Research Article

Fourier Transform Infrared Spectral Analysis of Polyisoprene of a Different Microstructure

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Some polyisoprene samples of different microstructure contents were studied by Fourier transform infrared (FTIR) and 1 H NMR. On the basis of detailed analysis of FTIR spectra of polyisoprene, the shift of absorption peaks caused by microstructure content’s variation was discussed. The contents of the polyisoprene samples’ microstructure which was determined by the 1 H NMR was used as the standard. Through the choice, calculation, and comparison with the corresponding absorption peaks of FTIR, a method based on the results of the analysis has been developed for the determination of the microstructure contents of polyisoprene by FTIR.

1. Introduction

As it is well known, polyisoprene (PIp) is one kind of important rubbers, and there are four kinds of microstructure in its molecular chain which are cis-1,4-, trans-1,4-, 1,2-, and 3,4-polyisoprene. The main ingredient of nature rubber is cis-1,4- or trans-1,4-polyisoprene. For example, Hevea brasiliensis (the Brazilian rubber tree) is polyisoprene with more than 5,000 cis-1,4-repeat units except for the transinitiator residue of repeat units ranging from 1 to 4, depending on the plant species. Gutta-percha, Balata, or Malaysian rubber is polyisoprene with trans-1,4-repeat units [1–4]. Since English chemist Michael Faraday found that the structure unit of nature rubber was C5H8, the research of synthetic polyisoprene keeps active [1–7].

Except for the synthesis of high content of cis-1,4- or trans-1,4-polyisoprene to imitate and replace nature rubber, the research on synthesis of polyisoprene with variable microstructure contents keeps attractive in order to obtain some materials of special properties. For example, with 3,4-unit content’s increasing, the curing rate and low temperature properties of polyisoprene decrease, but hardness and elasticity increase, as well as tensile properties, tension set, and tearing strength maintain are slightly changed. Particularly, the water resistance and hermeticity of polyisoprene with high 3,4-unit content can compare with butyl rubber [8–11]. The application of polyisoprene with high 3,4-unit content in tread can improve the skidding resistance, traction property, and cutting growing resistance and also can decrease the generation of heat by friction So it is the new varieties of rubber for a fuel-saving, environmental protection and safety tire.

Most of the studies on microstructure of polymers are characterized by nuclear magnetic resonance (NMR) spectrophotometer and FTIR [12, 13]. The first extensive IR spectroscopic studies of synthetic polyisoprenes were undertaken by Binder, Cornell, and Koenig. In comparison with other polymers, much less work has been reported on polyisoprene [14]. In this paper, polyisoprenes of some different microstructure content are analyzed by FTIR in details. Through comparison the intensity of corresponding microstructure characterization peak in FTIR with in NMR, the experience relation equation is founded and the method of calculating the microstructure content of polyisoprene by FTIR is also established.
2. Experimental

2.1. Materials. All the polyisoprene samples with variable microstructure content were polymerized according to [15–18].

2.2. Characterization

2.2.1. FTIR. Tensor 27 (Bruker, German) has been used in the analysis. The samples are tested by ATR-FTIR, with 4 cm\(^{-1}\) resolution, and scanned 32 times.

2.2.2. \(^1\)H NMR. AV 500 (Bruker, German) has been used in the analysis. \(^1\)H NMR spectra of the polyisoprene in CDCl\(_3\) were obtained at 500.13 Hz, and chemical shifts were referred to TMS.

The \(^1\)H NMR spectrum of polyisoprene which contains 1,4-, 1,2-, and 3,4-unit is shown in Figure 1. \(\delta 5.2 \sim 5.0\), \(\delta 5.0 \sim 4.8\), and \(\delta 4.8 \sim 4.6\) peak areas are assigned to the olefinic hydrogen of 1,4-, 1,2-, and 3,4-unit, respectively. Determining the intensity of these spectral lines, then calculating 1,4-, 1,2-, and 3,4-unit content with formula (1), and the results are shown in Table 1:

\[
X_{1,4-\text{Pip}} = \frac{\int \delta 5.2 \sim 5.0}{\int \delta 5.2 \sim 5.0 + \left( \int \delta 5.0 \sim 4.8 + \int \delta 4.8 \sim 4.6 \right)/2} \times 100\%
\]

\[
X_{1,2-\text{Pip}} = \frac{\int \delta 5.0 \sim 4.8/2}{\int \delta 5.2 \sim 5.0 + \left( \int \delta 5.0 \sim 4.8 + \int \delta 4.8 \sim 4.6 \right)/2} \times 100\%
\]

\[
X_{3,4-\text{Pip}} = \frac{\int \delta 4.8 \sim 4.6/2}{\int \delta 5.2 \sim 5.0 + \left( \int \delta 5.0 \sim 4.8 + \int \delta 4.8 \sim 4.6 \right)/2} \times 100\%
\]

3. Results and Discussion

3.1. Analysis of FTIR Spectra of Polyisoprene. Polyisoprene has four kinds of microstructure which are cis-1, 4-, trans-1, 4-, 1, 2-, and 3, 4-polyisoprene, as shown in Figure 2.

Figure 3 shows seven FTIR spectra of polyisoprene with different microstructure content.

The characterization and attribution peaks of FTIR spectra of polyisoprene are listed in Table 2.

It can be seen from Figure 3 and Table 2 that the difference of FTIR behavior of the polyisoprene microstructures is obvious. However, only 910, 888, and 840 cm\(^{-1}\) peaks can be used for quantitative calculation of microstructure content of polyisoprene. It is because that the peaks for quantitatively calculation must have moderate intensity, little interfering factors by other peaks or conditions, and so on. Except for those differences shown in Table 2, Table 3 shows some frequency excursion caused by microstructure content changing.

3.2. Quantization Calculation of Microstructure Content of Polyisoprene by FTIR. According to the Beer-Lambert law, the integrated intensity \(A\) of a characteristic band can be expressed as follows:

\[
A = bc \int_0^{\infty} \epsilon (v) \, dv.
\]

Here, \(\epsilon\) is the absorption coefficient, \(b\) is the thickness, \(c\) is the concentration, and \(v\) is the wavenumber.

Choosing a peak which has moderate intensity and is not affected by configuration, conformation or other structure factors as internal standard of thickness, then formula (2) can be changed to the following:

\[
[A] = \frac{A_1}{A_0} = c_1 \left[ \int_0^{\infty} \epsilon (v_1) \, dv_1 \right] \cdot \frac{\int_0^{\infty} \epsilon (v_0) \, dv_0}{ \left[ \int_0^{\infty} \epsilon (v_0) \, dv_0 \right]} = c_1 \cdot k.
\]

Here, “1” means characteristic band and “0” means internal standard band. “K” is the correction factor and can be calculated by \(^1\)H NMR dates. As described above, 910, 888, and 840 cm\(^{-1}\) peaks can be used for quantitatively calculating microstructure content of polyisoprene. Table 2 shows that there is seldom peak which can meet the request of internal standard peak. In this paper, 2727 cm\(^{-1}\) is used as internal standard peak. The integrated intensity \(A\) are calculated by the software of FTIR, and the integration methods are shown in Figure 4.
Figure 2: The structural formula of polyisoprene.

Table 2: The explanation of absorption peaks of FTIR spectrum of polyisoprene.

| Wavenumber/cm$^{-1}$ | Attribution | Wavenumber/cm$^{-1}$ | Attribution |
|----------------------|-------------|----------------------|-------------|
| 3080                 | –C–H stretching vibration of carbon-carbon double bond in 1,2-unit | 1150        | Stretching vibration of CC main chain in trans-1,4-unit |
| 3070                 | CH$_3$ stretching vibration of –C≡C– in 3,4-unit | 1140        | Stretching vibration of CC main chain in cis-1,4-unit |
| 3035                 | CH stretching vibration of –C≡C– in 1,4- or 1,2-unit | 1044        | Stretching or wagging vibration of CH$_3$C≡C in trans-1,4-unit |
| 2727                 | Sympathetic vibration | 1036        | Stretching or wagging vibration of CH$_3$C≡C in cis-1,4-unit |
| 1663                 | C≡C stretching vibration of 1,4-unit | 1003        | Stretching vibration of C–C in 3,4-unit |
| 1644                 | C≡C stretching vibration of 3,4- or 1,2-unit | 910         | Out-of-plane bending vibration of CH$_3$ in the –CH=CH$_2$ (1,2-unit) |
| 1413                 | Bending vibration of C–H in the =CH$_3$ group of 3,4- or 1,2-unit | 888         | Out-of-plane bending vibration of CH$_2$ in the –C=CH$_2$ (3,4-unit) |
| 1383                 | Scissoring vibration of CH$_3$ in trans-1,4-unit | 843         | Out-of-plane bending vibration of C–H in the –CH=CH– group of trans-1,4-unit |
| 1375                 | Scissoring vibration of CH$_3$ in cis-1,4-, 3,4- and 1,2-units | 837         | Out-of-plane bending vibration of C–H in the –CH=CH– group of cis-1,4-unit |
| 1325                 | Scissoring vibration of CH$_3$ or CH in trans-1,4-unit | 600         | Torsion or twisting vibration of CCC group in trans-1,4-unit |
| 1311                 | Scissoring vibration of CH$_3$ or CH in cis-1,4-unit |             |             |

Table 3: The change of peaks of FTIR spectra according to the microstructure contents of polyisoprene.

| Explanation\peak value | Spectrum A | Spectrum B | Spectrum C | Note |
|------------------------|------------|------------|------------|------|
| Microstructure content |            |            |            |      |
| 3,4-unit%              | 5          | 24         | 67         | 3,4-unit% increase by progressively |
| 1,2-unit%              | 5          | 23         | 15         | 1,2-unit% increase by degrees |
| 1,4-unit%              | 90         | 53         | 18         | 1,4-unit% decrease by degrees |
| Dissymmetry stretching vibration of –CH$_3$ | 2962.125 | 2964.053 | 2965.982 | Blue shift of peak (the value is 2978 cm$^{-1}$ in trans-1,4-unit) |
| C≡C stretching vibration | 1644.982 | 1644.018  | 1643.054  | Red shift of peak |
| Scissoring vibration of CH$_3$ | 1376.925 | 1374.997  | 1374.033  | Red shift of peak (the value is 1383 cm$^{-1}$ in trans-1,4-unit) |
| Out-of-plane bending vibration of CH$_3$ in the –C=CH$_2$ (3,4-unit) | 889.023 | 888.059  | 887.095  | Red shift of peak |
| Out-of-plane bending vibration of C–H in the –CH=CH– group of 1,4-unit | 836.955 | 840.812  | 848.849  (flat top) | Blue shift of peak |
Figure 3: FTIR spectra of polyisoprenes of variable microstructure content. (A) cis-1,4- = 100% 3,4- = 0% 1,2- = 0%; (B) trans-1,4- = 99.6% 3,4- = 0.2% 1,2- = 0.2%; (C) 1,4- = 90% 3,4- = 5% 1,2- = 5%; (D) 1,4- = 53% 3,4- = 24% 1,2- = 23%; (E) 1,4- = 30% 3,4- = 59% 1,2- = 11%; (F) 1,4- = 24% 3,4- = 63% 1,2- = 13%; (G) 1,4- = 18% 3,4- = 67% 1,2- = 15%.

Figure 4: Samples of absorption values of peaks of polyisoprene.

Figure 5: The absorption coefficient calculation of (a) 910 cm\(^{-1}\), (b) 888 cm\(^{-1}\), and (c) 840 cm\(^{-1}\) peaks of FTIR spectra of polyisoprene.

The samples shown in Table 1 are calculated with this method, and the results are given in Figure 5.

After regression of measured points of testing points based on a least-squares method, the formula of microstructure content is shown as follows:

\[
\begin{align*}
X_{1,2,\text{PIp}} &= 2.21[A]_{910\text{ cm}^{-1}} - 6.10, \\
X_{3,4,\text{PIp}} &= 1.92[A]_{888\text{ cm}^{-1}} - 3.40, \\
X_{1,4,\text{PIp}} &= 6.55[A]_{840\text{ cm}^{-1}} + 2.29.
\end{align*}
\]  

Because of 910, 888, and 840 cm\(^{-1}\) peak overlaps partly, the errors of calculated values of integrated intensity \(A\) will increase when the peak’s intensity is too small. Therefore, the
microstructure content shall be calculated with two higher peaks. In the 1,2- and 3,4-unit, the double bond is on the branched chain and belongs to asymmetry substitute, so their dipole moment's shift is bigger than that of 1,4-unit. As a result, the integrated intensity of 910 and 888 cm^{-1} peak is far stronger than 840 cm^{-1} peak when the contents of their corresponding units are the same. Therefore, the calculation of microstructure content of polyisoprene shall choose the former two peaks.

4. Conclusion

The change of microstructure content of polyisoprene can cause a lot of differences in FTIR spectra. The described method by FTIR can be used to determine the microstructure content of polyisoprene. 910 and 888 cm^{-1} peaks of 1,2- or 3,4-unit have higher absorption ability than 840 cm^{-1} peaks of 1,4-unit; therefore 910 and 888 cm^{-1} peaks shall be used first for the quantitative analysis of microstructure content of polyisoprene. The quantitative calculation formulas were also obtained.

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