

Effect of Reactivity of Different Types of Hydroxyl Groups of HTPB on Mechanical Properties of the Cured Product

SREELATHA S. PANICKER, K. N. NINAN

Propellant and Special Chemicals Group, Vikram Sarabhai Space Centre, Thiruvananthapuram-695 022, India

Received 4 March 1996; accepted 31 May 1996

ABSTRACT: The amount of three types of hydroxyl functional groups (G_{OH} , H_{OH} , and V_{OH}) in hydroxyl terminated polybutadiene (HTPB), remaining in samples acetylated to the same extent under two different conditions, viz., fast acetylation using acetyl chloride in presence of *N*-methyl imidazole catalyst and slow acetylation by acetic anhydride, differed significantly. For the fast acetylation there is a uniform reduction in all the three types of hydroxyls, probably because the reaction becomes random at rapid rates and the reactivity of the different types of hydroxyls does not play a major role. However, in the slow reaction, the reduction of *G*-type hydroxyls was 30% more than the expected value and there was a corresponding increase in the amount of *V*-type hydroxyls remaining in the acetylated product, showing reactivity of OH in the order of $G > H > V$. When the reaction is slow, it becomes selective and the change in reactivity of the three types of OH groups is reflected in the extent of conversion. The mechanical properties and the crosslink density data show a reduction in the samples containing lesser amounts of G_{OH} , confirming the branching nature of G_{OH} , which is involved in the crosslinking reaction. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1313–1320, 1997

Key words: hydroxyl terminated polybutadiene (HTPB)—reactivity of OH groups—hydroxyl groups— ^1H -NMR spectra of HTPB—mechanical properties

INTRODUCTION

Hydroxyl terminated polybutadiene (HTPB) is currently the most widely used solid propellant binder.¹ Apart from its use in propellant manufacture, HTPB finds applications in various areas like the tire, fabric, and electrical industries.^{2–4} Literature on the functionality distribution of free radically prepared HTPB (FR-HTPB) shows that it contains non-, mono-, di-, tri-, and polyfunctional molecules.^{5–11} Our studies^{8–11} on functionality distribution have shown that FR-HTPB contains a substantial quantity of tri and polyfunctional molecules in the polymer, a fact which is well supported by the fact that FR-HTPB can be

cured to get a highly crosslinked structure using a difunctional curative like toluene diisocyanate (TDI). The effect of functionality and molecular weight distribution on the properties of HTPB has been studied by several workers.^{8,9,12–14} Literature^{15–18} on HTPB shows that a free radically prepared HTPB contains only primary OH groups. Pham et al.^{16,17,19–21} have carried out an extensive study on the nature of different types of hydroxyl functions present in HTPB with the help of NMR spectroscopy (^1H and ^{13}C). They have identified^{16,17} three types of primary OH groups in FR-HTPB. They are (i) geraniol type (G_{OH}), (ii) 2-hexene-1-ol type (H_{OH}), and (iii) vinyl type (V_{OH}). The proportions of these three hydroxyl functions were also estimated from the accumulated ^1H NMR spectra.¹⁶ The nature of these hydroxyl functions gave information concerning the likely initiation, chain transfer, and termination mecha-

Correspondence to: K. N. Ninan

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/101313-08

nisms of the radical polymerization of butadiene by H_2O_2 in alcohol media.

Since the nature of the three OH functions are different, the reactivity of the three groups are expected to be different. Evaluation of the relative reactivity of the different types of hydroxyl groups present in HTPB is of great importance in understanding the gelation time and pot life of the propellant mix made with HTPB as the polymeric fuel binder. Pham et al.^{19,20} have done a thorough study of the kinetics of the reaction of HTPB with different reagents like silylating agents and isocyanates in bulk and in different solvent media. The study showed different reactivities for the three OH functions whose reactivity is in the decreasing order of $G > H > V$. This was further confirmed by comparing with the reactivities of model alcohols.²¹ A relative distribution of the three alcohol functions in FR-HTPB⁶ synthesized under varying conditions, and how these differences translate into the properties of the cured resin, have been studied by Rao et al.²²

In this work, the effect of the nature of the three hydroxyl functions on the mechanical properties of the cured product is studied. The hydroxyl groups of HTPB were partially acetylated to various extents with two types of acetylating reagents having different reactivities. The partially acetylated products obtained from the two methods were crosslinked using toluene diisocyanate, and the mechanical properties of the cured products were studied. The aim of the work was to find out the reactivity of different OH groups under the two different reaction conditions and to find the effect of the nature of these groups on the mechanical properties of the cured product.

EXPERIMENTAL

Materials

HTPB: Manufactured at NOCIL, Bombay, by the free radical polymerization of butadiene gas using H_2O_2 as initiator in isopropanol solvent. This process was developed by VSSC¹ and the technology transferred to NOCIL. Acetyl chloride: Glaxo (purified by distillation after refluxing with PCl_5). Acetic anhydride: AR grade, Qualigens. Tetrahydrofuran (THF): HPLC grade, Spectrochem. Toluene: AR grade, Qualigens. *N*-methyl imidazole (NMI): AR grade, Fluka. Toluene diisocyanate (TDI): 80 : 20 mixture of 2,4 and 2,6 isomers supplied by M/S AG Bayer.

Preparation of Partially Acetylated Samples of HTPB

Method 1

About 100 g of HTPB was dissolved in dry THF. To this solution, calculated amounts of acetyl chloride (required for 10% and 20% partial acetylation) and NMI (5 mL) catalyst were added. The flask was shaken for a few minutes and refluxed for 1 h to complete the reaction. After the reaction, THF was evaporated off and the residue obtained was dissolved in ether. The ether solution was washed with water and dried using anhydrous sodium sulfate. The acetylated product formed was recovered by removing ether using a vacuum rotary evaporator. By using this procedure, 10% and 20% acetylated HTPB were prepared and are designated in this work as 10% AC and 20% AC.

Method 2

To a solution of HTPB in toluene, acetic anhydride required for 10% and 20% acetylation was added and maintained at 60°C in a constant temperature bath for several hours. Completion of the reaction was confirmed by the absence of acetic anhydride in the reaction mixture using the morpholine test.²³ Approximately 72 h were required for the completion of the reaction. The products obtained are designated as 10% AA and 20% AA.

Characterization of HTPB and Partially Acetylated Samples

Infrared (IR) Spectroscopy

The IR spectra of the samples were recorded on a Perkin-Elmer 283 IR spectrophotometer.

Hydroxyl Value

Hydroxyl values of HTPB and partially acetylated samples were determined by the acetylation method using a 1 : 8 acetic anhydride-pyridine mixture.²³ The reaction mixture was refluxed on a water bath for about 3 h. Excess acetic anhydride was hydrolyzed and the total free acid was titrated against sodium hydroxide solution using phenolphthalein indicator. Correction was made for the free acid present in the sample.

Ester Value²³

The HTPB ester was dissolved in toluene and saponified by refluxing with 0.1 *N* alcoholic KOH on

a water bath for 3 h. Excess KOH was titrated against 0.1 *N* alcoholic HCl using phenolphthalein as indicator.

Acid Value²⁴

HTPB was dissolved in a 3 : 2 mixture of toluene and methanol and the resulting single phase solution was titrated with standard alcoholic KOH using phenolphthalein indicator.

Molecular Weight and Molecular Weight Distribution (MWD)

Molecular weight averages and molecular weight distributions of the samples were determined using a Waters Associates GPC²⁵ (model 244). Four micro Styragel columns of pore sizes 10⁴ Å, 10³ Å, 500 Å, and 100 Å were employed. Tetrahydrofuran was used as the solvent at a flow rate of 2 mL/min. A dual detector system of differential refractive index (DRI) and UV detectors was used. One hundred μL of 1% solution was used for each analysis. The column set was calibrated by Universal calibration.²⁶

NMR Analysis

Proton NMR spectra of the samples in CDCl₃ (10% solution) were recorded with a JEOL GSX400 instrument at 400 MHz. Chemical shifts were measured relative to TMS as the internal reference. The measurements were done using the FT pulsed NMR technique (number of scans 2000, time of acquisition 2.05 s) at ~ 25°C.

Curing of HTPB and Partially Acetylated Samples

The samples were mixed thoroughly with TDI (OH/NCO ratio of 1 : 1). The mixture was then degassed for a short while to remove air bubbles and poured into molds. Curing was performed at room temperature (in a desiccator) for 24 h followed by oven curing at 70°C for 24 h.

Mechanical Properties

Mechanical properties such as tensile strength, elongation, and stress at 100% elongation were measured on a Universal Testing Machine (Instron UTM) using dumb-bell shaped specimens prepared from the resin slabs.²⁷

Crosslink Density

Crosslink density (moles of effective network chains per cubic centimetre) of the cured samples was obtained by calculating the volume fraction of the swollen polymer. Crosslinked polymer specimens of size ~ 5 mm × 5 mm × 5 mm were soaked in toluene. After 24 h the swollen samples were taken out and weighed, (*W_s*) after gently wiping off the solvent. The weight of the deswollen polymer (*W_{ds}*) was obtained by removing the solvent present by drying in a vacuum oven at 100°C for 4 h. From the weights of the swollen and deswollen specimens the swell ratio (*Q*) was calculated.

$$Q = (W_s/W_{ds}) - 1 \quad (1)$$

The weight fractions of the polymer (*W₂*) and solvent (*W₁*) were calculated from the equation

$$W_2 = \frac{1}{1 + Q} \quad \text{and} \quad W_1 = 1 - W_2$$

The volume fraction of the polymer (*V₂*) in the swollen specimen was then obtained as

$$V_2 = \frac{W_2/\rho_2}{(W_2/\rho_2) + (W_1/\rho_1)} \quad (2)$$

where ρ_1 and ρ_2 represent the densities of the solvent and the polymer, respectively.

From the value of volume fraction under equilibrium-swollen conditions, the crosslink density (ν_e) and molecular weight between the crosslinks (*M*) were calculated by the Flory-Rhener relation,²⁸

$$\nu_e = \frac{-[\ln(1 - V_2) + V_2 + \chi V_2^2]}{V_s(V_2^{1/3} - V_2/2)} = \frac{\rho_2}{M_c} \quad (3)$$

where *V_s* is the molar volume of the solvent and χ is the polymer-solvent interaction parameter, related to the solubility parameter of the polymer (δ_p) and the solvent (δ_s) as,^{29,30}

$$\chi = 0.34 + (V_s/RT)(\delta_p - \delta_s)^2 \quad (4)$$

where *R* is the gas constant and *T* is the absolute temperature. The solubility parameter could be equated to the cohesive energy density by the relation³¹

$$\delta = (E_{\text{coh}}/V)^{1/2} \quad (5)$$

The cohesive energy and molar volume (V) parameters were estimated by the group additivity method. The values of the functional groups (OH and OAc) are not included, as their concentrations are very low.

$$\begin{aligned} (E_{\text{coh}})\text{HTPB} &= E_{\text{coh}}(\text{CH}=\text{CH}) + 2[E_{\text{coh}}(\text{CH}_2)] \\ &= 10200 + 2(4190) = 18580 \text{ J/mol.} \end{aligned}$$

Similarly, molar volume of HTPB (V) is given by,^{31a}

$$\begin{aligned} V = \sum V_i &= V_{(\text{CH}=\text{CH})} + 2[V_{(\text{CH}_2)}] \\ &= 60.65 \text{ cm}^3/\text{mol.} \end{aligned}$$

$$\delta_{\text{HTPB}} = (18580/60.65)^{1/2} = 17.5 \text{ J}^{1/2}/\text{cm}^{3/2}$$

For toluene,^{31b}

$$\delta_{\text{toluene}} = 18.1 \text{ J}^{1/2}/\text{cm}^{3/2}$$

and

$$V_s = 106.3 \text{ cm}^3/\text{mol}$$

From all these values, the interaction parameter " χ " for HTPB was calculated using eq. (4).

$$\chi = 0.355$$

The values of interaction parameters for different acetylated samples were calculated by substituting V_2 and V_s values in eq. (4). From this the crosslink density and molecular weight (M_c) between crosslinks of various compositions were calculated.

RESULTS AND DISCUSSION

Preparation of Partially Acetylated HTPB

Two different methods were adopted for the partial acetylation of HTPB. Acetylation using highly reactive acetyl chloride in presence of NMI catalyst is designated as the fast method or random method. In this case the reaction will be very fast and the G , H , and V hydroxyl groups can get acetylated in a random way. Acetylation using slow reacting acetic anhydride at 60°C is described as "slow reaction" or "selective reaction." Here reaction conditions are made slow so that acetylation

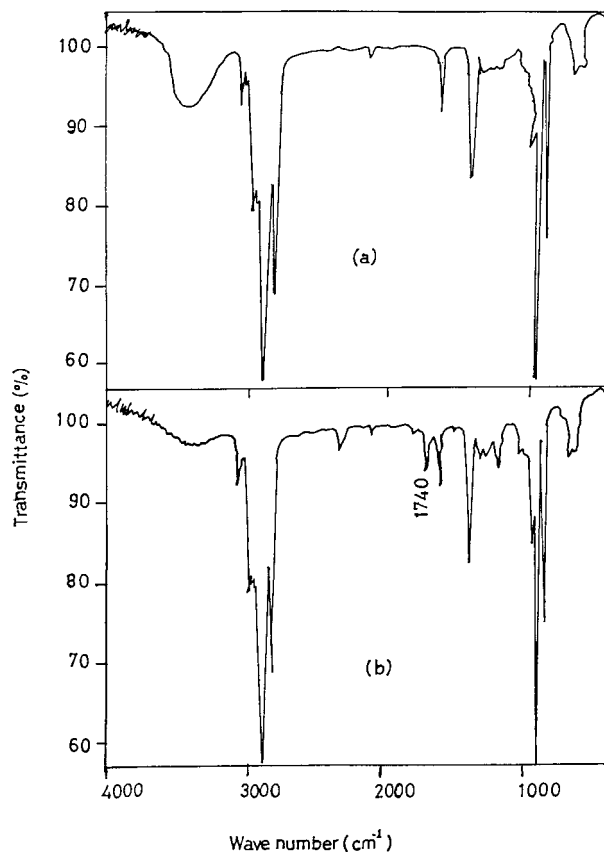


Figure 1 Typical IR spectrum of (a) HTPB and (b) partially acetylated HTPB.

can occur selectively on G , H , or V hydroxyl groups. In this case it is expected that the more reactive among the three OH groups will be acetylated to a greater extent.

Characterization of Partially Acetylated HTPBs

The introduction of acetyl groups in HTPB was confirmed by spectroscopic and chemical methods. The IR spectra of the acetylated samples were similar to that of HTPB with an additional absorption band at 1740 cm^{-1} due to the acetyl group, which was found to increase with the extent of acetylation. Figure 1 (a) and 1 (b) represent typical IR spectra of HTPB and partially acetylated HTPB, respectively.

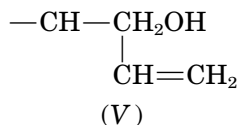
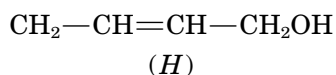
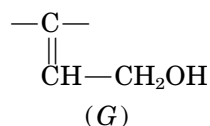
Acetylation of HTPB to different extents by the two methods was confirmed by estimating the hydroxyl and ester values of the samples. Table I shows the chemical analysis values of HTPB and partially acetylated samples. An increase in equivalent weight and decrease in average functionality ($f_n = \text{molecular weight/equivalent}$

Table I Characteristics of HTPB and Acetylated Samples

| Sample | HTPB | Fast/Random method | | Slow/Selective method | |
|---------------------------|-------|--------------------|--------|-----------------------|--------|
| | | 10% AC | 20% AC | 10% AA | 20% AA |
| OH value (mg KOH/g) | 41.3 | 39.0 | 34.9 | 37.6 | 32.0 |
| Ester value (mg KOH/g) | 0 | 3.3 | 7.6 | 3.4 | 8.0 |
| OH Eq.wt | 1358 | 1438 | 1607 | 1492 | 1753 |
| M_n (GPC) | 3070 | 2990 | 3240 | 2830 | 2760 |
| M_w (GPC) | 10410 | 11660 | 10350 | 9640 | 10520 |
| $d = M_w/M_n$ | 3.4 | 3.8 | 3.2 | 3.4 | 3.8 |
| f_n | 2.2 | 2.1 | 2.0 | 1.9 | 1.6 |

weight) was observed with increase in the extent of acetylation (corresponding reduction in the number of OH groups). Molecular weight values were almost the same within experimental error.

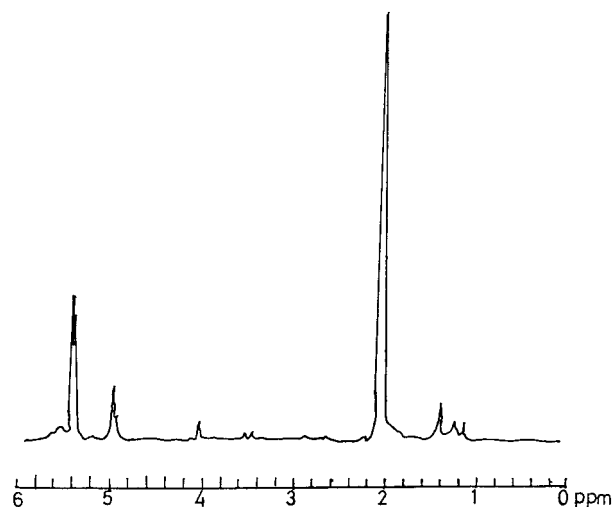
Analysis of the $^1\text{H-NMR}$ spectra enabled the determination of different types of hydroxyl groups present in the samples. A typical $^1\text{H-NMR}$ spectrum of HTPB recorded at 400 MHz is shown in Figure 2. The spectra contain small resonances at $\delta = 4.22$, 4.12, and 3.5 ppm, which are attributed by Pham et al.^{16,17} to the carbon bonded protons of primary alcohol and are described as geraniol type (*G*), hexene-2-1 type (*H*), and vinyl type (*V*) with the following structures:



A magnification of the resonances of methylene groups carrying the hydroxyl functions is represented in Figure 3, which shows that the three OH regions are well separated in the $^1\text{H-NMR}$ spectrum. The doublet resonance showed by the *G*-type OH (G_{OH}) is attributed¹⁷ to the difference in the nature of 1,2 or 1,4 butadiene adjacent to it. In Figure 3, vinyl OH (V_{OH}) absorption is found to spread between 3.65 ppm and 3.45 ppm, per-

fectly separated into two groups, each group again separated into four peaks. Of these, the peaks at high field (between 3.45 and 3.55) are attributed to the absorption of a terminal —V—V_{OH} and the other peaks located at a lower field (between 3.65 ppm and 3.45 ppm) to the absorption of a terminal diad $\text{—(1,4)—V}_{\text{OH}}$.

Thus, the relative proportions of *G*, *H*, and *V* hydroxyl groups can be estimated from the intensities of their resonances at $\delta = 4.21$, 4.12, and 3.5 ppm, respectively. The intensities of OH functions present in different samples are normalized according to the ester content present in each sample. The reason for taking the ester values of the samples as the standard for finding the extent of acetylation was due to the easy and sharp endpoint determination of ester content by chemical analysis. In the analysis of OH groups by acetylation, the endpoint determination was difficult due

**Figure 2** Typical $^1\text{H-NMR}$ spectrum of FR-HTPB.

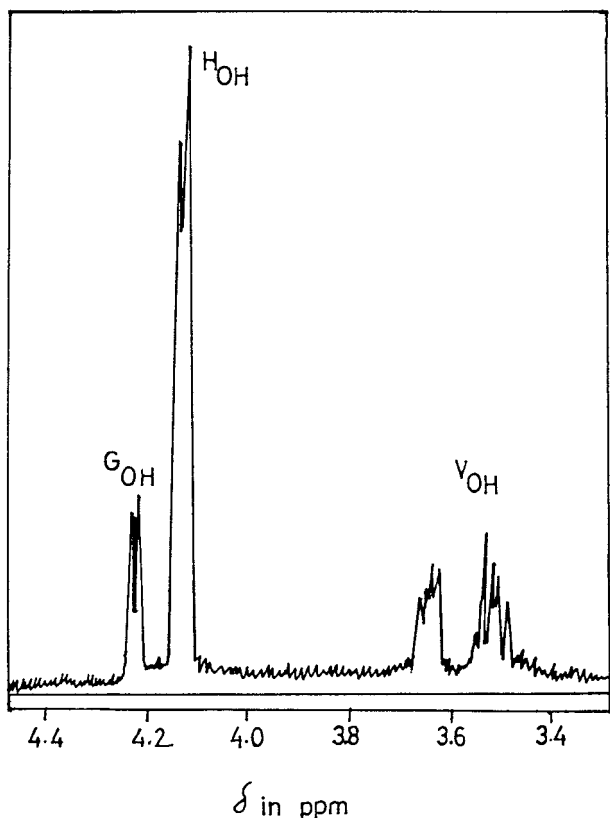


Figure 3 Typical $^1\text{H-NMR}$ spectrum of FR-HTPB showing magnification of OH resonances.

to the formation of emulsion. The percentage conversion to the acetyl derivative, based on the ester values, came close to the nominal values and hence the latter was used for the subsequent calculation of normalization of NMR peak intensities. The normalized peak intensities of different hydroxyl functions present in HTPB and partially acetylated samples are given in Table II.

Table II shows a steady decrease in the quantity of different hydroxyl groups as the extent of acetylation increases. However, the amount of G , H , and V hydroxyl groups remaining in the sam-

ples acetylated to the same extent by the two methods is different. This shows that the reactivities of the different OH functions vary with the conditions adopted in their reaction. If all the three functions reacted equally, the amount of G , H , and V hydroxyl remaining in the sample would have been same as the expected values (calculated on the basis of 10% and 20% reduction uniformly for all the three types of hydroxyls). Table III gives the experimental and expected (theoretical) values, and the difference between the two.

From Table III the following observations can be made: For the fast reaction condition, where the reaction is believed to proceed in a random manner, there is not much difference between the expected and experimental values of the relative amounts of the G -type of hydroxyls. In the case of H -type hydroxyls, the extent of reaction is slightly higher than the expected value for 20% AC (H -type hydroxyls remaining lower by 2.8%). A corresponding decrease is seen in the case of V -type hydroxyls. However, the magnitude of the difference is not significant enough (approximately 10% with respect to the expected value) to clearly conclude that H hydroxyl is more reactive than V hydroxyl under fast reaction conditions.

However, the situation is different when we go to the slow reaction conditions. For 20% AA, the G -type has reacted more than the expected amount (30% with reference to the theoretical value). The corresponding decrease in conversion is for the V -type, while there is no major change in the case of the H -type. From this we can conclude that the reactivity is in the order $G > H > V$ for the slow reaction. Under the conditions of acetylation by acetic anhydride, the reaction is slow enough to be selective, so that the change in reactivity of the hydroxyl groups is reflected in the extent of their conversion. However, when the reaction is very rapid, as in the case of NMI-catalyzed acetylation with acetyl chloride, the reaction

Table II Quantities (%) of the Hydroxyls Present in HTPB and Partially Acetylated Samples by $^1\text{H-NMR}$

| | HTPB | Fast/Random method | | Slow/Selective method | |
|---------------------------|------|--------------------|--------|-----------------------|--------|
| | | 10% AC | 20% AC | 10% AA | 20% AA |
| % of Acetylation | — | 8 | 19 | 9 | 20 |
| G_{OH} (4.2 ppm) | 21.6 | 20.1 | 16.6 | 18.7 | 12.2 |
| H_{OH} (4.1 ppm) | 39.3 | 35.9 | 28.6 | 34.6 | 30.3 |
| V_{OH} (3.5 ppm) | 39.1 | 34.0 | 34.6 | 36.7 | 37.5 |

Table III Theoretical and Observed Amount (%) of Different Hydroxyl Groups in Partially Acetylated Samples

| | Fast/Random method | | Slow/Selective method | |
|--------------------|--------------------|--------|-----------------------|--------|
| | 10% AC | 20% AC | 10% AA | 20% AA |
| G_{OH} (4.2 ppm) | | | | |
| Theoretical | 19.5 | 17.3 | 19.5 | 17.3 |
| Experimental | 20.1 | 16.8 | 18.7 | 12.2 |
| Difference | -0.6 | +0.5 | +0.8 | +5.1 |
| H_{OH} (4.1 ppm) | | | | |
| Theoretical | 35.4 | 31.4 | 35.4 | 31.4 |
| Experimental | 35.9 | 28.6 | 34.6 | 30.3 |
| Difference | -0.5 | +2.8 | +0.8 | +1.1 |
| V_{OH} (3.5 ppm) | | | | |
| Theoretical | 35.2 | 31.3 | 35.2 | 31.3 |
| Experimental | 34.0 | 34.6 | 36.7 | 37.5 |
| Difference | +1.2 | -3.3 | -1.5 | -6.2 |

becomes random and the reactivity of the individual types of hydroxyl groups does not play a major role so that all three types of hydroxyls react nearly to the same extent. Thus, in reality, the reactivity of the three types of hydroxyls are in the order $G > H > V$. This is in agreement with the results obtained by Descheres and Pham²⁰ who came to the same conclusion from their studies on the rate constants of the reaction of the three types of hydroxyls in HTPB (Arco R-45M) with isocyanate.

The lower reactivity of V in comparison to the G- and H-types is probably due to the steric hindrance of the vinyl branches in α -position of hydroxylated ends. The acetylated samples were cured using a difunctional curative TDI. The me-

chanical properties and swelling properties of the cured products obtained are given in Table IV.

Even though the samples are equally acetylated, the mechanical properties of the cured products vary considerably. Among the three types of OH present, G is branched and H and V are terminal. In a crosslinking reaction G contributes to the crosslinking, whereas H and V act as chain extenders only. Therefore, samples containing a higher proportion of the G-type will show higher tensile strength. The 10% acetylated sample, obtained from the random method (10% AC), which contains a higher percentage of G_{OH} , showed better mechanical properties compared to the 10% acetylated sample prepared from the selective reaction method (10% AA). Since more

Table IV Mechanical and Swelling Properties of the Cured Network

| HTPB | Fast/Random method | | Slow/Selective method | | |
|--|--------------------|--------|-----------------------|--------|-------|
| | 10% AC | 20% AC | 10% AA | 20% AA | |
| Tensile strength (kg/cm ²) | 8.9 | 7.0 | 4.5 | 5.5 | 3.1 |
| Elongation (%) | 320 | 500 | 675 | 326 | 590 |
| Modulus (kg/cm ²) | 4.3 | 2.2 | 1.5 | 1.8 | 0.9 |
| Hardness | 40 | 30 | 15 | 25 | 10 |
| Crosslink density ($\nu_e \times 10^{-4}$) | 1.83 | 0.91 | 0.60 | 0.78 | 0.35 |
| Mol. wt. between crosslinks (M_c) | 5280 | 10900 | 16200 | 12300 | 26700 |
| Swell ratio (Q) | 3.5 | 5.3 | 6.6 | 5.7 | 8.8 |
| Volume fraction of the polymer | 0.21 | 0.15 | 0.12 | 0.14 | 0.09 |

G_{OH} is consumed in 10% AA, the number of crosslink sites is low, and hence its crosslink density was found to be less compared to 10% AC. Similarly for 20% AC, the mechanical properties are higher than the 20% AA which contains a lesser amount of G hydroxyl groups. This experiment reestablishes the branching nature of G_{OH} , put forth by Pham et al.^{16,17} and shows the importance of microstructure on the mechanical properties of the polymer.

We thank the director, VSSC for the kind permission to publish this work. Thanks are due to Dr. C. P. R. Nair for the valuable discussions, K. B. Catherine for the GPC analysis, to Dr. M. Kanakavel for IR spectroscopy, to K. Ambika Devi for mechanical testing, and to the director RSIC, IIT, Madras for the NMR spectra. One of us (S.S.P.) thanks the Council of Scientific and Industrial Research, Govt. of India, for a Senior Research Fellowship.

REFERENCES

- R. Nagappa and M. R. Kurup, AIAA Paper No. 90-2331, 26th Joint Propulsion conference, Florida, 1990.
- S. Takeo and S. C. Yamashiro, Japan 71 32742 (1971).
- N. Masaji, T. Michio, M. Junji, N. Toshikazu, and N. Sumic, Ger. Offen, 1,961241, (1970) (*Chem. Abstr.*, **74**, 1971, 43056 t).
- W. Tamatsu, Japan, 74 01954, (1974), (*Chem. Abstr.*, **78**, 1973, 59265 d).
- R. D. Law, *J. Polym. Sci.*, A-1, **9**, 589 (1971).
- J. N. Anderson, S. K. Baczek, H. E. Adams, and L. E. Vescelius, *J. Appl. Polym. Sci.*, **19**, 2255, 2269 (1975).
- J. C. Carver, *Improved Specification for Composite Propellant Binders for Army Weapon Systems*, Report No. TR-RK-81-5, 1981.
- K. N. Ninan, V. P. Balagangadharan, and K. B. Catherine, *Polymer*, **32**, 628 (1991).
- K. N. Ninan, V. P. Balagangadharan, K. Ambika Devi, and K. B. Catherine, *Polym. Int.*, **31**, 255 (1993).
- S. S. Panicker and K. N. Ninan, *Polym. Int.*, **37**, 255 (1995).
- S. S. Panicker and K. N. Ninan, *J. Appl. Polym. Sci.*, **56**, 1797 (1995).
- D. M. French, *Rubber Chem. Technol.*, **12**, 71 (1969).
- Li Bei-zhu and Liu Zhong-Chun, "Analysis of Propellants and Explosives—Chemical and Physical Methods," *Proceedings of the 17th International Congress of ICT*, Fraunhofer Institut fur Treih-und Explosivstoffe, Germany, 1986, p. 9–1.
- D. Fakuma, K. Shirota, S. Suzuki, A. Iwama, and A. Saitoh, "Use of Plastic Materials for Propellants and Explosives," *Proceedings of the International Jahrestagung* (1981) p. 121.
- K. C. Ramey, M. W. Hayes, and A. G. Altenaue, *Macromolecules*, **5**, 795 (1973).
- G. Fages and Q. T. Pham, *Makromol. Chem.*, **179**, 1011 (1978).
- Q. T. Pham, *Makromol. Chem.*, **182**, 1167 (1981).
- L. S. Bresler, E. N. Barantsevitch, V. I. Polyansky, and S. S. Ivantchev, *Makromol. Chem.*, **183**, 2479 (1982).
- G. Fages and Q. T. Pham, *Makromol. Chem.*, **180**, 397 (1975).
- I. Descheres and Q. T. Pham, *Makromol. Chem.*, **187**, 1963 (1986).
- M. El Ghafari and Q. T. Pham, *Makromol. Chem.*, **184**, 1669 (1983).
- M. Rama Rao, K. J. Scariah, P. V. Ravindran, G. Chandrasekharan, S. Alwan, and K. S. Sastri, *J. Appl. Polym. Sci.*, **49**, 435 (1993).
- Sidney Siggia, *Quantitative Organic Analysis via Functional Groups*, 3rd Ed., John Wiley and Sons, New York, 1963, p. 187.
- ASTM D-2849-69, Part 36, *Annual Book of ASTM Standards*, American Society for Testing and Materials, 1982, p. 640.
- ASTM D-3536-76, vol. 8.03, *Annual Book of ASTM Standards*, American Society for Testing and Materials, 1989, p. 104.
- ASTM D-3593, Vol. 8.03, *Annual Book of ASTM Standards*, American Society for Testing and Materials, 1989, p. 122.
- ASTM-D412-80, Part-37, *Annual Book of ASTM Standards*, American Society for Testing and Materials, 1982, p. 57.
- P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953, p. 579.
- G. M. Briston and W. F. Watson, *Trans. Faraday Society for Testing and Materials* (1982).
- D. J. Hourston and Y. Zia, *J. Appl. Polym. Sci.*, **28**, 2139 (1983).
- D. W. Van Krayen, *Properties of Polymers*, Elsevier, New York, 1976, p. 130–132 (a) p. 55, (b) p. 582.