

# Determination of the Microstructure of Polybutadiene-ol Back-bone by FTIR and NMR Spectroscopy

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## ABSTRACT

The properties of polyurethanes strongly depend on the microstructure, functionality, and molecular weight of their initial polyol used. Therefore, in this work, microstructure of polybutadiene-ol, a pre-polymer used for producing special purpose polyurethanes was determined by two analytical methods, namely, FTIR and <sup>1</sup>H NMR spectroscopy. In the FTIR method, after obtaining  $\epsilon_i$  (molar absorption in each wavelength) of a specified polyol, the microstructure (*trans*, *vinyl* and *cis* content) of pre-polymer was measured by analyzing IR absorption bands in 966  $\text{cm}^{-1}$ , 912  $\text{cm}^{-1}$ , and 725  $\text{cm}^{-1}$  due to *trans*, 1,2-*vinyl* and *cis* configurations, respectively. In the <sup>1</sup>H NMR spectra of polyols, microstructure was determined using the ratio of peak areas of various protons (alkylic, olefinic and methylenic) as well as signals at 2.5-4.5 ppm which indicate the position of hydroxyl groups in the back-bone of the polyol. Determination by NMR spectroscopy is an easier method and the information obtained on microstructure of the polyol is more precise than the FTIR method. Finally we established an equation to convert values obtained by FTIR to NMR.

### Key Words:

polybutadiene-ol;  
microstructure;  
hydroxyl terminated;  
IR absorption;  
<sup>1</sup>H NMR.

## INTRODUCTION

Butadiene polyol is a low viscosity colourless polyol with number average molecular weight of 1,500-10,000 g/mol, being used in production of foams, unsaturated polyesters as well as polymer additives. Polyurethanes which are prepared

with these polyols exhibit excellent properties such as high abrasion resistance, high hydrolytic stability and good low-temperature flexibility, are being used as special purpose polyurethane elastomers.

Their molecular chains contain

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sufficient double bonds for further cross-linking reactions [1-3]. The type and properties of final products, in the form of elastomeric and thermosetting networks, very much depend on the microstructure, functionality, and molecular weight of the initial polyol used. Chemical structure of polybutadiene consists of three major configurations: *cis*, *trans*, and *1,2-vinyl* (*isotactic* and *syndiotactic*) isomers.

The contents of these configurations in the backbone of polymer chain as well as their distribution are effective parameters on the end-use of products and specially affecting the low temperature properties .

FTIR and  $^1\text{H}$  NMR spectroscopy are useful methods for measuring OH-number and functionality [4] as well as determining the microstructure of this type of polyol.

By FTIR analysis method the contents of *trans*, *1,2-vinyl* and *cis* are determined by analyzing the appropriate absorption bands in the  $966\text{ cm}^{-1}$ ,  $912\text{ cm}^{-1}$ , and  $725\text{ cm}^{-1}$  regions, respectively [5].

By NMR analysis method, the microstructure of polyol is obtained through measuring the ratio of peak areas of different types of protons such as: *trans* or *cis* alkylic at 2 ppm, *trans* or *cis* olefinic at 5 ppm and methylenic at 1.2 ppm [6,7]. Signals at 2.5 to 3.5 ppm region are related to protons adjacent to hydroxyl groups, which are detected precisely by a 500 MHz  $^1\text{H}$  NMR and specify the position of hydroxyl groups of polyol [8].

In this work the microstructure of various synthesized butadiene polyols were determined by both FTIR and 500 MHz  $^1\text{H}$  NMR spectroscopy and the results were interpreted.

## EXPERIMENTAL

### Materials

Butadiene polyol with different microstructures (A,B, and C samples) were prepared locally [9].

Butadiene polyol (sample K) with a known microstructure was purchased from Aldrich with microstructure T/V/C as 60/20/20.  $\text{CS}_2$ , *o*-dichlorobenzene, KBR, 2-propanol, 1,3-butadiene were purchased from Merck and  $\text{H}_2\text{O}_2$  (35%) from Degusa. All materials were used as received.

### Equipment

A Bruker 500  $^1\text{H}$  NMR spectrometer with TMS as internal reference was examined at 100°C.

A Bruker IFS-48 FTIR spectrometer was based on 10 scans per second with liquid cell (NaCl) of 0.05 cm in thickness.

A 1000-mL jacketed stainless steel reaction vessel (Buchiglususter bep 280) was equipped with three valves (one for monomer charge and others for polymer discharge and to purge off the unreacted butadiene), and a magnetic field driven stirrer, an anchor stirrer shaft, a rupture element, a manometer, a hot oil circulator (Haake) and a temperature probe were used.

### Preparation Method

Polybutadiene-ol was prepared in a 1000-mL jacketed stainless steel reaction vessel, by free radical polymerization of butadiene initiated by hydrogen peroxide (35 %) in 2-propanol as solvent. For carrying out the polymerization,  $\text{H}_2\text{O}_2$  was weighed followed by dilution in 2-propanol in the reactor (under  $\text{N}_2$ ).

Butadiene was condensed under pressure into the reactor and the heater, the stirrer and oil circulation around the reactor jacket were switched on. The oil heating rate was about 10°C/min. The stirring speed of the magnetic stirrer and the reactor temperature were adjusted at  $280\text{ min}^{-1}$  and 115°C, respectively as recommended. After 100 min the reactor was cooled immediately, the pressure was then dropped to around 2 bars, and the unreacted monomer was purged out and the liquid was drained off the vessel through the bottom valve. The liquid was stored overnight followed by separation of the two liquid phases (one aqueous and one non-aqueous). The product (non-aqueous phase) was purified by evaporation under vacuum (600 mbar) at 40 overnight [9].

### FTIR Method

As shown in Figure 1, *trans*-polybutadiene, *1,2-vinyl*-polybutadiene and *cis*-polybutadiene, are different in the observed peaks in wavelengths between 9 and 15 micrometers ( $600\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$ ), however, location of low *cis* has been shifted from  $740\text{ cm}^{-1}$  to  $725\text{ cm}^{-1}$ . At first,  $\epsilon$  (molar absorption) was calculated for each of corresponding wavenumbers using polyol of known microstructure through the Langmuir law.

Then the microstructure of polyols was determined

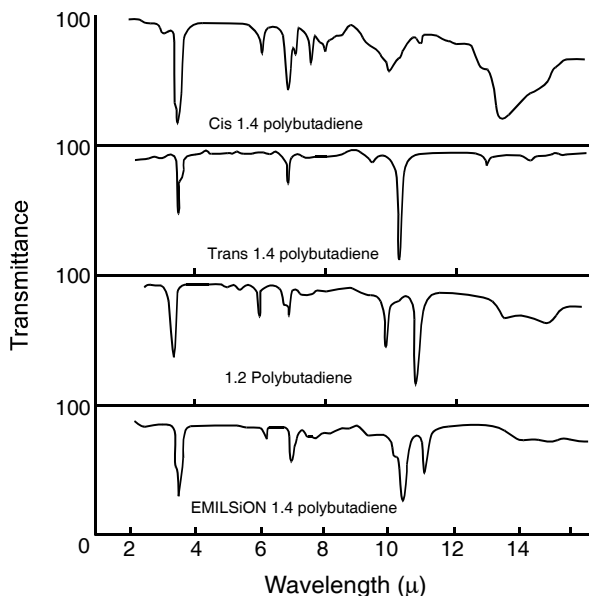


Figure 1. IR Spectra of *cis*, *trans* and 1,2-*vinyl* of polybutadiene.

using the magnitude of absorption in the appropriate wavelength of unknown sample.

Since absorption is directly proportional to the concentration, the content of different configurations are obtainable.

### Determination of the Molar Absorption and Absorption

Since no absorption was observed at 660-850  $\text{cm}^{-1}$  and 860-1400  $\text{cm}^{-1}$  regions of the FTIRs spectrum or any overlap with polymer bands in the FTIR spectrum of carbon disulphide [10],  $\text{CS}_2$  was chosen as a solvent (Figure 2). A solution of 0.024 g/L in concentration of the known microstructural butadiene polyol (K) was prepared. Then, FTIR spectrum was obtained using liquid cell. The following equations were used for determination of  $\epsilon$  and A.

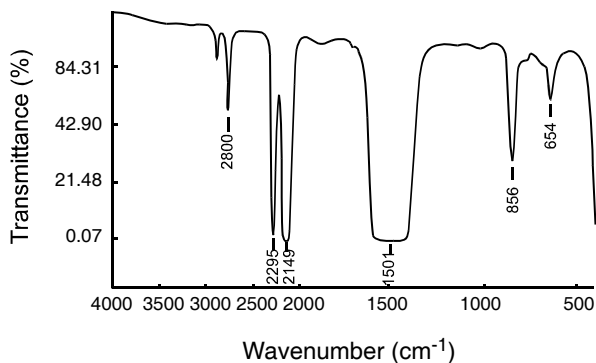


Figure 2. FTIR Spectrum of  $\text{CS}_2$ .

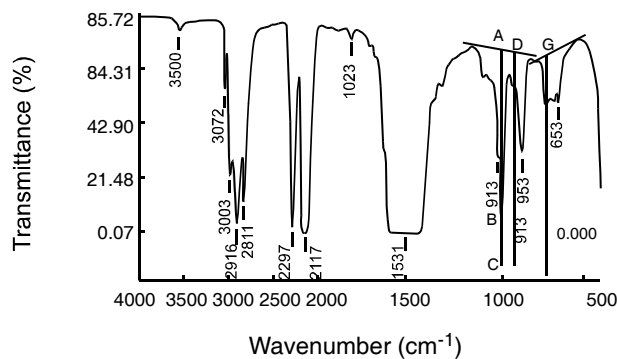


Figure 3. FTIR Spectrum of solution of sample K in  $\text{CS}_2$ .

where,

A = absorption; T = transmission.

where,

$A_i$  = absorption in each wavenumber;

$$A = \frac{1}{T} \quad (1)$$

$$\epsilon_i = \frac{A_i}{LC_i} \quad (2)$$

$\epsilon_i$  = molar absorption in each wavenumber;

L = cell width; and

$C_i$  = concentration of isomer in K.

According to eqn (1), using the magnitude of absorption in each peak and using eqn (2) (As shown in the Figure 3 and eqns (3-5)) for sample K,  $\epsilon$  at each wavenumber was calculated as follows:

$$\text{Trans} (\%) = \frac{\frac{A_1}{\epsilon_1}}{\frac{A_1}{\epsilon_1} + \frac{A_2}{\epsilon_2} + \frac{A_3}{\epsilon_3}} \quad (6)$$

$$\text{1,2-Vinyl} (\%) = \frac{\frac{A_2}{\epsilon_2}}{\frac{A_1}{\epsilon_1} + \frac{A_2}{\epsilon_2} + \frac{A_3}{\epsilon_3}} \quad (7)$$

$$\text{Cis} (\%) = \frac{\frac{A_3}{\epsilon_3}}{\frac{A_1}{\epsilon_1} + \frac{A_2}{\epsilon_2} + \frac{A_3}{\epsilon_3}} \quad (8)$$

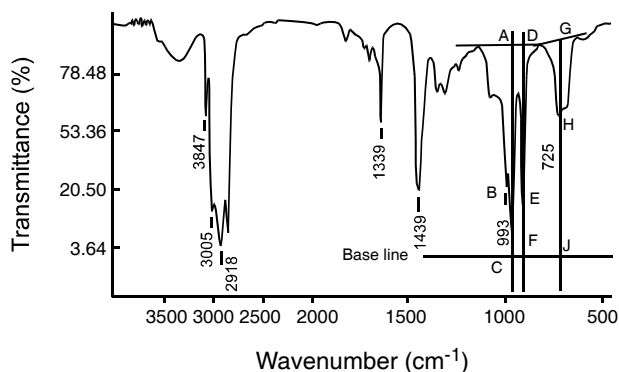


Figure 4. FTIR Spectrum of sample A.

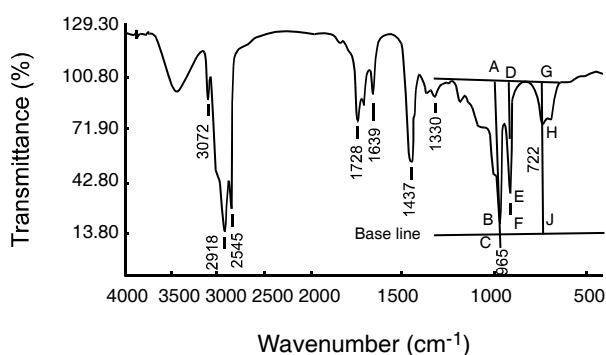


Figure 5. FTIR Spectrum of sample B.

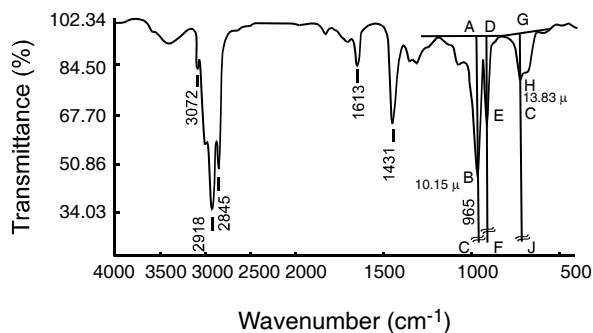


Figure 6. FTIR Spectrum of sample C.

$$\epsilon_{966} = 48$$

$$\epsilon_{912} = 81$$

$$\epsilon_{725} = 11$$

The absorption in each wavelength was calculated as follows:

$$A_1 = A_{966} = \log AC/BC$$

$$A_2 = A_{912} = \log DF/EF$$

$$A_3 = A_{725} = \log GI/HJ$$

Where, AC, BC, DF, EF, GJ and HJ are specified in Figures 3-6, Then, the obtained  $\epsilon$  and A were used to

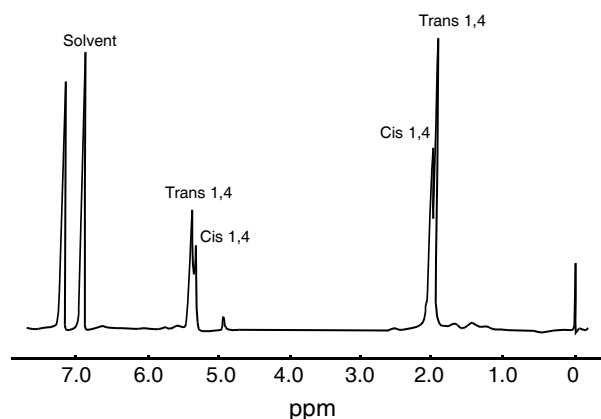


Figure 7. Portion  $^1\text{H}$  NMR spectrum of polybutadiene.

calculate the content of configurations (as %) as follows:

### NMR Method

To analyze the polyol by NMR method, samples were dissolved in 1,2-dichlorobenzene (5g/100mL). 1,2-dichlorobenzene was chosen as solvent since no absorption was observed in 1-7 ppm region of the NMRs spectrum or any overlap with polymer bands [10]. For locking, deuterated chloroform was used.

Figure 7 gives an illustration of  $^1\text{H}$  NMR spectrum of polyol. The resonance groupings centered at 1.4, 2, 4, 5.4, and 5.6 ppm represent 1,2-methylene, 1,4-methylene, hydroxyl, 1,2-terminal, 1,4-olefinic, and non-terminal vinyl protons, respectively [6,11]. The ratio of the peak area of the *trans* type protons to *cis* one in the 2 ppm or 5 ppm region indicates the value of ratio of *trans* to *cis* in the butadiene polyol.

Eqns (9) and (10) can be established between the peaks areas of olefinic protons to aliphatic protons [7].

$$\frac{I_{1.20}}{I_{2.10}} = \frac{2X}{X + 4Y} \quad (9)$$

$$X + Y = 1 \quad (10)$$

Where,  $I_i$  intensity, peak area of protons at  $i$  ppm,  $X$  is the *vinyl* content and  $Y$  is the total *cis* and *trans* content.

## RESULTS AND DISCUSSION

Figures 2 and 3 show FTIR spectra of  $\text{CS}_2$  and polyol solution in  $\text{CS}_2$ . Figures 4-6 show FTIR spectra of A, B

**Table 1.** Microstructure of samples A, B, C and K obtained by FTIR and <sup>1</sup>H NMR methods.

Sample	Content (%)	FTIR Method	<sup>1</sup> H NMR Method
A	<i>Trans</i>	53.11	48.12
	<i>1,2-Vinyl</i>	20.83	20.43
	<i>Cis</i>	21.03	31.44
B	<i>Trans</i>	54.5	45.9
	<i>1,2-Vinyl</i>	22	21.9
C	<i>Trans</i>	57	41.9
	<i>1,2-Vinyl</i>	18	17.3
K	<i>Trans</i>	58	50
	<i>1,2-Vinyl</i>	18	22
	<i>Cis</i>	24	28

(\*) A, B, C, Samples are synthesized with various microstructures.

and C samples (Table 1).

In each spectrum, adsorptions were calculated and then the content of various configurations was calculated according to eqns (5-7). Figures 8-10 show NMR spectra of A, B and C samples. By studying the values shown in these figures and eqn (9) the contents of various configurations were determined.

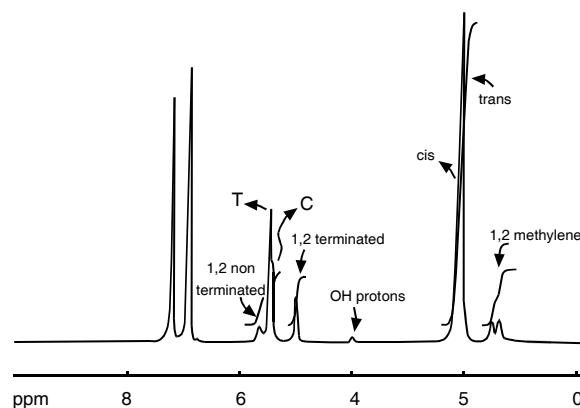
Table 1 presents the results of measured microstructures obtained by the two methods. The following equations were obtained by evaluating the data in the Table 1:

$$T_{FTIR} = 132 - 1.58 T_{NMR} \quad (11)$$

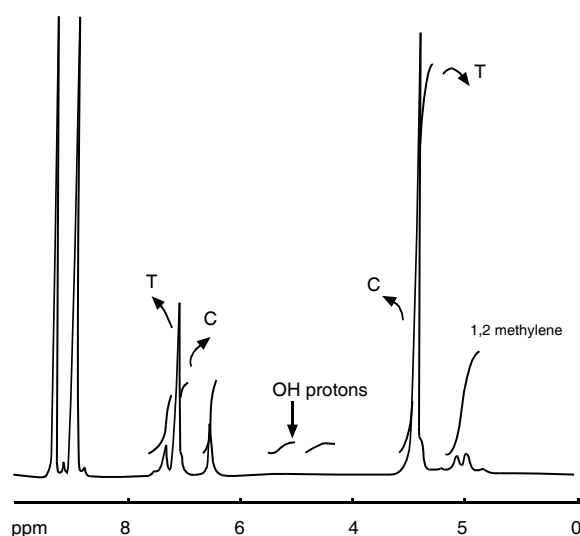
$$V_{FTIR} = -5.6 + 1.25 V_{NMR} \quad (12)$$

Where, T and V indicate the percentage of *trans* and *vinyl* contents, respectively. As it can be seen from Table 1, *vinyl* content obtained by both methods are relatively close together and the content of *trans* or *cis* are rather far apart. Furthermore, by comparison of microstructure of the known sample (K) with those values obtained by the investigated two methods, it is observed that *trans*, *vinyl* and *cis* contents obtained by NMR spectroscopy are closer to the real values.

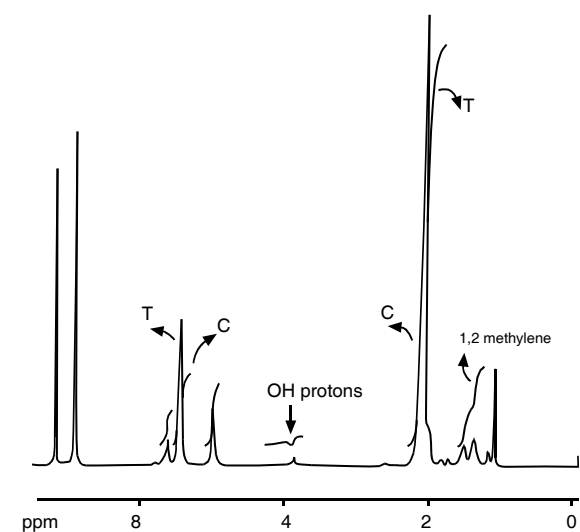
In FTIR method, peaks at 685 cm<sup>-1</sup> and 700 cm<sup>-1</sup> of



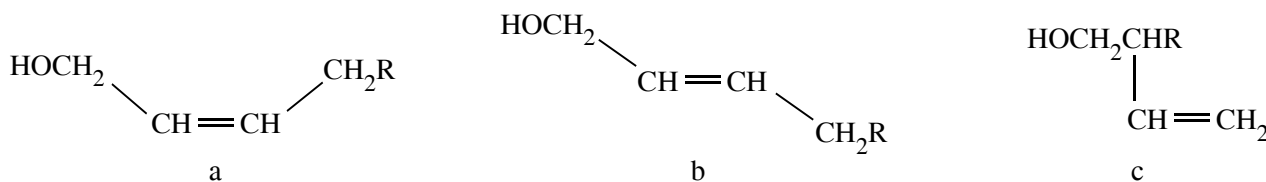
**Figure 8.** Proton NMR spectrum of sample A.



**Figure 9.** Proton NMR spectrum of sample B.



**Figure 10.** Proton NMR spectrum of sample C.



Scheme 1

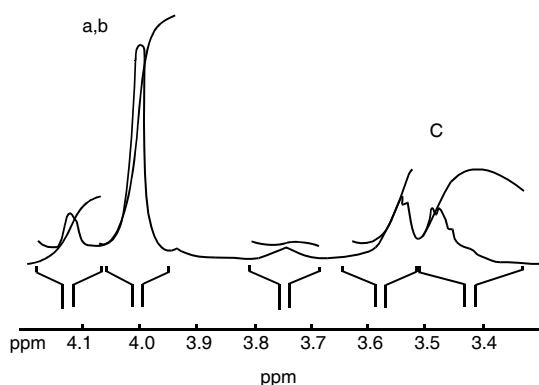
the corresponding *vinyl* isomer of the polyol have influence on the characteristic peak of *cis* that is seen in  $725\text{ cm}^{-1}$  and causes the deviation of the actual value. Hence, deviation increases, as the *cis* content of polyol increases.

Comparison of the isomer contents obtained by FTIR and NMR method, shows that the deviation of values of isomers in FTIR and NMR is 10% and 3%, respectively.

### The Position of the Hydroxyl Groups

Figure 11 shows the region of 2.5-4 ppm of butadiene polyol in NMR spectrum, which indicates the adjacent protons to hydroxyl groups of the polyol. In Scheme I, the first resonance peak (3.4 ppm) corresponds to a primary alcohol ( $\text{CH}_2\text{OH}$ ) adjacent to a saturated carbon (c), while 3.9 and 4 ppm bands are assigned to primary alcohols adjacent to olefins (a,b) [8].

Moreover, simultaneous existence of 4.3 and 5.9 ppm NMR peaks indicates the presence of OH groups attached to the back-bone of the chains in addition to the observed terminal groups.



**Figure 11.** 500 MHz  $^1\text{H}$  NMR spectrum of sample K in the region of 2.5-4.3.

## CONCLUSION

Microstructure could be well determined through the use of FTIR and NMR analysis techniques. Using the FTIR spectroscopy method is more practical and the obtained microstructure by NMR is more precise than the FTIR method. Correlation between FTIR and NMR results are found finally to convert the values obtained by two methods. It is possible to convert values yielded from FTIR to NMR by use of eqns (11) and (12). Also by use of NMR method, it is possible to determine the type of OH-groups pertaining to *1,2-vinyl* configuration, and those *cis* and *trans* configurations.

## ACKNOWLEDGEMENTS

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