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Determination of Average Degree of Polymerization and Average Number of Molecular Weight for Hydroxy Terminated Polybutadiene Polymer using ^{1}H NMR

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Average degree of polymerization and average number of molecular weight of hydroxy terminated polybutadiene, that prepared *via* radical polymerization were determined by using ^{1}H NMR spectrometry.

Key Words: Hydroxy-terminated polybutadiene, ^{1}H NMR, Average degree of polymerization, Average number of molecular weight.

INTRODUCTION

Hydroxy terminated polybutadiene (HTPB) was prepared *via* anionic, radical and sometimes cationic polymerization. This is very important in preparing adhesive, coating, tire and many industries[1]. Many researches were done on HTPB for determination of its physical constants as average degree of polymerization (Dp) and average number of molecular weight (Mn), *cis*, *trans* and vinyl double bonds per cent[2]. In past, GPC, VPO and light scattering methods were used for determination[3] of Dp and Mn. These methods are more time consuming. In this article, a facial method for the determination of Dp and Mn is reported using ^{1}H NMR spectra.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR-460 spectrometer (neat). ^{1}H NMR spectra were measured with a JEOL EX-90A spectrometer at 90 MHz ($CDCl_3$). The HTPB samples were prepared from Malekashtar university.

Hydroxy terminated polybutadiene is prepared[1] from 1,3-butadiene monomer *via* radical polymerization in the presence of H_2O_2. There are three types of double bonds in the polymer chain and also there are some OH groups in the ends of polymer chain. The double bonds are in *cis, trans* and vinyl groups form. The skeleton of HTPB[4] is shown in the Fig. 1.

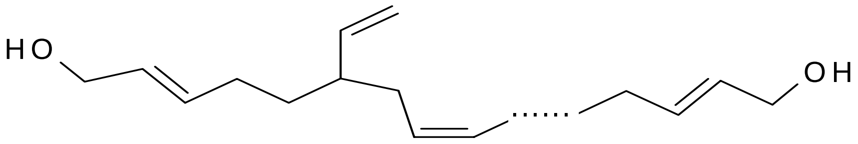

Fig. 1. Approximate structure of HTPB

In order to obtaining of the Dp and Mn, the following steps have been considered: (1) ^{1}H NMR and IR spectrums of HTPB (radically polymerization) was prepared and discussed, (2) alcoholic functionality (1°, 2°, 3°) of HTPB was obtained from its IR spectrum and (3) functionality or average number of OH groups in one chain of HTPB polymer was studied.

RESULTS AND DISCUSSION

The calculation of chemical shifts by using standard tables and the spectra (IR, NMR) have been interpreted. Results are given in Table-1. All the results are in consistence with interpretation of ^{1}H NMR spectra in the literature[5,6].

TABLE-1
INTERPRETATION OF ^{1}H NMR SPECTRA OF
HYDROXY TERMINATED POLYBUTADIENE

Possible structure	Calculated chemical shift[6]	Observed chemical shift	Peak no.
$\ldots CH_2\text{–}CH\text{–}CH{=}CH_2\ldots$	1.35	1.2-1.6	A
$\ldots CH_2\text{–}CH_2\text{–}CH\text{–}CH_2\text{–}CH_2\ldots$	2.08, 2.05	2.0	B
$\ldots\ldots CH_2OH$	4.13, 4.20	4.1	C
$\ldots\ldots CH\text{–}CH{=}CH_2$	5.02, 5.30	5.0	D
$\ldots CH{=}CH\ldots,\ \begin{array}{c} \vert \\ CH \\ \vert \\ CH{=}CH_2 \end{array}$	5.43-5.46	5.4-5.5	E

IR spectral data of HTPB have been summarized in Table-2. The IR peaks at 3750, 3140, 3000, 1440, 1320, 1350 cm^{-1} and especially 1360 cm^{-1} show that alcoholic groups are 1°.

Although the 2° and 3° alcoholic groups signals may be overlap with the another spectral bands, but ^{1}H NMR and carbon decoupled spectra show the 2° and 3° alcoholic groups are less than 1° alcoholic groups[2,4].

Functionality is used to determine of Dp and Mn. HTPB that was prepared *via* radical polymerization and found that functionality[7] of HTPB is 2. This means that each chain of polymer has 2 OH groups in the ends. It is inconsistent with reported results. In this reports, the functionality was 1.9-2.6, 2, 4 but in average functionality for HTPB is found to be 2.

TABLE-2
INTERPRETATION OF IR SPECTRUM (FIG.3) OF HYDROXY TERMINATED POLYBUTADIENE

* possible functional group	Observed frequency (cm^{-1})
Alcoholic OH, vibrational stretching without hydrogen bonding	3750 (3720–3770)
Vibrational stretching of OH with intramolecular hydrogen bonding	3140–3520
Vibrational stretching of olefinic CH	3075 (3040–3120)
Vibrational stretching of alcoholic OH with intermolecular hydrogen bonding	3000 (2980–3040)
Vibrational stretching of OH of–CH_2	2840 (2800–2880)
Vibrational stretching of vinyl, *cis* and *trans* C = C	1640 (1600–1680)
Vibrational bending of CH group of alcoholic group	1440 (1380–1480)
Vibrational bending of double bond (C=C) vinyl and bending of CH from alcoholic groupes	1350, 1320 (1300–1360)
Vibrational bending of double bond (*trans*) and vibrational bending of C-O from 1° alcohol that is attach to C=C or other functional group	960 (940–1080)
Vibrational bending of (C=C) vinyl	860 (880–940)
Vibrational Bending of double bonds and vibrational bending of (C-H) out of plane	680, 740 (600–800)

^{1}H NMR spectra (Fig. 2) of HTPB is concluded that all of the hydrogens in polymer are related to the possible structure as given in Table-1. It is appeared that peak C was corresponded to hydrogens (CH_2) that are attached to OH groups. This peak is for 4H, because functionality of polymer is 2, that means in each side of chain has one alcoholic group and the carbons attach to OH groups have two hydrogens[8,9]. The area of all peaks (peaks A-E) is 0.5306 cm^2 (eqn. 1) divided by area of peak C, which is found to be 0.008 cm^2. Then the result multiplied by 4, which shows that hydrogens of two carbon atoms is two end of polymer chain and are attached to alcoholic groups. Then the total of hydrogen in average chain of polymer is calculated. Finally, dividing N by 6 (the number of hydrogens in each monomer), the number of monomers in average chain of polymer is obtained.

$$N = \frac{4M}{L}$$

$$\overline{D}_p = \frac{N}{6} \Rightarrow \overline{D}_p = \frac{4M}{6L} \qquad (1)$$

M = total area of all peaks, L = area of peaks corresponding hydrogens (CH_2) attached to OH groups, N = total of hydrogen in polymer chain.

$$\overline{D}_p = \frac{4 \times 66.33}{6} = 44.21$$

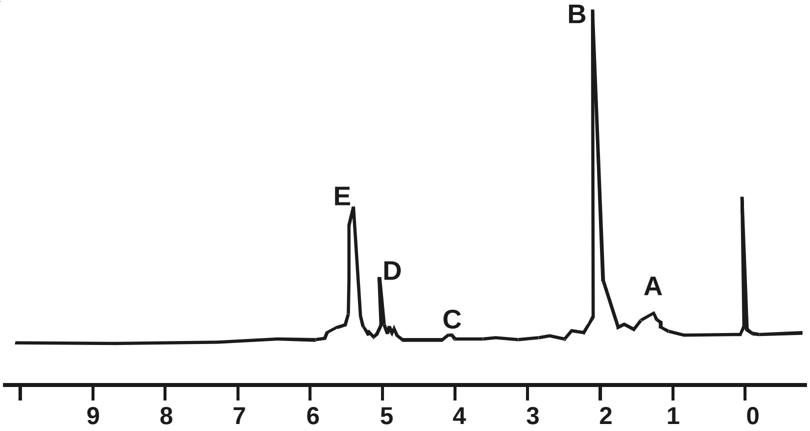

Fig. 2. ^{1}H NMR spectrum of hydroxy-terminated polybutadiene

For the determination of Mn, molecular weight of 1,3-butadiene monomer (54 g) is multipled by to Dp (44.21). Then the result is added to molecular weight of two OH groups, 2 OH = 2 × 17 = 34, as shown below:

$$\overline{M}n = (\overline{D}p \times 54) + 34$$
$$= (44.21 \times 54) + 34 = 2439 \text{ g mol}^{-1}$$

In summary, a new and facial method is developed for the determination of Dp and Mn for HTPB using ^{1}H NMR and IR techniques.

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