

Microstructural analysis of polybutadienes

Benefits at a glance

- Non-destructive analysis with no sample preparation
- High information content: distinct bands for each isomer
- Reproducibility

Introduction

Polybutadienes are among the most important industrial polymers,^{1,2} accounting for over 4 billion pounds of rubber and 2 billion pounds of Among rubbers, only styrene-butadiene rubber (a butadiene copolymer) is produced in greater quantity. Polybutadiene's resiliency makes it ideal for high-stress applications, such as the treads and sidewalls of tires and the cores of golf balls.

The 1,3-butadiene monomer can undergo two different polymerization reactions: 1,2- and 1,4-polymerization. In most systems, both reactions occur and the product contains a mixture of structure types.

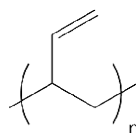
1,2-Polymerization



1,3-butadiene monomer

The less important reaction is 1,2-polymerization.

The product of 1,2-polymerization has a polyethylene backbone with a pendant vinyl group. The unsaturation is located in the side chain. The pendant vinyl group is on an asymmetric carbon atom, so the polymer can be isotactic, syndiotactic, or atactic. High-vinyl polybutadienes tend to be less thermally stable than those with lower vinyl content.

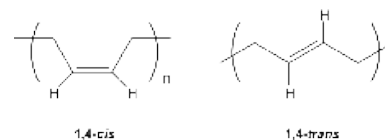


1,2-vinyl

Atactic high-vinyl polybutadiene can be produced by adding *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the reaction solution, forming a complex with the lithiated living chain ends and favoring 1,2-addition.

1,4-Polymerization

The more important polymerization reaction of buta-dienes is 1,4-polymerization.



This reaction is generated by anionic polymerization in non-polar solvent with alkyl lithium initiators. The products of 1,4-polymerization retain a double bond in the backbone. The two possible products are 1,4-*cis*- and 1,4-*trans*-polybutadiene. The *cis* isomer has a lower T_m and T_g and lower crystallinity than the *trans* isomer and is an excellent elastomer. High *cis* polybutadiene exhibits excellent cut growth resistance (resistance to the expansion of a cut, tear, or crack when the material is in use), which is especially important in tires.

Spectroscopy of polybutadienes

Several spectroscopic methods have been used to determine microstructure in polybutadiene samples,² including ^1H and ^{13}C NMR, IR, and Raman spectroscopy. By comparing these different spectroscopic methods, Frankland et al. showed that only ^{13}C NMR and Raman yield reproducible, accurate results.

① All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

Nuclear magnetic resonance spectroscopy

Both ^1H NMR and ^{13}C NMR have been used to analyze polybutadienes. The major drawback to ^1H NMR is that the 1,4-*cis* and 1,4-*trans* olefinic proton peaks, which are found near 5.4 ppm, can be difficult to resolve without using high frequencies. However, this region can be used to determine the 1,4 and 1,2-vinyl content by comparing it to the 1,2-vinyl peaks around 4.9 ppm.

^{13}C NMR, unlike ^1H NMR, can be used to distinguish 1,2-vinyl, 1,4-*cis*, and 1,4-*trans* units. The ^{13}C NMR data requires about 12 hours a major drawback if this method is to be used in quality control at the process line.

Infrared spectroscopy

IR has been used successfully to monitor polymerization reactions, but is less suitable for polybutadiene microstructure determination. The 1,4-*trans* $\nu(\text{C}=\text{C})$ vibration has a center of symmetry, so it is symmetry forbidden and cannot be observed in the IR. The microstructure has to be determined using other criteria. Several methods have been proposed. The $\delta(\text{C}-\text{H})$ bending modes of each of the three microstructural units can be detected using IR, but because the corresponding spectral bands result from combinations of the three microstructures and possibly other structures as well, deriving information from them is very difficult. Several methods have been developed for IR analysis of butadiene, but the results are inconsistent between methods and the results obtained by IR are often at variance with the results from NMR and Raman spectroscopy.²

Raman spectroscopy

Raman spectroscopy is especially useful for characterizing polybutadienes because the $\nu(\text{C}=\text{C})$ bond stretching of 1,2-vinyl, 1,4-*cis*, and 1,4-*trans* units are strong Raman scatterers. These vibrations generate strong Raman bands at 1639, 1650, and 1664 cm^{-1} , respectively. Because Raman scattering intensity is directly proportional to sample concentration, the intensities of these bands can be used for quantitative analysis of a polybutadiene sample. Because the bands overlap, multivariate analyses or curve-fitting techniques are normally employed to obtain accurate measurements of band areas.

Figure 1 shows the Raman spectral region used to identify the microstructure of polybutadiene. The Raman spectrum was acquired with a Raman analyzer, using a 785 nm NIR laser and three averaged 5 second acquisitions. Curve fitting was performed using the GRAMS™ software package. The curve-fitting algorithm assumed a Gaussian band shape. The data obtained by Raman is reproducible to within $\pm 1\%$.² The sampling options are compatible with *in situ* process monitoring.

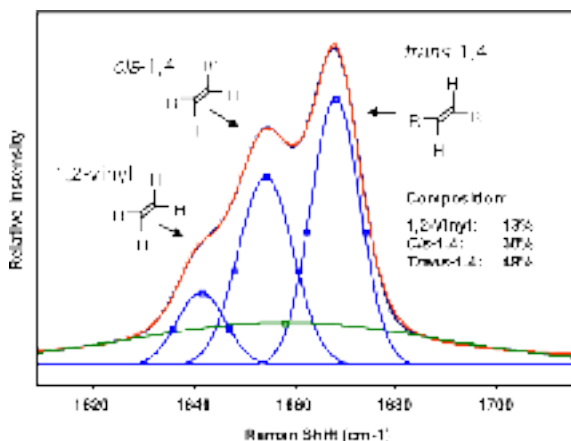


Figure 1: Raman spectral region used to identify microstructure of polybutadienes. The red curve is the original Raman data and the blue curves indicate the bands derived by curve fitting. The green curve is assigned to the baseline.

Conclusion

Raman spectroscopy is the clear choice for determining the microstructure of polybutadiene samples, especially for process applications. It is sensitive to the concentrations of all three major types of poly-butadienes and yields useful, quantitative information in minutes with excellent reproducibility.

Reference

1. International Institute of Synthetic Rubber Products (IISRP). "What is Synthetic Rubber?" <http://www.iisrp.com/synthetic-rubber.html> (accessed March 2003).
2. Frankland, J.A.; Edwards, H.G.M.; Johnson, A.F.; Lewis, I.R.; Poshychinda, S. "Critical assessment of vibrational and NMR spectroscopic techniques for the microstructure determination of polybuta-dienes." *Spectrochimica Acta*, Vol. 47A, **1991**, 1511.