

Tacticity, Isomeric Structural Units and Molecular Weight Determination of Hydroxyl Terminated Polybutadiene by High Field FT-qNMR Spectroscopy†

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High field FT-qNMR (800 MHz) was used to determine the content of vinyl-1,2-unit in free radical as well as anionic hydroxyl terminated polybutadiene polymer. Two dimensional $^1\text{H}/^{13}\text{C}$ -HMQC was used to study the complex NMR spectrum. The $^{13}\text{C}\{^1\text{H}\}$ DEPT-135 experiment was carried out to differentiate between the methylene and methine carbon resonances. The tacticity was investigated by splitting the olefinic methylene carbons of 1,2-vinyl unit and was tested with Bernoullian and first-order Markov statistical model of chain propagation. The configurational sequence assigned to various methylene carbon resonances of the polymer are in good agreement with that calculated by the statistical models. The functionality, number-average degree of polymerization ($\overline{\text{DP}}_n$) and molecular weight ($\overline{\text{M}}_n$) of the polymer were determined by FT-qNMR technique and the results were compared with those obtained by gel permeation chromatography.

Key Words: Hydroxyl terminated polybutadiene, Tacticity, Microstructure, Number-average molecular weight, NMR.

INTRODUCTION

The hydroxyl terminated polybutadiene (HTPB) prepolymer is synthesized from 1,3-butadiene by either free radical or anionic polymerization method. The polymerization of 1,3-butadiene gives rise to products which have a 1,4-polybutadiene or 1,2-polybutadiene structure or a mixture of these structures. The 1,4-addition product comprises the *cis*-1,4- and *trans*-1,4-configuration, whereas 1,2-addition leads to vinyl-1,2-configuration with different tacticity *i.e.* isotactic, atactic, syndiotactic parts in the polymer backbone. The chemical structures of HTPB, synthesized by free radical and anionic polymerization method, are depicted in Fig. 1, where α , β and γ are the number of *trans*-1,4-; vinyl-1,2-; and *cis*-1,4-micro structural units respectively.

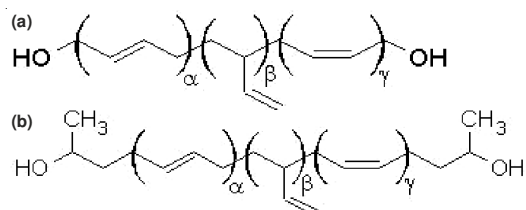


Fig. 1. Molecular structure of (a) free radical HTPB and (b) anionic HTPB prepolymer

The elastomeric properties of HTPB based polyurethanes (PUs) largely depend on microstructure and tacticity of the substrate HTPB prepolymer. Therefore, knowledge on the polymer structure and composition is essential for synthesis of polyurethanes with required properties and understanding the various advantages. The microstructure of HTPB has been investigated by infrared, ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy¹⁻³. *Hitherto*, the actual physical characteristics of HTPB are not precisely known, particularly its tacticity and absolute number-average molecular weight ($\overline{\text{M}}_n$). These parameters need to be explored further for better understanding on its subtle difference in elastomeric behaviour in different industrial applications. The $^{13}\text{C}\{^1\text{H}\}$ NMR with higher field magnets in which the ^{13}C nuclei resonate at a frequency of at least 50 MHz can be used for both quantitative and qualitative analysis of the polymers by integrating peak clusters representing specific carbon types. However, for quantitative analysis, many requirements are to be met *i.e.* (a) proper shimming, (b) a sufficient relaxation delay (at least $5 \times T_1$), (c) a suitable digital resolution, (d) elimination of nuclear overhauser enhancement, (e) adequate S/N ratio, (f) accurate and unbiased phasing of spectrum and (g) accurate method of integration.

The present work aims to study the polymer tacticity, functionality and number-average degree of polymerization ($\overline{\text{DP}}_n$)

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and thus, \overline{M}_n of the polymer by using high field (800 MHz) ^1D NMR techniques *i.e.* ^1H -qNMR, $^{13}\text{C}\{^1\text{H}\}$ -qNMR and, $^{13}\text{C}\{^1\text{H}\}$ -DEPT (distortionless enhancement by polarization transfer) and ^2D NMR techniques *i.e.* $^1\text{H}/^{13}\text{C}$ -HMQC (hetero-nuclear multiple quantum coherence). This study will certainly provide deeper insights in understanding the architecture of HTPB prepolymer and thus its behaviour in various industrial applications.

EXPERIMENTAL

NMR experiments: The NMR spectra were recorded on a Bruker 800 MHz NMR spectrometer. The HTPB samples (10 % (w/v) for the ^1H NMR and 30 % (w/v) for the $^{13}\text{C}\{^1\text{H}\}$ NMR analysis) were recorded in CDCl_3 at room temperature. The ^1H NMR acquisition parameters were: spectral width = 16 ppm, acquisition time = 2 s, relaxation delay = 1 s, pulse width = 90° and number of scans = 1000. Similarly, $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded using spectral width = 220 ppm, acquisition time = 2 s, relaxation delay = 10 s, pulse width = 90° and number of scans = 300. HMQC spectra of HTPB samples (30 % (w/v) in CDCl_3 at room temperature) were recorded on a Bruker 500 MHz with a 5 mm inverse Z-gradient probe. Spectral widths: F2 (^1H) = 8000 Hz, F1 (^{13}C) = 27500 Hz. Time domains: (^1H) = 1024 and (^{13}C) = 515, acquisition time (^1H) = 0.23 s, delay (^1H) = 2s. In processing, the FID was zero-filled to 32 K data points and the resulting 32 K time domain was Fourier transformed. Additionally, Gaussian apodization was also applied in both ^1H and ^{13}C domains.

Gel permeation chromatography: The molecular weight of the polymers were determined by gel permeation chromatography with tetrahydrofuran as the mobile phase (flow rate = 1 mL/min) with monodisperse polystyrene standards and a refractive-index detector.

RESULTS AND DISCUSSION

Fig. 2b shows the $^{13}\text{C}\{^1\text{H}\}$ -DEPT spectrum of free radical HTPB (Fr-HTPB) prepolymer recorded in CDCl_3 with complete signal assignments, where the methine carbons and both methyl and methylene carbons appear as positive and negative phase respectively. Fig. 2a shows the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (200 MHz, CDCl_3) of the prepolymer. For convenience, resonances in the spectrum can be divided in to three distinct regions, *i.e.* (a) an olefinic region: δ 113-144, (b) a carbon bearing hydroxyl end group region: δ 56-65 and (c) an aliphatic region: δ 24-44.

In the olefinic region, the DEPT spectrum showed a set of positive signals in the range of δ 142-144, that assigned to methine ($-\text{CH}=\text{}$) carbons, whereas a set of negative signal at δ 113-115, is due to the methylenic ($=\text{CH}_2$) carbon of vinyl-1,2- unit. The fine splitting of the signals is due to the tacticity of the monomer units. A set of positive signals in the range of δ 125-134 was ascribed to the compositional splitting of the two olefinic carbons ($-\text{CH}=\text{CH}-$) in central *cis*-1,4- or *trans*-1,4-unit, present in different combination of homotriads, heterotriads and symmetric and non-symmetric isolated triads⁴. In Fig. 2a, the integrated peak areas corresponding to olefinic methine *i.e.* A and B and olefinic methylene carbons *i.e.* C can be measured separately. Therefore, the content of vinyl-1,2- unit in HTPB can be determined from $^{13}\text{C}\{^1\text{H}\}$ NMR as: vinyl-1,2-unit (%) = $(A+C) \times 100 / (A + B + C)$.

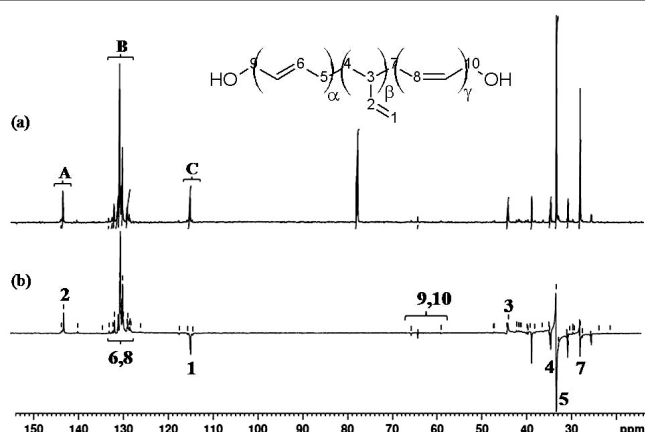


Fig. 2. NMR (CDCl_3 , 200 MHz) spectrum of free radical HTPB (a) $^{13}\text{C}\{^1\text{H}\}$ NMR, (b) $^{13}\text{C}\{^1\text{H}\}$ DEPT-135 NMR

Fig. 3 shows the $^1\text{H}/^{13}\text{C}$ -HMQC spectrum of HTPB prepolymer in olefinic region. In the olefinic region, the ^{13}C resonances at δ 113-144, showed three contours, which correspond to δ 4.9-5.7 range in the ^1H NMR spectrum. The fine splitting is attributed to configurational sequences and tacticity of the polymer. Thus, ^{13}C resonances observed in the $^1\text{H}/^{13}\text{C}$ -HMQC spectrum (Fig. 3) at δ 142.8-142.04 (A), δ 132-127 (B) and δ 114.9-114.2 (C) correspond to that of protons in the ^1H NMR spectrum at δ 5.7-5.4 (A'), δ 5.44-5.41 (B') and δ 5.0-4.9 (C'), respectively. Therefore, vinyl-1,2-unit content in HTPB can also be determined from ^1H NMR as vinyl-1,2-unit (%) = $2C' \times 100 / [2(A'+B')+C']$. The vinyl-1,2-content determined from $^{13}\text{C}\{^1\text{H}\}$ NMR for free radical HTPB, anionic HTPB-I and II is 17.93, 63.82 and 66.64 % respectively, whereas from ^1H NMR, it is 19.85, 65.55 and 67.59 % respectively. The results are in good agreement to each other. So the experimental conditions adopted and integration values are credible. As evident from the NMR study, the anionic HTPB would have more sensitivity to tacticity as it is very rich in vinyl-1,2- content.

Fig. 4 shows the expanded region of the methylene group resonances of anionic HTPB-I and free radical HTPB prepolymer. The peak of methylene carbon of vinyl-1,2- units

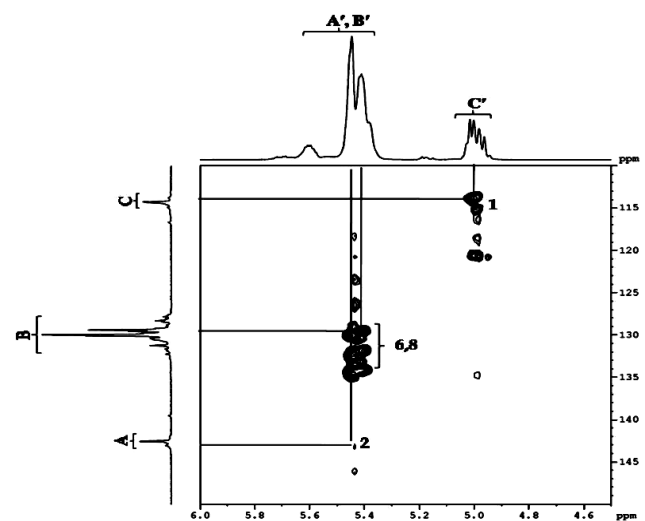


Fig. 3. $^1\text{H}/^{13}\text{C}$ -HMQC spectra of free radical HTPB prepolymer: olefinic region

TABLE-1
TACTICITY ANALYSIS OF METHYLENE GROUP OF ANIONIC HTPB-I AND FREE RADICAL HTPB PREPOLYMER

Polymer	Peak no.	Chemical shift (ppm)	Observed	Calculated intensity		Assignments
				Bernoullian	First-order markov	
Anionic HTPB-I	1	115.265	0.063	0.062	0.070	mrrm
	2	115.090	0.069	0.067	0.045	rrrr
	3	114.971	0.095	0.129	0.112	mrrr
	4	114.592	0.131	0.129	0.144	rmrr
	5	114.483	0.123	0.121	0.133	mrrm
	6	114.386	0.111	0.125	0.108	mmrr
	7	114.305	0.197	0.125	0.178	rmrm
	8	113.985	0.076	0.121	0.103	mmmr
	9	113.842	0.134	0.121	0.103	mmmm+rmmr
Free radical HTPB	1	114.984	0.108	0.270	0.109	mrrm+mrrr+rrrr
	2	114.395	0.360	0.375	0.264	rmrr+mmrm+mmrr
	3	114.302	0.464	0.125	0.559	rmrm
	4	113.817	0.068	0.230	0.061	mmmr+mmmm+rmmr

is splitted into nine peaks and in statistical analysis, it has pentad sequence distribution. The downfield group of lines is assigned to the syndiotactic triads (rr): δ 115.3-114.9 followed by atactic (mr): δ 114.6-114.3 and isotactic triad (mm): δ 114.0-113.8. Moreover, the fine structures observed clearly indicates the sensitivity of methylene carbon to the placements of higher than triad sequences. In statistical subject, probabilities of meso (P_m) and racemic (P_r) sequence are defined as, $P_m = (2mm + mr)/2$ and $P_r = 1 - P_m = (2rr + mr)/2$ respectively. Further, in Markov first-order model, the statistics is controlled by two independent parameters $P_{m/r}$ and $P_{r/m}$, which can be calculated from the triad content *i.e.* $P_{m/r} = 1 - P_{r/m} = mr/(2mm + mr)$ and $P_{r/m} = 1 - P_{m/r} = mr/(2rr + mr)$. The areas of NMR peaks (rr, mr and mm) are proportional to the molar ratios of their sequences. So, each triad content was calculated by normalizing the peak area. The theoretical values of Bernoullian and first-order Markov pentad intensities were then calculated and fitted with the experimental intensities for methylene carbon to assign the various pentad placements. The results are summarized in Table-1. The calculated values of P_m for Fr-HTPB, An-HTPB-I and II are equal to 0.480, 0.492 and 0.468 respectively. These results indicate that racemic addition is almost higher than the meso one. Basically for an ideal random condition, P_m is equal to 0.5. So, the HTPB prepolymers are close to the stereo sequences of an ideal atactic chain.

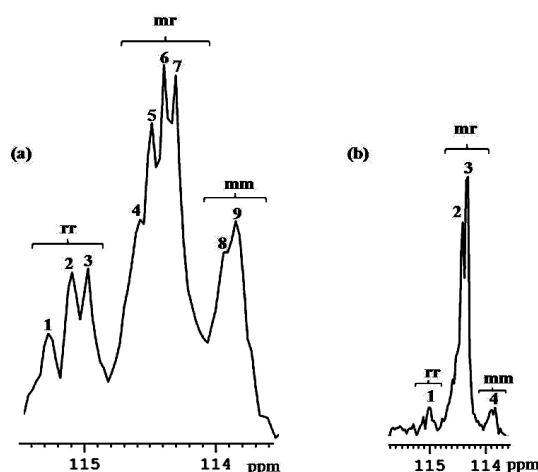


Fig. 4. Expanded NMR ($CDCl_3$, 200 MHz) spectrum (a) $^{13}C\{^1H\}$ NMR of anionic HTPB-I, (b) $^{13}C\{^1H\}$ NMR of free radical HTPB prepolymer

An useful parameter *i.e.* $\delta = 2(m)(r)/(mr)$ referred to as the persistence ratio, was introduced by Coleman and Fox. For any Bernoullian chain, $\delta = 1$, where as for first-order Markov chains $1/\delta = P_{m/r} + P_{r/m}$. The persistence ratio for Fr-HTPB, An-HTPB-I and II is found to 0.61, 0.89 and 0.89 respectively. However, it is difficult to say with certainty whether Bernoullian or first-order Markov propagation statistics is followed, although the data in Table-1 shows that it is close to those of first-order Markov statistics. Further, the average length of meso (N_m) and racemic (N_r) sequences were calculated as $N_m = (2mm + mr) / mr$ and $N_r = (2rr + mr)/mr$ respectively. For an ideal atactic structure, the length average values of meso and racemic sequences are basically equal to 2. The calculated values of N_m/N_r for Fr-HTPB, An-HTPB-I and II are 1.17/1.26, 1.75/1.81 and 1.68/1.91 respectively, which further confirms that the polymer have atactic stereosequence. In all the cases, the concentration of atactic sequences is higher than the isotactic and syndiotactic ones.

Polymer functionality and molecular weight: In the carbon bearing hydroxyl end group region (δ 56-65), the $^{13}C\{^1H\}$ -DEPT spectrum for Fr-HTPB showed only the negative resonances. Therefore, all the resonance signals belong to the adjacent methylene carbon to hydroxyl end group of HTPB prepolymer ($-CH_2-OH$). According to the Pham⁵, the free radical HTPB prepolymer can be approximated to three types of hydroxyls namely G, H and V types.

Fig. 5 shows the expanded $^1H/^{13}C$ -HMQC spectrum of δ 56-65 region along with the assignment of carbon signals. The ^{13}C resonance at δ 58.50 is attributed to methylene carbon of G-hydroxyl, while other resonances at δ 63.67 and δ 65.06 are assigned to the methylene carbon of H- and V-hydroxyl structures, respectively. Further, three signals seen in the $^1H/^{13}C$ -HMQC spectrum at δ 65.06, 63.67 and 58.5 correspond to that of protons at δ 3.4-3.7, 4.1-4.0 and 4.2, respectively. So, the relative amounts of G, H and V types hydroxyls can readily be calculated from either $^{13}C\{^1H\}$ NMR or 1H NMR spectrum. The G/H/V content calculated for Fr-HTPB from $^{13}C\{^1H\}$ NMR is 16.46/53.27/30.27 and from 1H NMR is 13.74/57.24/29.02 respectively, which are in good agreement with each other. The G-type hydroxyls represent the trifunctional (branching) components. The fraction of triols and diols can be readily calculated from the relative amounts

of G, H and V- types hydroxyls obtained from NMR spectra by the following reasoning: if f is the fraction of G type hydroxyls, then the total number of chains in the polymer is proportional to half the chain ends *i.e.* $(H+V)/2$ and is equal to $(1-f)/2$. Hence, the fraction of triols (n_3) will be equal to $2f/(1-f)$. Thus, the average functionality ($\bar{F}_n(OH)$) of the HTPB prepolymer can be readily calculated by using the classical relation defining functionality, *i.e.*, $[\bar{F}_n(OH)] = \sum n_i F_i / \sum n_i$, where n_i is the mole fraction of HTPB with hydroxyl functionality F_i and $\sum n_i = 1$. So, we have $\bar{F}_n(OH) = [(n_2 \times 2) + (n_3 \times 3)] / (n_2 + n_3)$ with $n_2 + n_3 = 1$, where n_2 and n_3 are the fractions of diols and triol respectively. For Fr-HTPB, the calculated value of $n_2 = 0.7$ and $n_3 = 0.3$. So, the average functionality would be 2.3. The number-average degree of polymerization (\overline{DP}_n) is defined as the ratio of the sum of olefinic protons integrals to that of hydroxylated methylene protons. Therefore, the number-average molecular weight ($\bar{M}_n(NMR)$) would be equal to $\bar{F}_n(OH)[(C' + 2(A'+B') \times 54 / (2(G' + H' + V'))) + 17]$, where A' , B' , C' , G' , H' and V' are the integrated peak area of the peak clusters as shown in Figs. 3 and 5. Similarly for An-HTPB prepolymers, the number average molecular weight *i.e.* $\bar{M}_n(NMR) = \bar{F}_n(OH)[(C' + 2(A'+B') \times 54 / (2(\text{area of secondary OH group})) + 59)]$ with $\bar{F}_n(OH)$ equal to 2. The $\bar{M}_n(NMR)$ for Fr-HTPB, An-HTPB-I and II was found to 4632, 7231 and 4779 g/mol respectively. Fig. 6 shows the gel permeation chromatography normalized curves for three HTPB prepolymers under investigation.

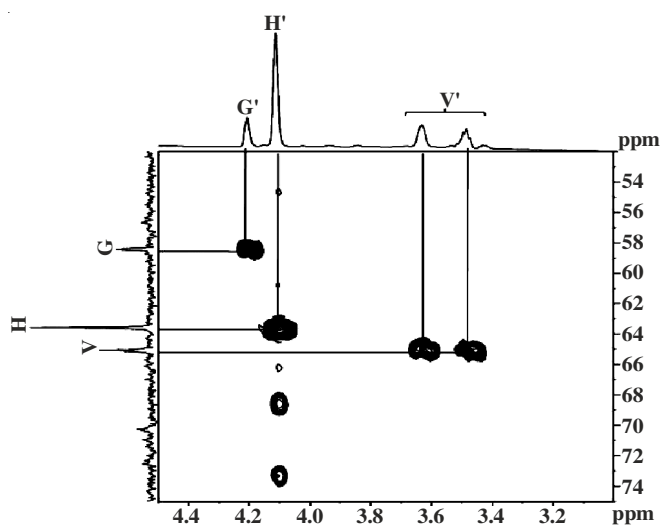


Fig. 5. $^1H/^{13}C$ -HMQC spectra of free radical HTPB prepolymer: carbon bearing hydroxyl end group region

The $\bar{M}_n(NMR) / \bar{M}_n(GPC)$ average ratio for free radical HTPB is found to be 0.79, which is well compared with the literature value⁶ of 0.67, where as for, An-HTPB-I and II, it is 1.23 and 1.18, respectively. This deviation may be due to the narrow distribution of anionic HTPB-I and II as shown in Fig. 6. The polydispersity index (PI) obtained by gel permeation chromatography for anionic HTPB-I and II are 1.6 and 1.8, respectively.

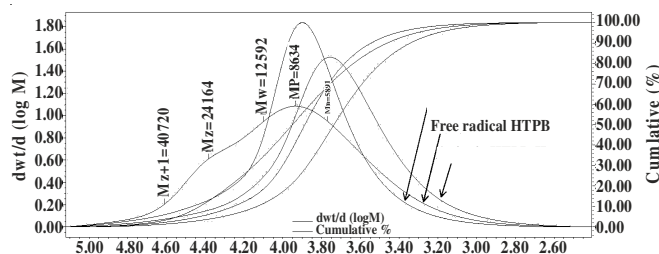


Fig. 6. Overlaid gel permeation chromatography curves of Fr-HTPB, anionic HTPB-I and II prepolymer

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REFERENCES

- G.M.M. Sadeghi, J. Morshedian and M. Barikani, *React. Funct. Polym.*, **66**, 255 (2006).
- W.D. Vilar, S.M.C. Menezes and L. Akcelrud, *Polym. Bull.*, **35**, 481 (1995).
- B.A. Breton, M. Audenaert and Q.T. Pham, *Macromol. Chem. Phys.*, **197**, 1651 (1996).
- J.A. Frankland, H.G.M. Edwards, A.F. Johnson, I.R. Lewis and S. Poshyachinda, *Spectrochim. Acta*, **47A**, 1511 (1991).
- Q.T. Pham, *Makromol. Chem.*, **179**, 1011 (1978).
- N. Kebir, I. Campistron, A. Laguerre, J.F. Pilard, C. Bunel, J.P. Couvercelle and C. Gondard, *Polymer*, **46**, 6869 (2005).