	163
3,3-Dimethyl-1-butene	287-5S	910	145
4-Methyl-1-pentene	532-5S	910	143
4,4-Dimethyl-1-pentene	547-5S	912	153
1-Heptene	520-5S	909	153
1-Octene	521-5S	910	155
1-Nonene	551-5S	909	160
1-Decene	552-5S	910	159
1-Undecene	555-5S	909	168
Average for R—CH=CH_2		910	155

[a] From a study of the infrared absorption spectra in the 3-, 6-, and 10- to 15-micron regions, it is believed that N.B.S. samples 536 and 537 have the configurations listed in this table rather than the reverse configurations as the samples are at present labeled. Rossini (*14*) is conducting a further investigation to establish the true configuration.

Ozonization (*1*, *13*) and perbenzoic acid (*7*, *8*) methods have been applied to the chemical determination of 1,2 addition in butadiene polymers. Infrared spectroscopic methods of analysis have also been described by various workers.

Thompson and Torkington (*17*) published spectra showing the presence of a large amount of 1,2 addition in sodium-polymerized butadiene, but did not give quantitative methods. Field, Woodford, and Gehman (*4*) attempted to determine the relative amounts of 1,2 and 1,4 addition in polybutadiene by measuring the relative intensities of absorption at 996 and 967 cm.$^{-1}$, and comparing with results on known mixtures of 1-octene and 2-octene. However, they did not distinguish between cis and trans forms, and only the trans isomer has strong absorption at 967 cm.$^{-1}$ Anderson and Seyfried (*3*) described infrared methods for the determination of unsaturation in complex samples such as hydrocarbon synthesis naphthas. They recognized that absorption at 967 cm.$^{-1}$ is characteristic of trans internal double bonds, whereas the cis form absorbs near 700 cm.$^{-1}$ Extinction coefficients for a number of pure compounds were averaged for use in the analyses. Such methods are extremely useful for mixtures with more than one component having a given type of unsaturation.

As shown by Table I, the characteristic infrared extinction coefficients for olefins of low molecular weight vary somewhat for the individual compounds. It therefore seemed desirable to determine extinction coefficients for the specific polymers being analyzed. Such methods have now been developed, and found satisfactory for the analysis of polybutadiene, and butadiene-styrene copolymers (in which styrene is also determined). In the near future it is planned to extend these methods to substituted butadiene polymers such as polyisoprene.

Early attempts to use infrared spectroscopy in studying polymer unsaturation were seriously handicapped by the lack of suitable pure reference compounds. One of the first standards obtained was a commercial material, stated to be "95% pure 2-octene." Later work showed this sample to contain about 50% 1-octene, and of course nothing was known regarding the relative amounts of *cis*- and *trans*-2-octene. However, through the efforts of the National Bureau of Standards and A.P.I. Project 46, several pure olefin samples are now available and their number is being steadily increased.

The infrared spectra of the olefins listed in Table I show characteristic differences, depending upon the type of olefin, in three regions. The $C=C$ stretching frequencies in the 6-micron region are weak and not sufficiently well characterized to be useful in analysis. The C—H stretching frequencies in the 3-micron region are considerably more intense and are characteristic when examined with high resolving power. However, the C—H bending absorption bands in the 10- to 15-micron region are very intense and apparently highly specific, if only hydrocarbons are being analyzed. Much less is known about the C—H bending frequencies in samples containing strongly polar atoms such as oxygen or halogen.

MATERIALS STUDIED

The hydrocarbons of low molecular weight studied in this work were all National Bureau of Standards standard samples and are listed in Table I. Polymers of butadiene and copolymers of butadiene-styrene from a variety of sources have been measured and the results are shown in Tables II to V. All samples were examined in carbon disulfide solution. The polymers were purified by solution in carbon disulfide, filtration through 300-mesh silk to remove gel, precipitation with methanol, and final re-solution in carbon disulfide. In actual analyses the removal of gel in this manner would cause erroneous results, if the gel were of different composition than the sol portion of the polymer, as might well be the case. However, for this experimental work results on the sol portion were satisfactory. In some cases the gel was so finely divided that it could not be removed by filtration and this gel was left suspended in the polymer solution for the analysis. Polymers may also be examined as thin films, molded in optically flat molds, or deposited from solution. In comparison with carbon disulfide solutions, the solid films have spectra with slightly different absorption frequencies. Preliminary data indicate that extinction coefficients may be considerably different.

Table II. Comparison of Results on Polybutadiene Samples

Sample	Polymerization Temp., ° C.	% cis (by Difference)		% 1,2		% trans	
		a	*b*	*a*	*b*	*a*	*b*
26-E-57-76	−19	0.8	7.6	19.6	16.4	79.6	76.0
26-E-41-56	−10	3.1	9.2	20.6	17.0	76.3	73.8
J-946-4	+5	7.7	16.0	20.8	16.0	71.5	68.0
26-E-77-96	+5	7.0	14.4	21.3	18.3	71.7	67.3
14-R-3	+50	14.8	21.5	23.2	20.0	62.0	58.5
14-R-6	65	19.6	27.3	23.8	19.1	56.6	53.6
14-R-5	97	23.8	33.8	24.8	18.0	51.4	48.2

Table III. Comparison of Results on Butadiene Styrene Copolymers

Sample	Polymerization Temp., ° C.	% Styrene[a]	% 1,2		% trans	
			a	*b*	*a*	*b*
GR-S	50	23.4	16.8	13.7	49.6	46.3
GR-S-10	50	21.8	15.7	12.1	45.4	42.1
J-888-3	5	23.3	16.1	12.5	58.3	54.7
J-889-3	−18	24.3	14.8	11.8	63.5	58.3
J-948-B-2	+5	7.6	17.9	15.2	67.1	63.6
J-947-2	+5	3.8	20.2	16.5	68.7	64.7

[a] Results reported by Hart and Meyer (*6*). % 1,2 and % trans based on octene standards; styrene estimated from refractive index.

[b] Results based on original data obtained for Hart and Meyer, recalculated according to present method, using polymer standards.

Table IV. Complete Analyses of Polybutadiene Samples

Sample	Source[a]	Polymerization Temp., ° C.	% cis	% 1,2	% trans	Total Found
P-7	P	−20	7.5	17.5	77.6	102.6
P-6	P	−10	7.4	17.6	74.3	99.3
7 HRZF-1	A	+50	18.5	19.9	59.2	97.6
XP-132-L 7	A	50	18.6	19.7	59.3	97.6
HM-7	G	70	23.5	19.9	57.3	100.7
IC	G	70	21.2	19.1	53.7	94.0
63PC-1D4	A	87	24.2	20.5	56.2	100.9
63PC-4D4	A	90	22.5	20.5	55.6	98.6
21444[b]	R	..	15.2	65.8	17.9	98.9
184C[b]	I	30	13.9	67.6	19.9	101.4

[a] Sources of samples measured.
A. Government Laboratory, University of Akron.
G. General Laboratories, U. S. Rubber Co., Passaic, N. J.
I. University of Illinois, C. S. Marvel.
P. Produced by Phillips Petroleum Co.
R. Rubber Reserve (imported from Russia).

[b] Sodium-catalyzed; all other samples emulsion-polymerized.

Table V. Complete Analyses of Butadiene-Styrene Copolymers

Sample	Source[a]	Polymerization Temp., ° C.	% Styrene	% cis	% 1,2	% trans	Total Found
K-2524	F	−38	26.6	12.0	11.0	54.0	103.6
J-1351-5-4	N	+5	26.1	9.7	12.0	50.9	98.7
J-1446-4	N	10	25.8	11.8	12.0	50.0	99.6
63PB7D3-4	A	109	24.7	22.6	14.3	39.8	101.4

[a] Sources of samples measured.
A. Government Laboratory, University of Akron.
F. R. L. Bebb, Firestone Tire and Rubber Co.
N. U. S. Rubber Co., Synthetic Rubber Division, Naugatuck, Conn.

INSTRUMENTAL TECHNIQUES

Infrared measurements were made using a Model 12A Perkin-Elmer spectrometer equipped with a blackened Thermistor bolometer, Western Electric amplifier Model KS-10281, and a Speedomax Type A recorder. The recorder chart and Littrow mirror are driven through Selsyns to ensure accuracy of the wave-length calibration on the charts. Radiation is chopped at 15 cycles per second by means of a synchronous rotating sector at the globar. This recording system is stable, sensitive, and completely free from zero drift. Although prisms of lithium fluoride, calcium fluoride, and potassium bromide were used for some of the preliminary studies, all analyses reported here were made using a sodium chloride prism, with slit widths of 0.210 mm. at 967 cm.$^{-1}$, 0.215 mm. at 911 cm.$^{-1}$, and 0.360 mm. at 724 cm.$^{-1}$ corresponding, respectively, to equivalent half-intensity widths of 7, 6, and 4.5 cm.$^{-1}$ (Measurements were made on the 909 cm.$^{-1}$ band of 1-heptene for slit widths from 0.100 to 0.600 mm. Extrapolation to zero slit width indicated about 20% higher extinction coefficient than that found using the standard slit width of 0.215 mm.)

In order to reduce short wave-length scattered radiation a plane grating (*18*) of 3610 lines per inch is used in place of the flat mirror which directs the light from the globar to the condensing mirror. Correction was made for residual stray light (about 0.6%), and also for a slight nonlinearity in response of the bolometer-amplifier combination (maximum correction 0.5%). Under these conditions it was found that Beer's law is obeyed accurately at optical densities less than 0.8. Measurements were made by two different methods. In the scanning method a portion of the spectrum including the band to be measured was recorded and measurements were made at the peak relative to a similarly recorded spectrum for the same cell containing pure carbon disulfide. Measurements were made also with the recorder running and the spectrometer drive stopped at the frequency of maximum absorption for the particular band being measured. The cell containing the sample solution was alternately placed in front of the slit, then removed, and the corresponding intensities were read from the chart. These readings were then repeated using the same cell filled with the pure solvent. If the chart showed any change in the cell-out reading, the readings were corrected for this change.

The vapor-tight cells used, made with amalgamated lead spacers, were filled by means of a glass syringe, and closed by clamping a sheet of tin foil–covered rubber against the rim of the hypodermic needle hub opening of the cell. Six different cells were used, varying in thickness from 0.0052 to 0.0905 cm., so that in most cases measurements could be made at optical densities between 0.4 and 0.7. Cell thicknesses were determined interferometrically (*16*) except for the 0.0905-cm. cell, which was measured microscopically.

For the National Bureau of Standards hydrocarbons, molar extinction coefficients were calculated:

$$\epsilon = \frac{\log I_0/I}{cl}$$

where c is the solution concentration in gram-moles per liter, l is the length in centimeters of absorbing path (cell depth), I is the intensity of radiation transmitted by the solution, and I_0 is the intensity of radiation transmitted by the pure solvent.

For the polymer samples, the specific extinction coefficient, E, is calculated like the molar extinction coefficient, except that the concentration is expressed in grams per liter.

EXPERIMENTAL

The data reported by Hart and Meyer (*6*) were obtained by a method similar to that since described by Anderson and Seyfried (*3*), using 1-octene as a standard for the determination of 1,2 addition, and *trans*-4-octene as a standard for the determination of trans-1,4 addition. Measurements were made by scanning, as described above, except that no grating was used, and the amplifier response was not corrected for lack of linearity. Stray light, as measured with a lithium fluoride shutter, was subtracted from all readings. An empirical calibration curve was used, thus avoiding dependence on Beer's law and automatically compensating for amplifier and stray light errors. It was realized that slight errors were probably inherent in the assumption that extinction coefficients for polybutadiene were identical with those found for 1-octene and *trans*-4-octene. For the determination of cis-1,4 addition, low molecular weight standards are much less satisfactory.

The method finally developed uses polybutadiene standards for the determination of unsaturation, and has been extended to cover the determination of styrene in copolymers, and cis-1,4 addition of butadiene, as well as giving more accurate values than the original method for 1,2 and *trans*-1,4 addition.

Polybutadiene exhibits infrared absorption bands at 724, 911, and 967 cm.$^{-1}$, the relative intensities of which vary, depending on the method of preparation of the polymer. The band at 967 cm.$^{-1}$ is attributed to *trans*-1,4-polybutadiene as suggested by Pitzer (*12*) and since confirmed by Anderson and Seyfried (*3*), and by study of the spectra of the olefins listed in Table I, and numerous A.P.I. spectra (*2*). The band at 911 cm.$^{-1}$ has been similarly attributed to 1,2-polybutadiene. For emulsion polybutadiene prepared at high temperatures, the sum of 1,2- plus *trans*-1,4 polymer (estimated from the 911 and 967 cm.$^{-1}$ bands) is considerably lower than for other polybutadiene samples; by difference, the amount of cis-1,4 polymer should be relatively high. This material shows an absorption band at 724 cm.$^{-1}$, which is very weak in the other samples, and is considered characteristic of *cis*-1,4-polybutadiene.

From measurement of the absorption at the three positions (724, 911, and 967 cm.$^{-1}$) it is possible to calculate the isomeric composition of a sample of polybutadiene, by solution of three simultaneous equations

$$E_{724} = \underline{CE^c_{724}} + VE^v_{724} + TE^t_{724} \qquad (1)$$

$$E_{911} = CE^c_{911} + \underline{VE^v_{911}} + TE^t_{911} \qquad (2)$$

$$E_{967} = CE^c_{967} + VE^v_{967} + \underline{TE^t_{967}} \qquad (3)$$

where C, V, and T represent the respective weight fractions of cis-, vinyl (1,2), and trans polymer in the sample; E_{724}, E_{911}, and E_{967} represent specific extinction coefficients found for the sample at the three frequencies; and E^c_{724}, E^v_{911} . . . etc., represent specific extinction coefficients for the three pure isomers of polybutadiene at the same three frequencies.

The underscored coefficients $\underline{E^c_{724}}$, $\underline{E^v_{911}}$, and $\underline{E^t_{967}}$ are the important characteristic coefficients for *cis*-, vinyl-, and *trans*-polybutadiene and are determined as described below. The other "correction" coefficients are so small that considerable errors can be tolerated without seriously affecting the final result. All except E^v_{724} were estimated by using average values from low molecular weight olefins. The 1-alkenes all have a moderately strong band near 724 cm.$^{-1}$, whose exact position varies from different samples; so E^v_{724} cannot be satisfactorily estimated from low molecular weight compounds. With 1,2-polybutadiene, this interfering band is found at 680 cm.$^{-1}$ Measurements were made on a sample of sodium-polymerized polybutadiene, assuming that the 680 cm.$^{-1}$ band is symmetrical, so that $E^v_{636} = E^v_{724}$, and that only 1,2-polybutadiene absorbs at 636 cm.$^{-1}$ Measurements at 636 cm.$^{-1}$ were made using a potassium bromide prism and slits of the same equivalent half-intensity width as for the sodium chloride prism measurements at 724 cm.$^{-1}$

Preliminary values of the major extinction coefficients, $\underline{E^c_{724}}$, $\underline{E^v_{911}}$, and $\underline{E^t_{967}}$, were obtained by dividing the corresponding average molar extinction coefficients for low molecular weight olefins by the molecular weight of butadiene. Using these preliminary values, the three equations given were solved to determine preliminary values for per cent *cis*- and per cent *trans*-polybutadiene in a sample of sodium-polymerized polybutadiene and the major component, 1,2-polybutadiene, was estimated by difference. This figure (per cent 1,2) was substituted in Equation 2 in order to calculate a new value for $\underline{E^v_{911}}$. In a similar manner E^t_{967} was re-evaluated using a sample of low temperature emulsion polymer, whose major component, *trans*-1,4-polybutadiene, was determined by difference, and E^c_{724} was calculated from data on a sample of high temperature emulsion polymer, on which per cent cis was determined by difference. Values were averaged, respectively, for three samples relatively high in cis, two samples high in vinyl, and four samples high in trans, to obtain new values for E^c_{724}, E^v_{911}, and E^t_{967}. Using the new extinction coefficients, the above series of calculations was repeated until further successive repetitions did not result in further change in the E values. For each repetition, a new value of E^v_{724} was also used, based on the new figures for per cent 1,2 in the sodium polymers.

Copolymers of styrene and butadiene are treated as four-component systems, and measurements are made at 699 (for styrene determination), 724, 911, and 967 cm.$^{-1}$ In this case four simultaneous equations result:

$$E_{699} = \underline{SE^s_{699}} + CE^c_{699} + VE^v_{699} + TE^t_{699}$$

$$E_{724} = SE^s_{724} + \underline{CE^c_{724}} + VE^v_{724} + TE^t_{724}$$

$$E_{911} = SE^s_{911} + CE^c_{911} + \underline{VE^v_{911}} + TE^t_{911}$$

$$E_{967} = SE^s_{967} + CE^c_{967} + VE^v_{967} + \underline{TE^t_{967}}$$

where S represents the weight fraction of styrene in the polymer, and the other symbols have the same meanings as before.

E^s values were determined directly on carbon disulfide solutions of pure polystyrene, and the other E_{699} values were calculated from measurements on a series of polybutadiene samples which had been analyzed as described above.

An electrical computer (12-equation electrical computer, Model 30–103, obtained from Consolidated Engineering Corp., Pasadena, Calif.) has been used for this work, although solution of the equations is not difficult by successive approximations or the use of determinants. For most purposes the correction terms can be determined with sufficient accuracy by using estimated values for the weight fractions S, C, V, and T, and the final values calculated directly. Table VI lists the extinction coefficients found.

DISCUSSION

The above method involves the tacit assumption that no other components are present and that the samples examined had the theoretical total unsaturation, one double bond per butadiene unit. Lee, Kolthoff, and Mairs (*9*) have reported that sodium- and emulsion-polymerized polybutadiene, respectively, have approximately 92 and 98% of the theoretical unsaturation. If these representative values apply to the samples used in the present work, then the results reported for 1,2 addition are too high by about 8% of the amounts reported; results for cis and trans would not be affected. If accurate total unsaturation values were determined for the samples used as standards, more accurate extinction coefficients could be calculated on that basis. However, in view of the uncertainties and difficulties inherent in the chemical determination of unsaturation, as well as lack of experience with such methods, it seemed preferable tentatively to assume that the purified polymer samples used had the theoretical unsaturation, and accept the possible errors resulting. The 1,2 polymer, which would be the only one affected if the results of Lee, Kolthoff, and Mairs are applicable, is a relatively minor and unvarying constituent except in the case of sodium polymers.

The method for styrene is believed to be more reliable than the refractive index method (*10*), for it has been shown (*6*) that the refractive index of polybutadiene varies with temperature of polymerization. The ultraviolet absorption method (*11*) for combined styrene is presumably applicable to low temperature polymers, but is more subject to interference by traces of antioxidant than is the infrared method.

Table VI. Polymer Extinction Coefficients[a]

	699 cm.$^{-1}$	724 cm.$^{-1}$	911 cm.$^{-1}$	967 cm.$^{-1}$
Polystyrene	2.703	0.038	0.064	0.050
cis-1,4-Polybutadiene units	0.385	0.551	0.037	0.058
1,2-Polybutadiene units	0.153	0.050	3.193	0.098
trans-1,4-Polybutadiene units	0.005	0.007	0.055	2.542

[a] Extinction coefficients were measured for carbon disulfide solutions and are defined as follows:

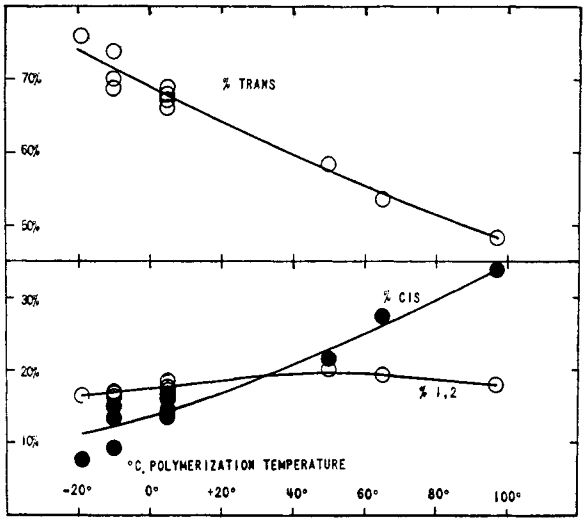
$$E = \frac{d}{xl}$$

d = optical density = $\log \frac{I_0}{I}$
I = intensity of radiation transmitted by solution
I_0 = intensity of radiation transmitted by pure solvent in same cell
x = solution concentration in grams per liter
l = cell thickness in cm.

RESULTS

Tables II and III compare some of the data obtained by Hart and Meyer (*6*) with results obtained by recalculating the original data according to the new method. Because no measurements were made on these samples at 699 or 724 cm.$^{-1}$, the equation involving E_{724} was replaced by the equation $S + C + V + T = 1.000$ (thus determining cis by difference), and the weight fraction of styrene, as estimated by refractive index measurement, was substituted for S, in order to estimate the correction terms for the copolymer samples. The new method gives somewhat higher values for cis, and lower values for 1,2 and trans, but confirms the general conclusion that lowering the temperature of polymerization lowers the cis–trans ratio.

Tables IV and V give the results of complete analyses by the new method, where cis, 1,2, and trans (and styrene, if present) were determined. In most cases the summation is reasonably close to 100%. These results further confirm the previous conclusion (*6*) regarding the effect of polymerization temperature.



Fignre 2. Effect of Temperature on Polybutadiene Structure

Infrared spectroscopy provides a valuable means of polymer analysis. By this method it is possible to distinguish between standard and "cold" GR-S in unknown samples. In studying other possible methods of polymerization it is now readily possible to determine the effect of various conditions on polymer composition, and thus guide research in the most fruitful channels.

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