QUANTITATIVE ANALYSIS OF POLYBUTADIENES
USING DIFFERENCE INFRARED SPECTRA

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The infrared absorptions due to out of plane deformation vibrations at 742, 912 and 967 cm^{-1} are frequently employed for quantitative determination of *cis*-1,4, *trans*-1,4 and 1,2 units, respectively in linear polymers. A rather restricted utility of the methods based on these absorptions has been a subject of a series of papers. The main difficulty that makes analyses unreliable is the dependence of the absorption band shape, the position of a maximum, and the value of extinction coefficients upon the polymer composition[1−3]. This has also been observed in low molecular 1-alkenes[4]. Also the assignement of absorption bands to one type of units has been questioned[5,6]. It has recently been reported that even the skeletal vibrations, attributed to certain polymer units, strongly depend on the vicinal groups *i.e.* whether these units are surrounded by the same type of units or whether they are isolated from one another by other type of units[7]. The same dependence can be expected in the case of deformation vibrations. These difficulties have stimulated the development of other methods of analyses[1,8−11] all of them being, however, based upon the following deformational vibrations. As we believed that the measurement of valence vibration absorptions would give better results we employed the 3003 cm^{-1} band for determination of *cis*-1,4 units (component B) and the 3025 cm^{-1} band for *trans*-1,4 units (component A). For the purpose of quantitative analysis we used the differential method which allows a very exact measurement of the spectra.

EXPERIMENTAL

Samples analysed. Europene *cis*-1,4 (Anic, Italy Ravena), Buna CB 10 (Chemische Werke Hüls), Polybutadiene JSR-BRO-1 (Japan Synthetic Rubber Co., Ltd., Tokyo, Japan), Diene 35 NFA (Firestone Tyre and Rubber Co., Akron, Ohio, U.S.A.), Polybutadiene *cis* 4-1203 (Phillips Petroleum Co., Bartlesville, Oklahoma, U.S.A.), Intene 35 NF-A (International Synthetic Rubber Ltd., Southampton Hants., G.B.), Cariflex 1 220 (Shell Chemical Co., France), Št.-I-69 was a polymer prepared in the presence of $Al(C_2H_5)3 — CoCl_3$ catalytic system in benzene.

Standards. *cis*-1,4-Polybutadiene Cariflex contained, according the manufacturer's specification, 97% *cis*-1,4, 2% *trans*-1,4 and 1% of 1,2 units. *trans*-1,4-Polybutadiene was prepared by polymerization in the presence of a rhodium catalyst; the polymer did not show any measurable absorptions due to *cis*-1,4 and 1,2 units. The IFP polybutadiene contained 5% of *trans*-1,4 units that were determined by the baseline method using the 967 cm^{-1} band.

Methods. The spectra were taken on a double beam spectrometer Zeiss UR-10 using an LiF prism for measurements in the region 2950—3100 cm^{-1}. An NaCl prism was used for experiments in 700—900 cm^{-1} region. Two cells fitted with sodium chloride windows were used throughout the work (0·0996 cm pathlength, unless otherwise stated). Classical analyses were performed with 0·25 and 0·50% solutions of samples in carbon disulphide. The difference spectra were taken using c. 0·2% tetrachloromethane solutions of standards as well as samples. The cell placed in the reference beam was, for measurements by the difference method, always filled with a solution

of the *trans*-1,4-polybutadiene standard. A correction aperture was set to a constant position throughout all the experiments. The recorder deflection in the region where absorption did not occur was always adjusted to $50-75\%$ by using a wire mesh placed in the reference beam. In the presence of *trans*-1,4-polybutadiene in the reference beam and *cis*-1,4-polybutadiene in the recording beam, a pronounced maximum of transmission is seen at 3025 cm^{-1} ($\tilde{v}_2$) and a minimum at 3003 cm^{-1} ($\tilde{v}_1$) (Fig.1). The 3003 cm^{-1} band was used for the baseline method of analysis (Fig. 2). Calibration diagrams for *cis*-1,4 and *trans*-1,4-polybutadiene mixtures have been made both for the measurements by the baseline method and for the difference method (Fig. 3).

The extinction coefficient of the 1,2-polybutadiene standard was measured at 912 cm^{-1} by taking spectra of carbon disulphide solutions of the IFP polymer. The baseline method was used to evaluate the results. The 912 cm^{-1} band was assumed to be common for both polybutadiene syndiotactic and isotactic form. Absorptions at frequencies $\tilde{v}_1$ and $\tilde{v}_2$ resp. were calculated using the method of extinction differences taking the frequency $\tilde{v}_r = 3200 \text{ cm}^{-1}$ as a reference. At this frequency none of the possible polybutadiene structures has a specific absorption.

The difference method enables to determine the ratio of *cis*-1,4 and *trans*-1,4 units after subtraction the 1,2 units contents. No other impurities (*e.g.* cyclic forms) must be present in the sample being analysed. The overall double bond content was thus checked by the iodine-monochloride[12] method and by taking NMR spectra[13] using a 60 Mc instrument.

Calculation. The relationship for difference spectrum is similar to that derived for two components[14]:
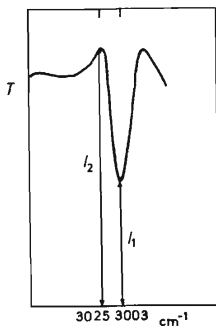

FIG. 1

Difference Spectrum

0·20% Solution of *cis*-1,4-polybutadiene placed in the recording beam and 0·2% solution of *trans*-1,4-polybutadiene placed in the reference beam. Solvent: tetrachloromethane.
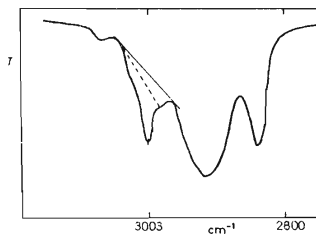

FIG. 2

Infrared Spectrum of Diene NFA

0·5% Solution in carbon disulphide.

$$\frac{1}{c'd'} \log \frac{I_2}{I_1} = [(\varepsilon_1)_A - (\varepsilon_2)_A] \left[\frac{cd}{c'd'} x_A - x'_A \right] +$$

$$+ [(\varepsilon_1)_B - (\varepsilon_2)_B] \left[\frac{cd}{c'd'} x_B - x'_B \right] +$$

$$+ [(\varepsilon_1)_C - (\varepsilon_2)_C] \left[\frac{cd}{c'd'} x_C - x'_C \right]. \qquad (1)$$

I_1 and I_2 resp. are intensities at $\tilde{v}_1$ and $\tilde{v}_2$ frequencies, resp. $(\varepsilon_1)_A$, $(\varepsilon_1)_B$, $(\varepsilon_1)_C$ are the extinction coefficients of A, B and C components at frequency $\tilde{v}_1$; similarly $(\varepsilon_2)_A$, $(\varepsilon_2)_B$, $(\varepsilon_2)_C$ are the extinction coefficients at frequency $\tilde{v}_2$; x_A, x_B and x_C are the molar fractions of components in the sample cell, whereas x'_A, x'_B and x'_C are the molar fractions of components in the reference cell. d and d' are the pathlengths of a sample and reference cell, resp. c and c' are the concentrations of the sample in a sample and reference cell respectively.

When $x'_A = 1$, $x'_B = 0$, $x'_C = 0$ the equation (1) is reduced to the form

$$x_A = [K \log (I_2/I_1) - K_2 r + K_1 - (K_3 - K_2) r x_C]/(K_1 - K_2) r, \qquad (2)$$
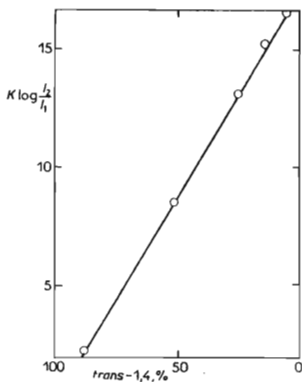

FIG. 3

Calibration Curve for Difference Spectra

0·2% Solution of the mixture of cis-1,4-polybutadiene and trans-1,4-polybutadiene placed in the recording beam, 0·20% solution of trans-1,4-polybutadiene placed in the reference beam.
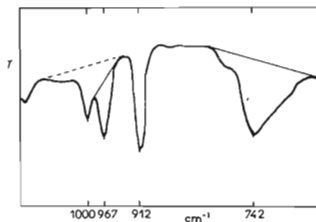

FIG. 4

The Spectrum of Št-I-69 Polybutadiene Containing Rather High Contents of 1,2 Form

0·4% Solution in carbon disulphide placed in a 0·2 cm cell (compensated by the solvent in a cell of the same path-length).

where

$$K_1 = [(\varepsilon_1)_A - (\varepsilon_2)_A], \quad K_2 = [(\varepsilon_1)_B - (\varepsilon_2)_B], \quad K_3 = [(\varepsilon_1)_C - (\varepsilon_2)_C]$$
$$r = cd/c'd', \quad K = 1/c'd'.$$

In the case of the method of extinction differences following relationship holds:

$$K_3 = [\log (I_r/I_1) - \log (I_r/I_2)]/cd, \tag{3}$$

I_r being the intensity at $\tilde{\nu}_r$ frequency; the constant K_3 was determined by measuring the absorption of the 1,2-polybutadiene standard (1·063). The constant K_1 was calculated from the difference spectra of 1,2-polybutadiene placed in the recording beam and trans-1,4-polybutadiene placed in the reference beam. Under these conditions ($x_C = 1$) the equation (1) is reduced to

$$\frac{1}{c'd'} \log \frac{I_2}{I_1} = -K_1 + K_3 r. \tag{4}$$

When $r = 1·060$ then $K_1 = 0·517$.

Similarly the constant K_2 was determined from the expression

$$\frac{1}{c'd'} \log \frac{I_2}{I_1} = -K_1 + K_2 r, \tag{5}$$

provided that only cis-1,4 component ($x_B = 1$) is placed in the recording beam and trans-1,4-isomer is used as a reference ($x'_A = 1$). For 100% pure cis-1,4 form the value of $(1/c'd') \log (I_2/I_1) = 16.85$ was used. This value was determined from the calibration curve of Cariflex (Fig. 3) extrapolating to 100%. For $r = 1·065$ the value of K_2 was found to be 16·3.

The 1,2-polybutadiene content x_C was first determined in the samples using a calibration curve at 912 cm^{-1}. By means of the experimentally found value of $\log (I_2/I_1)$ and known values of r and K, resp. (Table I) it was possible to calculate the trans-1,4-polybutadiene contents (x_A, see Eq. (2)); the content of the cis form was determined by extrapolation to 100%.

TABLE I

Analytical Data Concerning Analyses of Linear Polybutadienes
$\tilde{\nu}_1 = 3\,003$ cm^{-1}, $\tilde{\nu}_2 = 3025$ cm^{-1}, $c' = 0·198\%$ w/w, $c'd' = 0·0197$.

Sample	c	$r = cd/c'd'$	I_1, mm	I_2, mm	$\log (I_2/I_1)$	$\frac{1/c'd' \cdot}{\log (I_2/I_1)}$
Europene cis-1,4	0·201	1·015	30·2	56·0	0·270	13·7
Buna CB 10	0·201	1·015	29·0	56·5	0·289	14·66
JSR — BRO1	0·200	1·010	29·0	57·2	0·295	14·98
Diene 35 NFA	0·212	1·07	39·9	53·0	0·123	6·24
Cis 4 1203	0·200	1·010	29·8	56·8	0·280	14·20
Intene 35 NF-A	0·2005	1·013	39·7	52·3	0·120	6·08
Št-I-69	0·1995	1·013	36·7	56·0	0·184	9·39
Cariflex	0·211	1·065	27·1	56·9	0·322	16·33

RESULTS

The experimental data were obtained by employing classical baseline methods based on the absorption caused by deformation vibration at 740, 967 and 912 cm^{-1}, or 3 003, 967 and 912 cm^{-1} resp. Moreover, the difference method based on the measurements of the valence vibrations at 3 003 cm^{-1}, 3 025 cm^{-1} resp. was used. All the results are summarised in Table II. The com-

TABLE II

The Contents (% w/w) of trans-1,4 (A); cis-1,4 (B) and 1,2 (C) Structural Units in Polybutadiene

For the determination of cis-1,4 units the bands at 3 003 cm^{-1} (a) and the band at 742 cm^{-1} (b) were employed. The trans-1,4 units content was determined by means of the 967 cm^{-1} band.

Sample	Component	Difference spectra	Baseline method	
			a	b
Europene cis-1,4	A	10·3	4·7	4·3
	B	85·3	90·4	91·1
	C	4·4	4·9	4·6
Buna CB 10	A	6·5	3·3	3·1
	B	91·4	94·4	94·8
	C	2·1	2·3	2·1
JSR — BRO1	A	4·6	3·3	3·1
	B	94·0	95·3	95·5
	C	1·4	1·4	1·4
Diene 35 NFA	A	53·3	52·2	50·7
	B	36·3	36·5	38·8
	C	10·4	11·3	10·5
Cis 4 1203	A	6·5	3·9	3·7
	B	88·9	91·2	91·6
	C	4·6	4·9	4·7
Intene 35 NF-A	A	52·2	52·1	51·3
	B	37·5	36·7	37·6
	C	10·3	11·2	11·1
Št-I-69	A	21·3	14·9	15·2
	B	58·1	62·2	61·6
	C	20·6	22·9	23·2
Cariflex	A	2·02	—	2·0
	B	96·98	—	97·0
	C	1·00	—	1·0

parison of Figs 1 and 2 clearly shows that the difference method allows better evaluation of the results than the baseline method. The inaccuracy of the baseline method, namely in the region of 3003 cm^{-1} is clearly seen in Fig. 2 showing the spectrum of Diene 35 NFA. Similar shortcoming of the baseline method, this time illustrated on polybutadiene Št-I-69 (967 cm^{-1} band), is shown in Fig. 4. This polymer has rather high concentration of 1,2 addition units. Similarly the problem of evaluation by the baseline method at 967 cm^{-1} follows from Fig. 5, where the spectrum of polybutadiene containing high concentration of cis-1,4 form is shown.
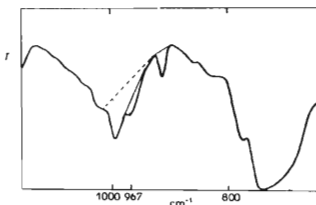

Fig. 5

Spectrum of cis-1,4 Polybutadiene
2·8% Solution in carbon disulphide.

The comparison of analyses results where all the three methods were used indicates, that whenever low concentrations of a measured unit is present, the classical methods give lower values than the method based on measuring the absorption due to valence vibration. The smallest differences between the values of trans-1,4 units content determined by the difference method (using the valence vibrations) and the baseline method (using the deformation vibrations), have been observed in the cases of Diene-NFA and Intene NF-A, resp. These polymers contain 50% of trans-1,4 units. Substantially greater differences are seen in the case of polymers containing predominantly cis-1,4 form but low concentration of trans-1,4 units.

The results obtained by the difference method employing absorption bands due to valence vibration are believed to be more correct because we assume that the extinction coefficients of these vibrations are less influenced by vicinal units of other types than in the case of deformation vibrations. The extinction coefficients of standards correspond to a polymer in which each unit is surrounded by identical units. Extreme cases of alternating polymers have shown, that the extinction coefficients of deformation vibrations markedly differ from these values. Hence, the lower concentration of these units, the greater probability of their isolation thus resulting into a lower accuracy of their determination on the basis of the absorption due to deformation vibration.

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FLOWING-BOUNDARY DIFFUSION CELL
AND THE DETERMINATION OF ZERO-TIME CORRECTION
IN FREE DIFFUSION MEASUREMENTS IN VERY DILUTE POLYMER SOLUTIONS
WITH A POLARIZATION INTERFEROMETER

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One of the decisive conditions of a successful measurement of free diffusion in solutions is an appropriate cell, which allows to form, at the beginning of the experiment, as perfect a boundary as possible between the solutions under investigation, thus approaching as much as possible the initial conditions $c = c_2^0$ for $x \leqq 0$ and $c = c_1^0$ for $x > 0$ at $t = 0$. As a number of authors have shown[1-4], best results are obtained with cells in which the boundary is formed by a slow outflow of the solution and the solvent through a narrow horizontal slit. In this way, the initial rough boundary is sharpened in the plane of the slit; the time $t = 0$ is given by the closing of the outflow. The sharpening can also be accomplished[5-8] by inserting a fine capillary from above into the centre of the measuring space; the solvent is then sucked through the capillary at a constant rate, and the capillary is slowly removed when the sharpening is completed. The latter method, however, is less suitable from the hydrodynamic point of view[7]; it is also hardly possible to avoid certain disturbances while removing the capillary.

The cells described above, although for the present being the best available, do not yield an ideally sharp boundary, so that the initial conditions cannot be perfectly met. The arising error is eliminated by introducing the so-called zero-time correction Δt (defined as the time necessary for the diffusion to proceed from a hypothetical, ideally sharp boundary until the moment at which the measurement begins); this value ought to be added to the measured time t. The calculation of the diffusion coefficient in which experimental times are used yields time-dependent quantities D' which with increasing t approach the correct value; the correction Δt is obtained together with