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LA103-E003
● SPECTROPHOTOMETRIC ANALYSIS
No.A321

Quantitative analysis of cis, trans, and vinyl in polybutadiene using the single-reflection ATR accessory

Application News No. A308, A304, A299, A294, and A271 previously introduced that the single-reflection ATR accessory is widely used, for qualitative analysis in particular, as it requires no pretreatment, can handle any sample shape, can analyze small sample volumes, and causes minimum damage to the prism. As an example of quantitative analysis, this Application News introduces the microstructural analysis of polybutadiene with the diamond-prism single-reflection ATR accessory (DuraSamplIR).

■ Polybutadiene

Polybutadiene is a generic term for 1,3-butadiene polymer having plastic and rubber properties. It exists with three different structures: cis (cis-1,4-polybutadiene), trans (trans-1,4-polybutadiene), and vinyl (1,2-polybutadiene). Polybutadiene with plastic properties that contains many vinyl structures is used in wrapping film, and high-density cis-structure polybutadiene with rubber properties is used in rubber products such as tires and belts.

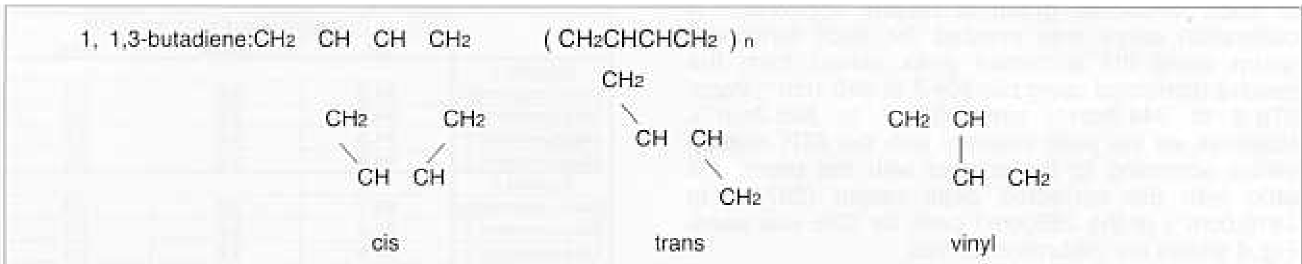

Fig.1 Polybutadiene

■ Infrared spectrum of polybutadiene

Fig. 2 shows the spectrum of polybutadiene with at least 90% cis content, measured with the DuraSamplIR. The 732.9cm^{-1} peak is the cis peak, the 912.3 cm^{-1} peak is the vinyl peak, and the 966.3 cm^{-1} peak is the trans peak.

Table 1 Analytical conditions

Resolution	:	4cm^{-1}
Accumulatic	:	40
Detector	:	DLATGS

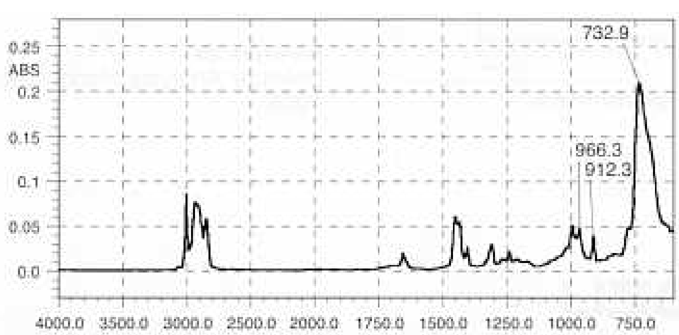

Fig.2 ATR spectrum of polybutadiene

■ Quantitative analysis of cis, trans, and vinyl in polybutadiene

Methods using NMR spectra and IR spectra are used to determine the proportions of cis, trans, and vinyl in polybutadiene. The Morero method using IR spectra is considered effective with a high cis content. This method involves transmission measurements of the sample dissolved to a certain concentration in carbon disulfide using a fixed cell with 1mm light-path length. The relative concentrations are calculated from the Ac, AT, and Av peak absorbance values for cis, trans, and vinyl, respectively, using the following expressions:

$$C=(1.7455Ac-0.0151Av) \quad -(1)$$

$$V=(0.3746Av-0.0070Ac) \quad -(2)$$

$$T=(0.4292A_T-0.0129Av-0.0454Ac) \quad -(3)$$

$$cis(\%)=C/(C+V+T)\times 100 \quad -(4)$$

$$trans(\%)=T/(C+V+T)\times 100 \quad -(5)$$

$$vinyl(\%)=V/(C+V+T)\times 100 \quad -(6)$$

This method uses transmission measurements with a fixed cell to achieve good sensitivity, and quantitative analysis with dispersive IR is also possible. However, tasks of weighing and dissolving the sample and cleaning the cell are unavoidable and a certain amount of carbon disulfide is required. The ATR method permits direct measurement, eliminating the need for pretreatment, and clean up involves just wiping the prism with a small amount of alcohol.

Fig. 3 shows the results of measuring four types of polybutadiene (each with 90% minimum cis concentration) with different, but known, concentration using the DuraSamplIR. The concentration difference of each functional group is clearly apparent. A calibration curve was created for each functional group using the corrected peak values from the spectra (corrected using cis: 804.7 to 640.1cm^{-1}; trans: 978.8 to 944.9cm^{-1}; vinyl: 927.7 to 895.2cm^{-1}). However, as the peak intensity with the ATR method varies according to the contact with the prism, the ratio with the corrected peak height (2873.3 to 2816.0cm^{-1}) of the 2850cm^{-1} peak for CH_2 was used. Fig. 4 shows the calibration curves.

Next, each type of polybutadiene was measured three times for quantitation of each functional group concentration.

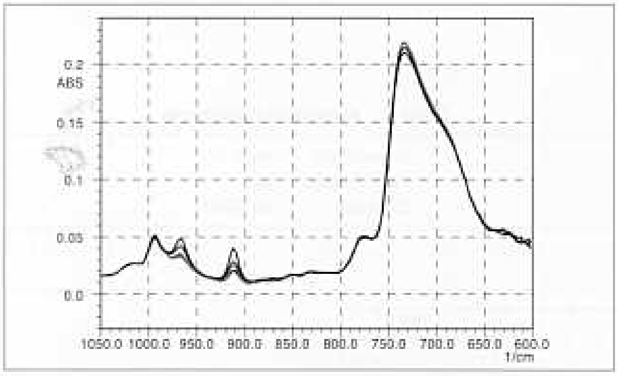

Fig.3 ATR spectra of polybutadiene

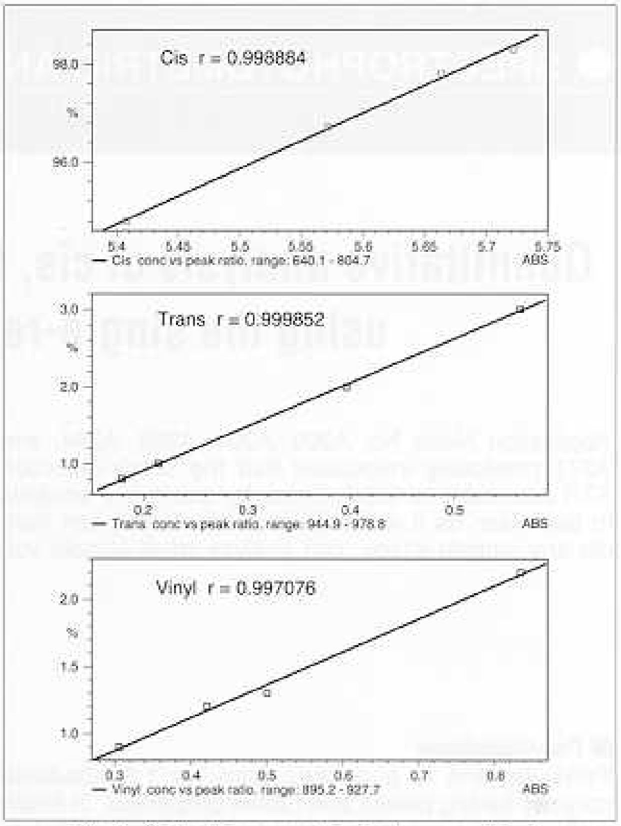

Fig.4 Calibration curves for cis, trans, and vinyl

Table 2 Quantitation results

	Corrected quantitation result (%)		
	cis	trans	vinyl
Sample 1			
Known concentration	94.8	3.0	2.2
Measurement 1	94.8	3.0	2.2
Measurement 2	94.8	3.0	2.2
Measurement 3	94.8	3.0	2.2
Sample 2			
Known concentration	96.7	2.0	1.3
Measurement 1	96.6	2.0	1.4
Measurement 2	96.6	2.0	1.4
Measurement 3	96.6	2.0	1.4
Sample 3			
Known concentration	97.8	1.0	1.2
Measurement 1	97.8	1.0	1.2
Measurement 2	97.8	1.0	1.2
Measurement 3	97.8	1.0	1.2
Sample 4			
Known concentration	98.3	0.8	0.9
Measurement 1	98.3	0.8	0.9
Measurement 2	98.3	0.8	0.9
Measurement 3	98.3	0.8	0.9

In a similar way to the Morero method, the quantitation results were corrected using equations (4) to (6) to give a total concentration of 100%. The results are listed in Table 2.

The quantitation value and repeatability were excellent for each sample.

References

Polymer Analysis Handbook, Kinokuniya, First Edition 1995

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