

# Correlation of Binder Mechanical Properties with Functionality Type and Molecular Weight Distribution for Hydroxy-Terminated Polybutadienes: $^{13}\text{C}$ -NMR and SEC Studies

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## SYNOPSIS

Hydroxy-terminated polybutadiene (HTPB) liquid prepolymers (I–IX), with closely similar OH values,  $\bar{M}_n$ , viscosity, and microstructure, were synthesized by  $\text{H}_2\text{O}_2$ -initiated free-radical polymerization of butadiene in an isopropanol–water solvent system. However, binders obtained by curing HTPB polymers showed wide variations in their sol content, cross-link density, and mechanical properties. These variations were attributed to the differences in functionality-type distribution (FTD) and molecular weight distribution (MWD) of the polymers. FTD was interpreted in terms of  $H$  [ $\text{HOCH}_2 - \text{CH}=\text{CH} - \text{CH}_2 \sim \sim \sim$ ],  $V$  [ $\text{HOCH}_2 - \text{CH}(\text{CH}=\text{CH}_2) \sim \sim \sim$ ], and  $G$  [ $\text{HOCH}_2\text{CH}=\text{C} \sim \sim \sim$ ]-type primary

hydroxyls.  $[V/G]$  showed excellent linear correlation with the elongation at break ( $E$ ) of the binders. The polymers exhibited bimodal MWD and this behavior was discussed in relation to two different initiation processes occurring. The high molecular weight fraction ( $F_h$ ) of the various polymers was determined by reverse-phase HPLC and showed good correlation with  $E$ . The sol content and cross-link density of the binders also showed good correlation with the parameter  $V/GF_h$ . The parameters  $[V/G]$  and  $F_h$  provide acceptance criteria for blending different batches of polymers for propellant formulations. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Hydroxy-terminated polybutadiene (HTPB) liquid prepolymers play an important role in the manufacture of composite solid propellants for rocket motors. Differences in the manufacture of these polymers and also batch-to-batch variability result in polymers varying in molecular weight distribution and functionality distribution.<sup>1,2</sup> These differences greatly affect the propellant processibility, pot life, cure behavior, mechanical properties, and aging characteristics.<sup>3</sup> Therefore, several studies were undertaken to (i) fractionate the polymers according to functionality: mono-, di-, tri-, etc., by column

chromatography, TLC, and HPLC<sup>4–7</sup>; (ii) obtain functionality distribution with respect to molecular weights by employing derivatized polymers and using size-exclusion chromatography (SEC)<sup>8–10</sup>; (iii) identify the nature and reactivity of the hydroxyl group by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy<sup>11,12</sup>—three types of primary alcohol groups were identified; and (iv) correlate the functionality and molecular weight distribution with the properties of the cured resins (gum stock properties).<sup>13</sup> Thus, HTPB may be considered to be a well-characterized polymer. However, studies on the relative distribution of the three types of hydroxyl functionalities in polymers synthesized under varying conditions and also how these differences translate into the properties of the cured resin are lacking.

In this communication, we report on the functionality-type distribution (FTD) of the HTPB polymer samples synthesized by  $\text{H}_2\text{O}_2$ -initiated free-

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radical polymerization of butadiene. These polymers show a bimodal molecular weight distribution (MWD) and this behavior is discussed in terms of two different initiation processes occurring. Also, the dependence of sol content, cross-link density, and the mechanical properties of the cured resins on the functionality type and bimodal distributions is presented.

## EXPERIMENTAL

### Synthesis of Polymers

HTPB polymers (I–IX) were synthesized by free-radical polymerization of butadiene initiated by  $H_2O_2$  in an isopropanol (IPA)–water solvent system. The relative proportions of the monomer, initiator, IPA, and water were kept nearly constant during the synthesis of all the polymers. Minor changes in the process parameters and inadvertent batch-to-batch variation resulted in polymers I–IX.

### Polymer Characterization

The number-average molecular weight ( $\bar{M}_n$ ) of the polymers was determined using a Knauer analog VPO with toluene as solvent at 65°C. Hydroxyl values were determined by the standard chemical method and functionalities were calculated using the  $\bar{M}_n$  obtained by VPO. Viscosity measurements at 30°C were carried out using a Brookfield HBT rotating spindle viscometer with spindle no. 2 at 50 rpm.

### Molecular Weight Distribution

The MWDs were determined from SEC using a set of two Styragel columns with permeabilities of 500 and 100 Å. THF was used as the eluant at a flow rate of 1 mL/min. Calibration was performed using polystyrene standards and the observed molecular weights were corrected for polybutadienes using the ASTM D3593 procedure.<sup>14</sup> An HP 1081B liquid chromatograph coupled to a Shimadzu CR2AX data processor was used for the measurements.

High-pressure liquid chromatographic (HPLC) measurements were carried out using a reverse-phase preparatory column (Shimpack PREP-ODS, Shimadzu), a Shimadzu LC6A instrument, and a Shimadzu CR2AX data processor. THF was the eluant at a flow rate of 9 mL/min.

### <sup>13</sup>C-NMR Spectra

Proton noise decoupled <sup>13</sup>C-NMR spectra of HTPB polymers (I–IX) were recorded at 22.5 MHz on an ~ 10% (w/v) solution in  $CDCl_3$  with TMS as the internal standard using a JEOL FX 90Q NMR spectrometer. Other relevant operating parameters were the following: sweep width, 5000 Hz; acquisition time, 1.6 s; pulse width, 18 s (corresponding to a nuclear tip angle of 60°); data points, 16K; pulse delay, 2.5 s; and number of scans, ~1000.

### Curing of HTPB Polymers

HTPB polymer samples were cured using toluene diisocyanate (TDI) at  $[NCO]/[OH]$  equivalence ratios of 0.75 and 1.0 at 70°C for 24 h. Propellant samples were obtained by curing HTPB polymer at a  $[NCO]/[OH]$  equivalence of 0.75 and with 86% solid loading.

### Characterization of Binders

The sol content of the binders was determined by Soxhlet extraction with toluene for 48 h. Cross-link density was determined by the swollen compression method.<sup>15</sup> The mechanical properties—tensile strength (TS), elongation at break ( $E\%$ ), and modulus—were determined according to the ASTM D412 procedure<sup>16</sup> using an Instron UTM Model 4201.

## RESULTS AND DISCUSSION

### Polymer Synthesis and Characterization

HTPB polymers (I–IX) were synthesized by free-radical polymerization of butadiene using hydrogen peroxide ( $H_2O_2$ ) as the initiator in an isopropanol–water solvent system. The relative amounts of butadiene,  $H_2O_2$ , water, and isopropanol were kept constant during the synthesis of the various polymers. The polymers were characterized by their hydroxyl value, number-average molecular weights,  $\bar{M}_n$ , by VPO, Brookfield viscosity, functionality, and microstructure by <sup>13</sup>C-NMR. The results, given in Table I, indicate that the properties of the polymers lie in a very narrow range.

### Formation of Urethane Networks

HTPB polymers (I–IX) were cured by reaction with TDI at 70°C for 24 h to obtain cross-linked

**Table I Properties of HTPB Polymers**

Polymer No.	OH Value (mg KOH/g)	$\overline{M}_n$ (VPO)	Viscosity at 30°C (cps)	$\overline{F}_n$	Microstructure (%)		
					<i>trans</i>	<i>cis</i>	Vinyl
I	44.1	2560	6330	2.01	50.6	30.0	19.4
II	47.2	2690	6240	2.26	55.2	27.0	17.8
III	43.7	2700	6460	2.10	53.3	27.6	19.1
IV	44.6	2660	5820	2.11	53.5	26.7	19.8
V	40.0	2590	5840	1.85	52.1	29.5	18.4
VI	41.2	2660	6100	1.95	52.7	28.1	19.2
VII	40.3	2620	6150	1.88	53.1	27.9	19.0
VIII	41.8	2680	5145	2.00	50.7	31.0	18.3
IX	39.5	2720	4514	1.95	55.6	27.5	16.8

polyurethane networks. The cure reaction was carried out at an [NCO]/[OH] equivalent ratio of 0.75 as well as the stoichiometric ratio of 1. The cured polymers were characterized by their sol content, cross-link density, and mechanical properties (tensile strength [TS], modulus, and elongation at break [E]). The results obtained are shown in Table II. Also included in the table are the mechanical properties of propellants obtained by curing HTPB polymers at an [NCO]/[OH] equivalent ratio of 0.75 and 86% solid loading. The results indicate striking variations in the sol content (11.3–38%), cross-link density ( $0.8 \times 10^{-5}$  to  $5.3 \times 10^{-5}$  mol/cc), and elongation (220–1130%) for polymers cured at less than the stoichiometric ratio even though the polymers have closely similar properties. Similar trends were observed at an [NCO]-to-[OH] equiv-

alent ratio of 1 as well as in the propellants. However, the differences are smaller. The changes in tensile strength are correspondingly much lower and do not show any consistent regularity. Thus, the results quite clearly confirm that functionality and MWDs in the polymer play a vital role in determining the mechanical properties of the corresponding cured systems. Hence, a detailed study of these two parameters was undertaken.

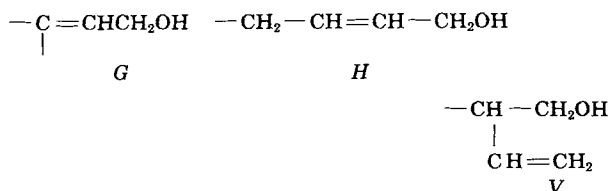
#### Functionality-Type Distribution (FTD)

Pham et al.<sup>11,12</sup> studied comprehensively the characterization of HTPB polymers by <sup>1</sup>H- and <sup>13</sup>C-NMR techniques. They identified three types of primary hydroxyls, namely, (i) geraniol type (*G*), (ii) 2-hexene-1-ol type (*H*), and vinyl type (*V*) with

**Table II Properties of Cured HTPB Polymers and Propellants**

Polymer	Cured HTPB Polymer						Propellant		
	[NCO]/[OH] = 0.75				[NCO]/[OH] = 1		[NCO]/[OH] = 0.75		
	Sol Content (%)	Crosslink Density (mol/cc $\times 10^5$ )	TS (KSC)	EL (%)	TS (KSC)	EL (%)	TS (KSC)	EL (%)	Modulus (KSC)
I	11.3	5.3	4.3	222	7.1	107	10.8	15	129
II	20.5	3.9	3.5	303	6.6	90	9.6	18	100
III	23.1	3.5	3.4	378	7.2	139	8.5	13	112
IV	20.4	4.4	3.5	534	7.4	140	11.3	24	92
V	18.8	3.9	3.3	630	6.8	170	—	—	—
VI	26.8	2.7	3.2	712	6.2	182	—	—	—
VII	31.4	1.3	3.9	725	7.0	200	11.7	27	87
VIII	—	—	3.5	750	5.8	212	—	—	—
IX	38.0	0.8	4.5	1130	6.3	323	9.5	38	50

the following structural units. The presence of secondary hydroxyls, if any was found to be small:



The three hydroxyl functions, *G*, *H*, and *V*, can be readily distinguished and their relative amounts estimated from their chemical shift differences in either  $^1\text{H}$ - or  $^{13}\text{C}$ -NMR spectra. Therefore, the  $^{13}\text{C}$  spectra of HTPB polymers I–IX were recorded in  $\text{CDCl}_3$  solvent and the relative proportions of *G*, *H*, and *V* were estimated from the intensities of their resonances at  $\delta = 58.6$ , 63.2, and 65.0 ppm, respectively. The results obtained are given in Table III and indicate considerable variations in the FTD among the various polymers.

### Correlation of FTD with Mechanical Properties

Among the three types of hydroxyls, *G*, *H*, and *V*, present in the polymer, *G* is branched, whereas *H* and *V* are terminals. Also, *G* contributes to cross-linking in the cured system, whereas *H* and *V* act as chain extenders only. Consequently, the higher the proportion of (*G*) in the polymer, the higher the tensile strength and the lower the elongation of the cured polyurethane network. On the other hand, *V* gives rise to urethane linkages with a single bond at

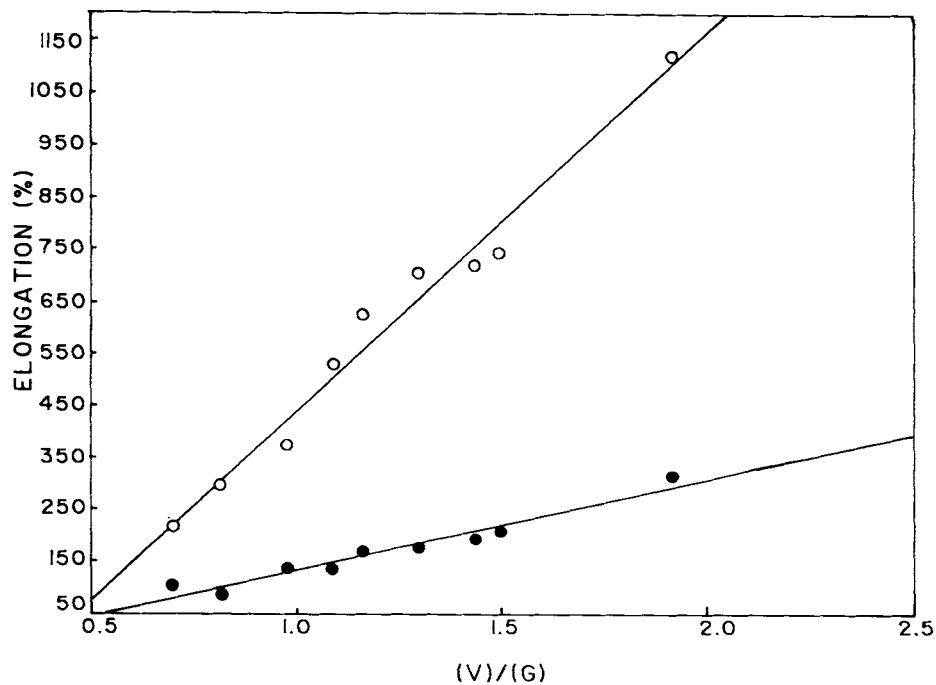
the  $\alpha$ -carbon ( $\text{ArNH COO CH}_2\text{---CH}\sim$ ), whereas *H* gives rise to a linkage with a double bond at the  $\alpha$ -carbon atom ( $\text{ArNH COO CH}_2\text{---CH=CH}\sim$ ). Hence, *V*-type functionality is expected to contribute to higher elongation. Therefore, the net effect of the different types of functionality causes an increase in elongation and a decrease in TS as the ratio of concentration of vinyl type to *G* type  $\{[V]/[G]\}$  increases. This, indeed, was found to be the case, as shown by the plot of elongation Vs  $\{[V]/[G]\}$  (Fig. 1). The excellent linearity of the plot with a correlation coefficient of 0.99 demonstrates the influence of the FTD on the gum stock properties.

Ninan et al.<sup>13</sup> presented a correlation between weight ratio of functionalities less than 3 (*CE*) and functionalities 3 and higher (*CR*) and the mechanical properties of the cured resin. The ratio *CE/CR* was obtained from SEC using 3,5-dinitrobenzoylester derivatives of HTPB polymers. Their data suggest that the ratio, *CE/CR*, can be roughly approximated to the mole ratio of difunctional to trifunctional moieties  $\{[\text{di}]/[\text{tri}]\}$  since (i) higher functionalities are associated with higher molecular weights and (ii) the mole fraction of functionalities higher than 4 is quite small. Therefore, the mole ratio  $[\text{di}]/[\text{tri}]$  was calculated from the relative proportion of *G* assuming that the polymer contains only di- and tri-functionalities. The results obtained for the mole ratio  $[\text{di}]/[\text{tri}]$  are given in Table III and are plotted against % elongation of the resin obtained by curing the polymer at an  $[\text{NCO}]/[\text{OH}]$  equivalence of 1, as shown in Figure 2. From this graph, elongations that correspond to the *CE/CR* value of Ninan et al.<sup>13</sup> were derived and are compared

**Table III** Functionality and Molecular Weight Distribution of HTPB Polymers

Polymer	Functionality-type Distribution				MWD			
	[ <i>G</i> ] (%)	[ <i>H</i> ] (%)	[ <i>V</i> ] (%)	[ <i>V</i> ] /[ <i>G</i> ]	[di]/ [tri] <sup>a</sup>	<i>F<sub>n</sub></i> (%)	[ <i>H</i> ] /[ <i>V</i> ]	[ <i>V</i> ] × 10 <sup>2</sup> /[ <i>G</i> ] <i>F<sub>n</sub></i>
I	24.0	59.1	16.9	0.70	0.58	35.9	3.50	1.95
II	25.0	54.6	20.4	0.82	0.50	33.4	2.68	2.46
III	24.3	51.8	23.9	0.98	0.56	30.8	2.17	3.19
IV	23.1	51.7	25.2	1.09	0.67	29.2	2.05	3.73
V	21.5	53.2	25.2	1.17	0.83	23.8	2.11	4.92
VI	20.6	52.7	26.7	1.30	0.93	24.1	1.97	5.39
VII	17.4	57.6	25.0	1.44	1.37	23.8	2.30	6.04
VIII	18.2	54.5	27.3	1.50	1.25	24.6	2.00	6.10
IX	14.4	57.9	27.7	1.92	1.97	24.9	2.05	7.73

<sup>a</sup> Calculated from the equation  $[\text{di}]/[\text{tri}] = (100 - 3[\text{G}])/(2[\text{G}])$ .

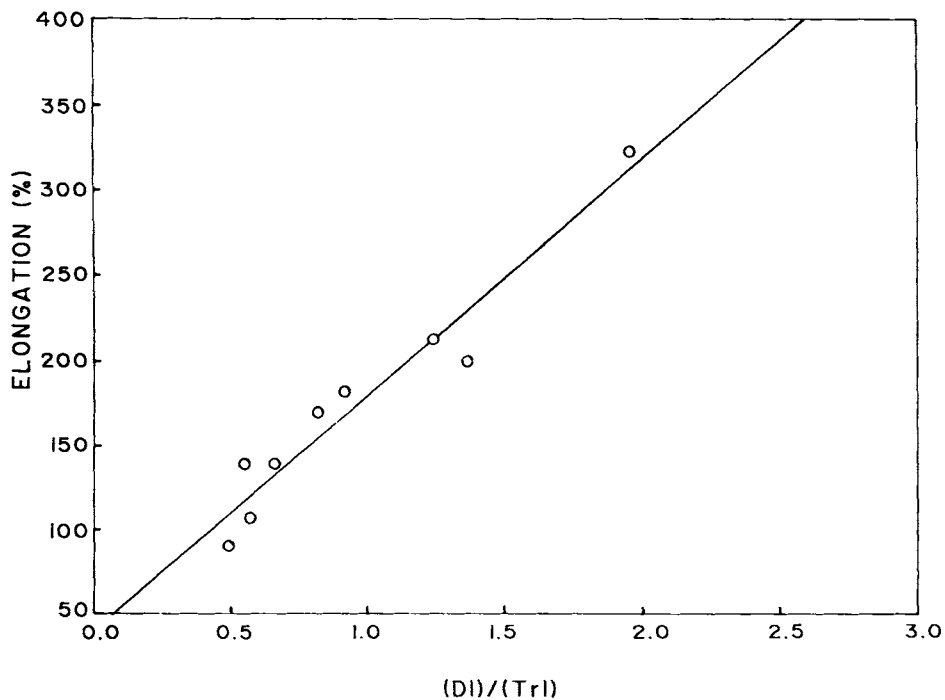


**Figure 1** Plot of  $[V]/[G]$  vs. elongation percent: (○)  $[NCO]/[OH] = 0.75$ ; (●)  $[NCO]/[OH] = 1.0$ .

with their observed and calculated values in Table IV. The satisfactory agreement between the two sets of data obtained by two different methods validates the methodology adopted by us.

#### Molecular Weight Distribution

The MWD of the HTPB polymer was determined by size-exclusion chromatography (SEC) and a rep-



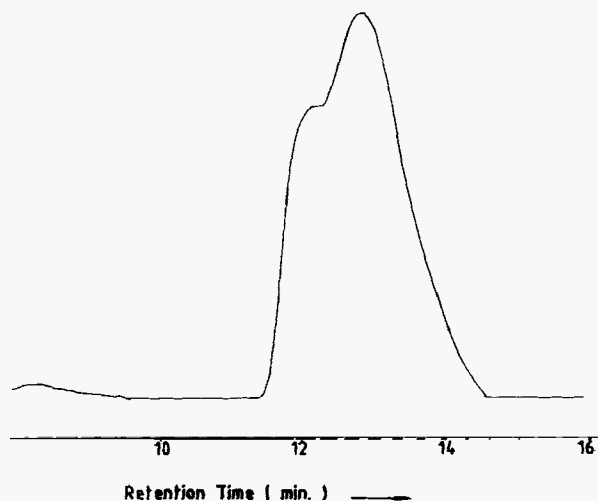
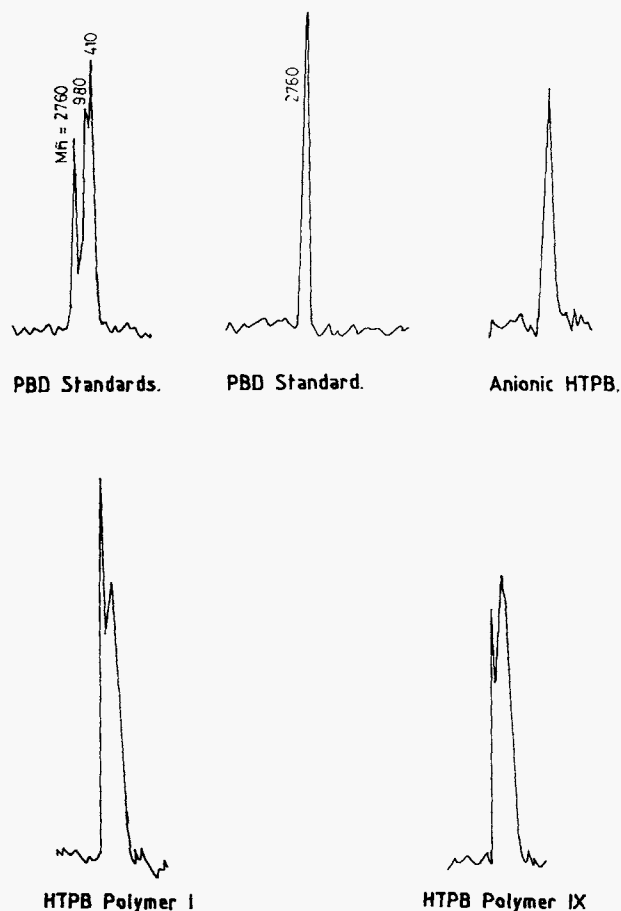
**Figure 2** Plot of  $[di]/[tri]$  vs. elongation percent at  $[NCO]/[OH] = 1.0$ .

**Table IV** Correlation of  $[CE]/[CR]$  with Elongation

Serial No.	$\frac{CE^*}{CR}$	Elongation (%)	
		Observed <sup>a</sup>	Calculated
			From Curve Fit <sup>a</sup>
		155	168
		226	209
		210	256
		230	256
		307	321

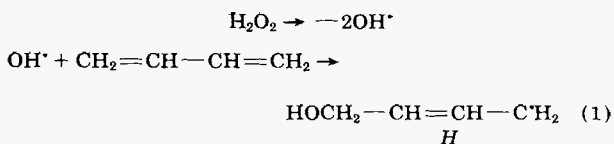
<sup>a</sup> Ref. 13.

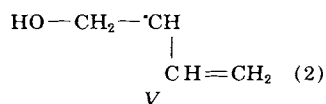
representative chromatogram is shown in Figure 3. A bimodal distribution of the molecular weights is clearly indicated. Attempts were then made to improve the resolution by reverse-phase HPLC using a Shim-pack Prep-ODS column and THF as the eluant. Figure 4 shows the improved resolution that could be obtained by this technique. Under identical conditions, polybutadiene standards of molecular weights 2760, 980, and 410 were also run and their chromatograms are included in Figure 4. The results indicate that, under the experimental conditions, separation takes place according to molecular weights. Also, commercially available anionic HTPB, which should have only a unimodal distribution, showed a single peak in the chromatogram, confirming the earlier observation. However, the present data are not adequate to infer that functionality does not influence the separation. The high

**Figure 3** SEC of HTPB polymer IX.**Figure 4** Reverse-phase HPLC of polybutadiene and HTPB polymers.

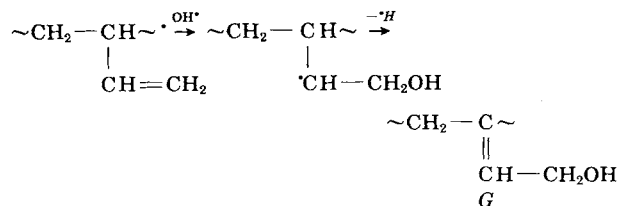
molecular weight fraction ( $F_h$ ) of the polymers was calculated from peak areas and the results are shown in Table III. The number-average molecular weights of the two fractions were determined by SEC and were found to be in the range 3000–3500 and 2000–2500. Considerable variation was observed in  $F_h$  values among various polymers.

The bimodal distribution of HTPB polymers may be because two types of initiation reactions are occurring in the polymerization process, as is evident from the occurrence of H- and V-type hydroxyls in the polymer. H-type hydroxyls arise from the addition of OH radicals to a butadiene monomer in a 1,4-fashion, whereas the V-type hydroxyl arises from a 1,2-addition as was suggested by Pham<sup>12</sup>:

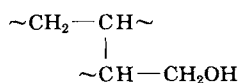




The *G*-type hydroxyl may arise from the addition of a OH radical to a vinyl-type double bond in a polymer chain and subsequent loss of a H radical:



The absence of structural units of type



in the polymers suggests that formation of *G* is not an initiation reaction. Thus, only reactions (1) and (2) can be considered as initiation reactions.

The relative importance of the two initiation reactions (1) and (2) can be judged from the relative

concentrations of *H*- and *V*-type hydroxyls. The ratio  $[H]/[V]$  can be obtained from  $^{13}\text{C}$ -NMR as indicated earlier and values obtained for the various polymers are given in Table III and are plotted against the fraction of high molecular weight,  $F_h$ , in Figure 5. The correlation of the  $[H]/[V]$  ratio with  $F_h$  shows interesting behavior. Thus, for polymers **V**, **VI**, **VIII**, and **IX**, which show nearly a constant value (24%) for  $F_h$ , also show a nearly constant value (2.0) for the ratio  $[H]/[V]$ . Also,  $F_h$  decreases as the ratio  $[H]/[V]$  decreases, although not linearly. The results indicate that high molecular weight polymers are obtained when *H*-type initiation (1) predominates and that lower molecular weight polymers are obtained when *V*-type initiation (2) also occurs to a comparable extent. This is quite reasonable because the greater the number of the initiating radicals the lower will be the observed molecular weights. However, the process parameters that influence the two types of initiation reactions are not yet understood and are under investigation.

#### Correlation of $F_h$ with Mechanical Properties

Earlier studies show that for HTPB polymers, prepared by  $\text{H}_2\text{O}_2$  initiation, the functionality of the polymer increases with increase in molecular weight. Extending this observation to the present case, it

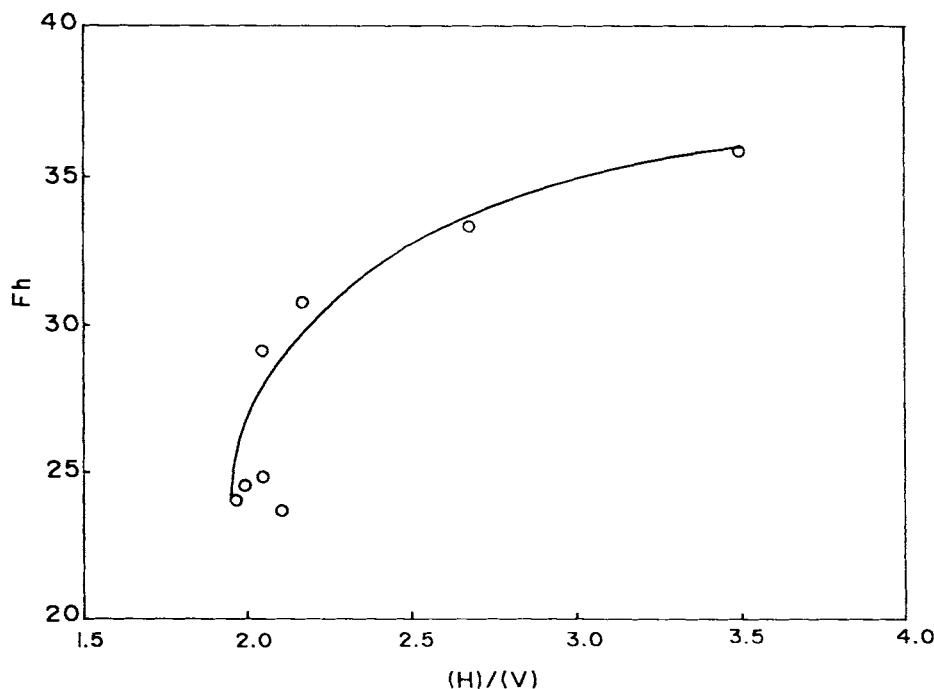
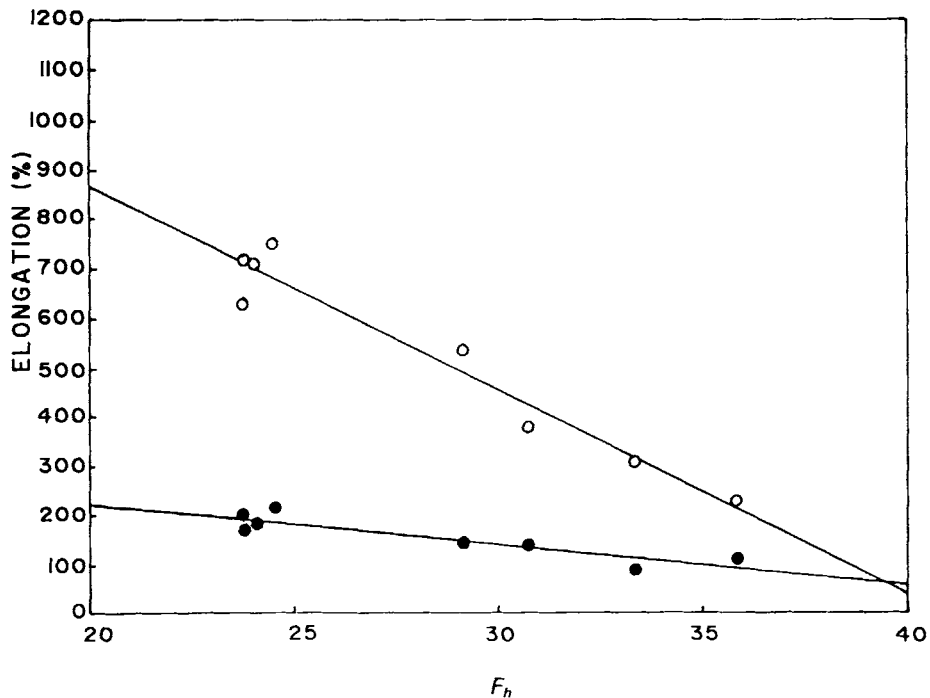


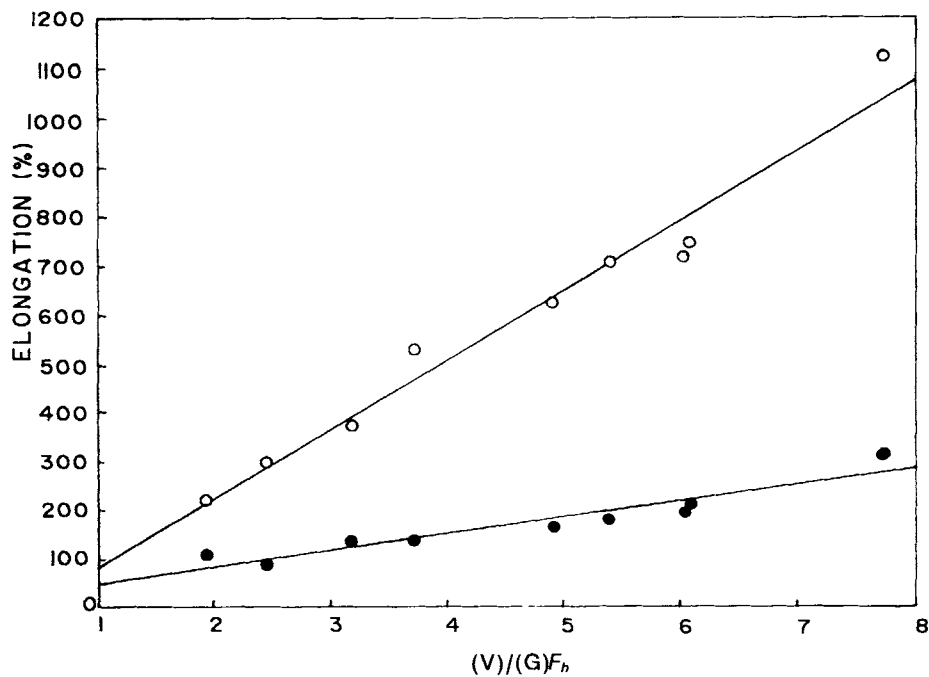
Figure 5 Plot of  $[H]/[V]$  vs.  $F_h$ .



**Figure 6** Plot of  $F_h$  vs. elongation percent: (○)  $[NCO]/[OH] = 0.75$ ; (●)  $[NCO]/[OH] = 1.0$ .

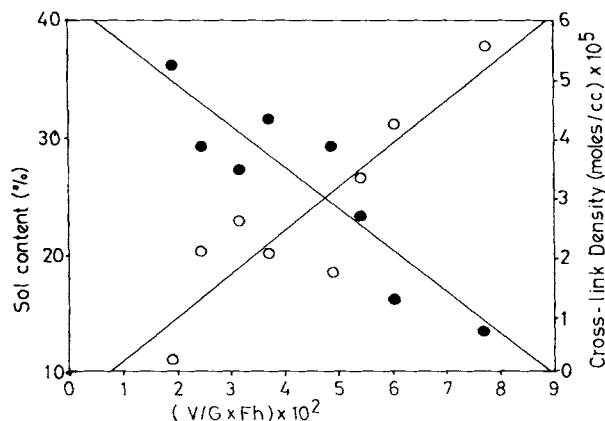
can be inferred that the greater the high molecular weight fraction ( $F_h$ ) the greater will be the proportion of higher functionalities in the polymer. This

is, indeed, found to be the case. Thus, as  $F_h$  decreased, the ratio of di-to-tri functionalities (cf. Table II) decreases. Therefore, a good correlation is



**Figure 7** Plot of  $[V]/[G]F_h$  vs. elongation percent: (○)  $[NCO]/[OH] = 0.75$ ; (●)  $[NCO]/[OH] = 1.0$ .





**Figure 8** Plot of  $[V]/[G]F_h$  vs. sol content and cross-link density: (O) sol content; (●) cross-link density.

expected between  $F_h$  and the mechanical properties of the cured resins. A plot of  $F_h$  vs. elongation of the cured resins, shown in Figure 6, confirms these observations.

Since FTD and MWD were found to be interdependent, a combination of these two variables should describe the polymer more completely. Thus, a plot of  $[V]/[G]F_h$  vs. elongation of the binders, shown in Figure 7, demonstrates the good correlation between these parameters.

#### Correlation of Sol Content and Cross-Link Density

Further characterization of the binder system was carried out by determining the sol content and cross-

link density of the network structures. The variation of these properties with the derived structural parameter is shown in Figure 8. Again, a good correlation was observed between measured properties and  $[V]/[G]F_h$ .

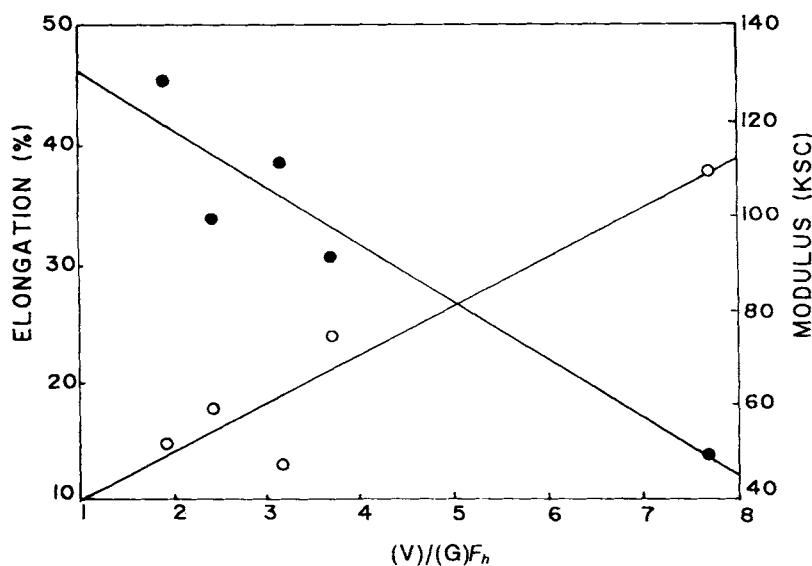
Thus, the results indicate that the properties of the binder system like sol content, cross-link density, and elongation at break can be satisfactorily correlated with the structural properties  $[V/G]$ ,  $F_h$  or  $[V]/[G]F_h$ .

#### Mechanical Properties of Propellants

The propellants were obtained by curing HTPB polymers at a  $[NCO]/[OH]$  equivalence of 0.75 with 80% solid loading. The elongation and modulus of the propellants exhibited good correlation with the structural parameter,  $[V]/[G]F_h$ , of the polymers, as shown in Figure 9.

#### CONCLUSIONS

The main conclusions that can be drawn from the present study are the following: (i) HTPB polymers show bimodal molecular weight distribution, due to addition of OH radicals in a 1,4- and a 1,2-fashion ( $H$  and  $V$ , respectively); (ii) High molecular weight fractions increase with increase in H-type addition. (iii) Elongation of binders, obtained by curing HTPB resins with TDI, increase with (a) an increase in the mol ratio of  $V$ - and  $G$ -type hydroxyls and (b) a decrease in the high molecular weight



**Figure 9** Plot of  $[V]/[G]F_h$  vs. elongation and modulus for HTPB propellants: (O) elongation; (●) modulus.

fractions and the structural parameters,  $[V]/[G]$  and  $F_h$ , provide acceptance criteria for the blending of different batches of polymers and for propellant formulations.

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