

Correlation of Binder Mechanical Properties with Microstructure for Poly(butadiene–Acrylonitrile–Methacrylic Acid) Terpolymer: ^{13}C -NMR and Pyrolysis-GC Studies

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SYNOPSIS

^{13}C -NMR spectroscopy (22.5 MHz) was used to characterize poly(butadiene (B)–acrylonitrile (A)–methacrylic acid (M)) liquid terpolymers prepared by emulsion polymerization. The sequence distribution of the monomers in the terpolymers was described in terms of triads BBB, ABA, ABB, BBA, MBB, and AMB and was found to vary with the mode of addition of methacrylic acid monomer. The NMR data was found to be in good agreement with a mechanism of polymerization in which methacrylic acid is preferentially involved in initiation reactions by a thiyl radical arising from the reaction of the chain modifier, 1-dodecanethiol, and cyanoisopropyl radical generated from AIBN initiator. Binders obtained by curing the liquid terpolymers with an epoxy resin showed widely varying mechanical properties with tensile strength varying from 4.3 to 0.6 kg/cm² and elongation at break from 130 to 450%. It was found that tensile strength increases and elongation decreases with the number of acrylonitrile units between the methacrylic acid crosslinks. Good correlation was obtained between triad population ratio $[\text{ABB} + \text{BBA}][\text{BB}^{\ast}\text{B}]/[\text{ABA}][\text{MBB}]$ and the mechanical properties of the binders. Pyrolysis-GC data at 550 and 600°C confirmed the results obtained from ^{13}C -NMR, and the mole ratio of butadiene to acrylonitrile in the pyrolyzates showed correlation with the properties of binders.

INTRODUCTION

Liquid polybutadiene polymers containing functional groups, like carboxyl or hydroxyl, play an important role in solid composite propellants for rocket motors. Binders obtained by curing these liquid polymers provide a matrix for the inorganic oxidizer, metallic fuel, and other dispersed solid components. In addition, they impart dimensional stability to the propellant grain. Many of the mechanical properties of the final cured propellant will be dictated by binder characteristics. It has been demonstrated that (i) propellant mechanical properties depend strongly on the prepolymer functionality (which should be nearly 2), molecular weight, and their distributions and (ii) the propellant processability is effected by

the prepolymer molecular weight, microstructure, and reactivity of the functional group.^{1,2} Hence, it is not surprising that excellent control must be exercised during the manufacture of the prepolymers, and their characterization is an important factor to assure satisfactory reproducibility of solid propellant properties.

In this communication, we report on the characterization of poly(butadiene–acrylonitrile–methacrylic acid) terpolymer by ^{13}C -NMR and pyrolysis-GC and the correlation of binder mechanical properties with microstructure of the polymer.

EXPERIMENTAL

Synthesis of Terpolymers

Terpolymers of butadiene (B), acrylonitrile (A), and methacrylic acid (M) were prepared at 50°C by

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emulsion polymerization using azobisisobutyronitrile (AIBN) as initiator, hexadecylbenzyltrimethylammonium chloride as emulsifier, 1-dodecanethiol as chain modifier, hydroxyammonium sulfate as chain stopper, and iron(III) ammonium sulfate as catalyst. Polymer I was prepared by almost continuous addition of the acid, whereas polymers II–V were prepared by intermittent addition of the acid, maintaining total concentration of the acid constant for all the polymers. Polymer VI was prepared with higher acid concentration and multiple addition. Polymers I–VI, after precipitation, were washed thoroughly with water and vacuum dried. Polymer VII is a commercially available terpolymer of butadiene, acrylonitrile, and acrylic acid, PBAN (Thiokol, USA).

Composition of Terpolymers

Acrylonitrile content of the polymers was obtained from nitrogen analysis and the acid content was determined by titration. Sulfur was estimated by conversion to BaSO₄.

Molecular Weight Determination

The number average molecular weight \bar{M}_n and the dispersity \bar{M}_w/\bar{M}_n were determined from GPC using a set of 4 μ styragel columns with permeabilities of 10⁴, 10³, 500, and 100 Å. THF was used as the eluent at a flow rate of 2 mL/min. Calibration was performed using polystyrene standards and the observed molecular weights were corrected for polybutadienes using ASTM D3593 procedure.³ The functionality of the polymers was determined from the calculated \bar{M}_n values and the acid values. A Waters ALC GPC 244 with R401 RI detector and M730 Data system was used for GPC measurements.

¹³C-NMR Spectra

Proton noise decoupled ¹³C-NMR spectra of the terpolymers were recorded at 22.5 MHz on 10% (w/v) solutions in CDCl₃ with TMS as internal standard using a JEOL FX 90Q NMR spectrometer. Other relevant operating parameters were: sweep width, 5000 Hz; acquisition time, 1.6 s; pulse width, 18 μ s (corresponding to a nuclear tip angle of 60°); data points, 16K; pulse delay, 2.5 s; and number of scans, 1000.

Pyrolysis-GC

About 0.6–0.7 mg of the polymer sample was pyrolyzed using a furnace pyrolyzer (Shimadzu PYR-

2A) coupled to a Shimadzu GC-5A gas chromatograph. The GC conditions used were: column: Porapac, 2 m \times 3 mm ID, SS; column temperature: 150–220°C programmed at a linear rate of 30°C/min; injection port: 250°C; detector: FID; and carrier gas: He at a flow rate of 45 mL/min. A Shimadzu data processor C-R1A was used for the computation of peak areas.

Viscosity Measurements

The viscosity of the resins were measured at 25°C using a Brookfield HBT rotating spindle viscometer using spindle no. 5 at 20 rpm.

Binder Properties

The binders were prepared by curing the terpolymer with the epoxy resin GY-250 (Ciba Geigy, India) at 100°C for 24 h. The tensile strength and percent elongation were determined according to ASTM D412 procedure.⁴

RESULTS AND DISCUSSION

Polymer Characterization

The terpolymers of butadiene, acrylonitrile, and methacrylic acid (polymers I–V) were prepared by emulsion polymerization. The synthesis of the polymers differ only in the mode of addition of the acid, the other experimental parameters remaining essentially the same. Some properties of the polymers are given in Table I. The results indicate that (i) the change in the mode of addition of the acid has not altered the composition of the polymers to any significant extent, (ii) the almost continuous addition of the acid has increased the molecular weight \bar{M}_n and functionality \bar{F}_n compared to polymers obtained by multiple addition of the acid, and (iii) higher initial concentration of the acid (polymer V) considerably reduces both \bar{M}_n and \bar{F}_n , indicating preferential involvement of methacrylic acid in initiation reactions. A similar observation was made in the emulsion copolymerization of acrylonitrile and methacrylic acid.⁵ These changes are quite understandable because it is known that mode of addition of a comonomer, continuous, multiple, or single, greatly influences the properties of the copolymers.¹

¹³C-NMR SPECTRAL STUDIES

Natural abundance Fourier transform noise decoupled ¹³C-NMR spectra of the polymers were recorded

Table I Properties of the Terpolymers

Polymer	AN (%)	Acid Value (mg KOH/g)	Viscosity (cps) at 25°C	\bar{M}_n	\bar{M}_w/\bar{M}_n	\bar{F}_n
I	11.8	33.8	174,000	4978	3.0	3.0
II	12.3	30.7	68,800	3396	3.0	1.86
III	10.6	29.8	28,938	3598	2.9	1.91
IV	12.5	31.7	36,160	3415	2.7	1.93
V	11.8	30.8	21,760	2781	2.4	1.53
VI	10.8	78.7	—	—	—	—
VII	12.0	36.0	40,000	3412	3.4	2.19

under identical instrumental settings. Figure 1 shows a typical ^{13}C -NMR spectrum of the terpolymer (polymer I). The spectrum is quite complex and shows absorptions in the olefinic region 110–150 ppm due to Sp^2 and Sp carbons; and in the region 10–50 ppm due to Sp^3 carbons. Assignments of the individual carbons are arrived at by comparison with data on copolymer systems containing the same monomers. The information derived therefrom is discussed below.

Olefinic Carbon Resonances

The olefinic carbons of butadiene are very sensitive to their environment and information can be obtained regarding the sequence distribution of the monomers by assigning the various absorptions to the possible triads. For this purpose, it is convenient to classify the triads into (i) triads containing butadiene (B) units only, (ii) triads containing butadiene and acrylonitrile (A) units, (iii) triads containing B and M units, and (iv) triads containing B, A, and M units.

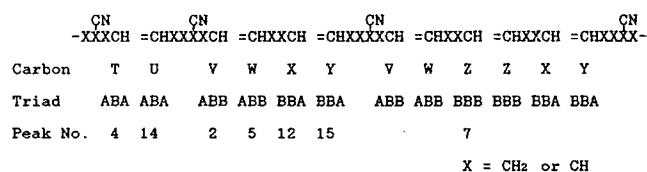
BBB Triads

BBB triads consist of butadiene in *trans*-1,4-, *cis*-1,4-, and vinyl-1,2- units and their chemical shifts in the terpolymer should closely correspond to values observed for polybutadiene (PBD). Elgert et al.⁶ have discussed the assignments of the olefinic carbons in PBD and a comparison of the spectrum (Fig. 1) of the terpolymer with the data of Elgert et al. leads to the assignment of the olefinic carbon peaks given in Table II. These assignments enable one to calculate the microstructure of the butadiene moiety in the terpolymer assuming that (i) T_1 and NOE enhancements for all the olefinic carbon atoms are same and (ii) peak heights are relative measures of intensities. The results obtained by this analysis for all the polymers are given in Table III and show

that the average configuration of butadiene is about 65% *trans*, 24% *cis*, and 11% vinyl for all the polymers studied. The slight preponderance of the *trans*-1,4- units compared to the value in pure PBD obtained by free radical polymerization can be attributed to the influence of acrylonitrile and methacrylic acid monomers and is in agreement with the results obtained for poly(butadiene-acrylonitrile)⁷ and poly(butadiene-methyl methacrylate)⁸ copolymer systems reported earlier.

ABA, ABB, and BBA Triads

The introduction of acrylonitrile (A) units into PBD gives rise to new olefinic carbon resonances and Karitzky and Weiss⁷ identified six distinct resonances for olefinic carbons adjacent to A units as shown in Scheme 1:



To assign the chemical shifts of the triads ABA, ABB, and BBA in the terpolymer, the data of Karitzky and Weiss were corrected by about -1.2 ppm. This correction arises due to the fact that the earlier authors recorded the spectra under external lock conditions and the central signal of CDCl_3 was observed at 78.3 ppm compared to 77.1 ppm observed in the present study. Moreover, they assigned the signal at 131.2 ppm to the BBB triad whereas in the present study it was assigned 130.0 ppm, a value which is in agreement with the assignments of Elgert et al.⁶ and Conti et al.⁹ Further confirmation of the triad assignments was obtained by recording the spectra of a completely alternating B-A copolymer and a copolymer with 30% acrylonitrile content. The results of the assignments are given in Table IV.

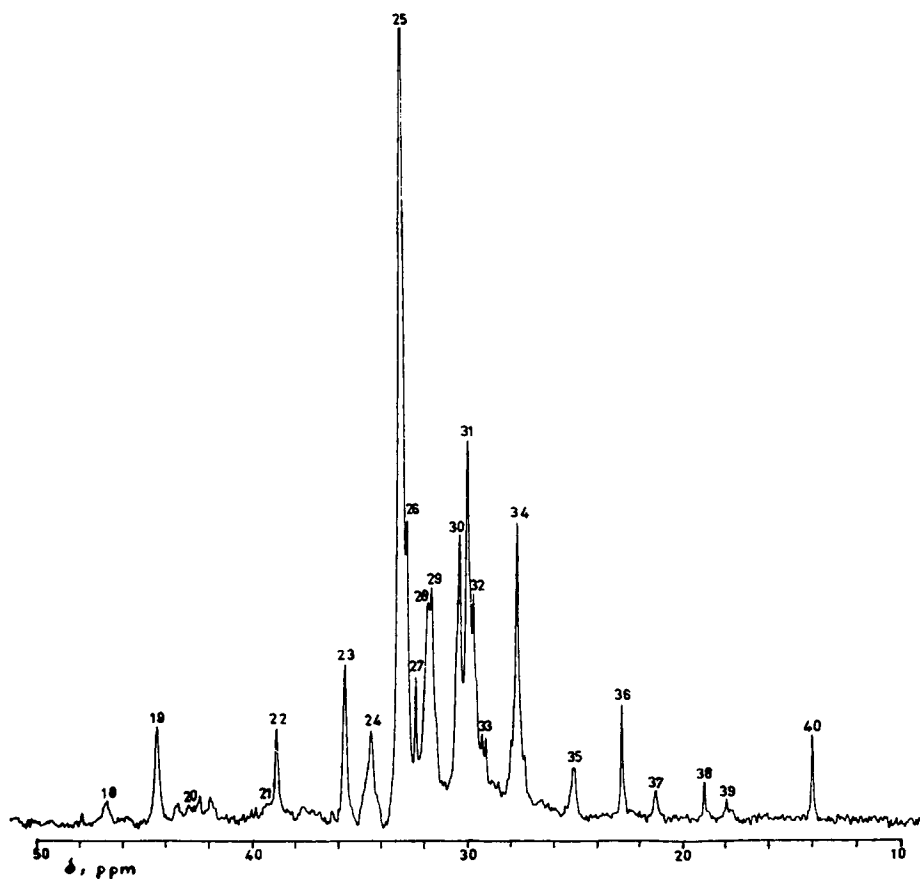
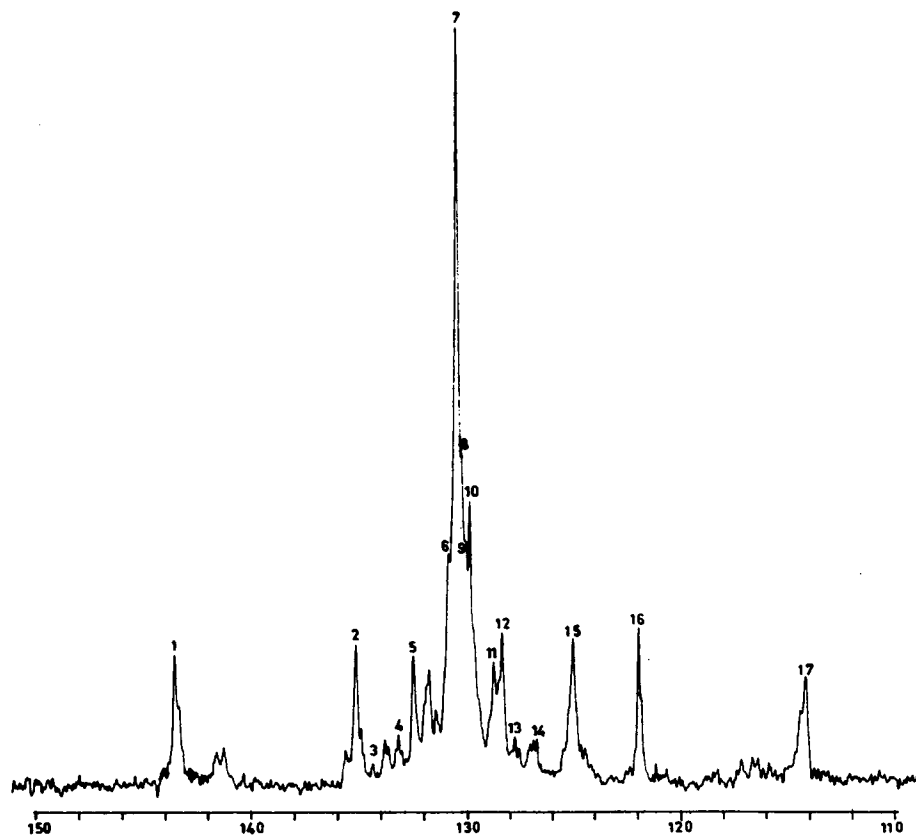


Figure 1 22.5 MHz proton noise decoupled ¹³C-NMR spectrum of Polymer I.

Table II Chemical Shift Assignments of Olefinic Carbons of BBB Triads in the Terpolymers

Peak No.	Chemical Shift δ (ppm)	Assignment ^a
1	142.56	c/tvc/t
6	130.35	c/ttv
7	129.95	ttc/t
8	129.70	c/ttv
9	129.49	c/tcc
10	129.38	c/tct
11	128.35	vtc
17	114.26	c/tvc/t

^a c = cis, t = trans, v = vinyl.

It is to be noted that, in the alternating B-A copolymer, the butadiene unit is exclusively in the trans configuration. However, it is likely that in random copolymers the butadiene unit can have either a 1,4-*cis* or a 1,2-vinyl configuration also. No attempt is made here to identify these triads in view of the low concentration of the acrylonitrile content.

The populations of the triads in the various polymers were evaluated by normalizing the intensities of carbons T-Z (Scheme 1) to the mole percent of butadiene in the terpolymer and the results are shown in Table IV. The overall consistency of the assignments can be checked since (i) the population of ABB triad must be equal to the population of BBA triad, i.e., the intensities of the peaks due to carbons V, W, X, and Y must be equal, and (ii) the intensities of carbons T and U must be equal. This can be seen to be reasonably true from Table IV.

Further, the fractional population of ABA triads $[ABA]/([ABB] + [BBA])$ which reflects the alternating character of the distribution of A units increases from polymer I to V (Table V). Thus, poly-

mer I prepared by almost continuous addition of the acid shows greater randomness of distribution of A units whereas polymer V prepared with higher initial concentration of the acid shows greater alternating nature of placement. Therefore, it can be concluded that the distribution of A units in the terpolymer can be controlled by the mode of addition of the acid.

MBM, MBB, and BBM Triads

Since the terpolymers contain only about 3 mol % methacrylic acid, to facilitate the assignments of the chemical shifts, a polymer (polymer VI) containing 7.9% of the acid was prepared. The ¹³C-NMR spectrum of the polymer is shown in Figure 2. The analysis of the spectrum, as outlined earlier, shows that the average configuration of the B units and the population of the triads ABA, BBA, and ABB are quite similar to other polymers (Table III). This indicates that no significant overlap of resonances involving M and A containing triads occur. Also, the ¹³C-NMR spectrum of a similar polymer recorded at 67.88 MHz shows no additional lines.¹⁰

If random distribution of M and A units in the terpolymer chain is assumed, the number of butadiene units connected to M units and to A units is expected to be in the ratio of 7.9 to 11.5, corresponding to the mole ratio of M and A in the polymer. However, a comparison of the spectra in Figures 1 and 2 shows that absorptions mainly at $\delta = 133.85$ ppm (peak no. 3) and 127.37 ppm (peak no. 13) show an increase in intensity when the acid concentration is increased and therefore correspond to triads involving B and M. This clearly indicates that the number of B units adjacent to M units is not commensurate with the concentration of the acid

Table III Microstructure of Butadiene Units in Terpolymers

Polymer	Microstructure (%)						
	From Olefinic Carbons			From Methylene Carbons			
	Trans	Cis	Vinyl	Trans	Cis	Vinyl	
I	63.7	25.2	11.1	65.3	22.8	11.9	
II	65.0	24.0	11.0	66.0	21.6	12.4	
III	63.7	23.2	13.1	63.7	24.0	12.3	
IV	64.9	23.7	11.3	65.5	22.2	12.3	
V	63.4	24.0	12.7	67.1	20.9	11.9	
VI	65.1	24.6	10.3	63.8	22.5	13.7	
VII	60.9	26.6	12.6	66.2	22.2	11.6	

Table IV Chemical Shift Assignments and Normalized Intensities of ABA, ABB, and BBA Triads

Peak No.	Chemical Shift δ (ppm)	Assignment	Carbon	Normalized Intensity for Polymers						
				I	II	III	IV	V	VI	VII
2	134.50	ABB	V	8.3	8.7	8.7	8.3	8.1	8.5	6.0
4	132.61	ABA	T	3.0	3.3	3.7	4.1	4.5	3.7	3.3
5	131.85	ABB	W	7.6	8.7	8.0	8.6	7.6	7.5	6.8
12	127.97	BBA	X	9.0	8.7	8.2	8.5	7.1	7.6	6.8
14	126.40	ABA	U	2.4	2.8	3.4	3.6	3.8	3.5	2.5
15	124.75	BBA	Y	8.6	8.9	8.4	8.7	8.2	8.9	6.2

suggesting that the acid units are present as either IMB (I = initiator radical) or AMB triads. The former possibility is consistent with other observations from Sp^3 carbon resonances as discussed later.

The absorption at $\delta = 133.85$ and 127.37 ppm may be tentatively assigned to MBB and BBM triads based on similarities with ABB and BBA triads. Further, a rough idea of the differences in the distribution of M units between various polymers can be evaluated by considering the ratio of the intensities of the BBB and MBB triads. The results are shown in Table V and indicate that the population of the MBB triads show an increase from polymer I to polymer V, showing the dependence on the mode of addition of the acid as is the case with the distribution of acrylonitrile.

Nitrile Carbon Resonances

The absorption observed at $\delta = 121.74$ ppm is assigned to the nitrile carbon of the acrylonitrile unit in the polymer. Lack of multiplicity of this CN signal suggests that A units are mostly present as BAB triads and no block AAA or significant amounts of AAB occur in the polymer.

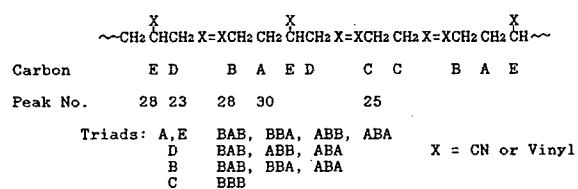
Sp^3 Carbon Resonances

BBB Triads

The assignment of methylene resonances for PBD containing a mixture of configurations was discussed by Suman and Werstler¹¹ and their data was used to identify the methylene resonances of B unit in the terpolymer. The assignments are shown in Table VI. These assignments are also in agreement with the values reported by Sato et al.¹² The microstructure of the B units in the terpolymer was computed and the results are given in Table III. The two sets of results obtained from the intensities of the olefinic carbons and from that of methylene carbons are in good agreement with each other, validating the assignments.

ABA, ABB, and BBB Triads

Katritzky and Weiss⁷ identified five different methylene resonances in the copolymer of butadiene and acrylonitrile as shown in Scheme 2:

**Table V** Triad Intensity Ratios for Terpolymers

Sample No.	Polymer	$\frac{[\text{ABB}] + [\text{BBA}]}{[\text{ABA}]}$	$\frac{[\text{BBB}]^a}{[\text{MBB}]}$	$\frac{[\text{BB}^*B]^b}{[\text{MBB}]}$	$\frac{[\text{BB}^*B]^b}{[t\text{-CH}_3]^c}$	$\frac{[\text{ABB}] + [\text{BBA}]}{[\text{ABA}]} \times \frac{[\text{BB}^*B]}{[\text{MBB}]}$
1	I	6.2	8.2	5.0	5.1	31.0
2	II	5.7	5.5	2.7	2.2	15.4
3	III	4.7	4.8	2.2	3.1	10.3
4	IV	4.4	4.7	2.3	2.0	10.1
5	V	3.7	4.2	2.1	1.8	7.8

^a Calculated from Sp^2 carbon resonances, $[\text{BBB}] = ttc/t$.

^b Calculated from Sp^3 carbon resonances.

^c $t\text{-CH}_3$ = terminal CH_3 .

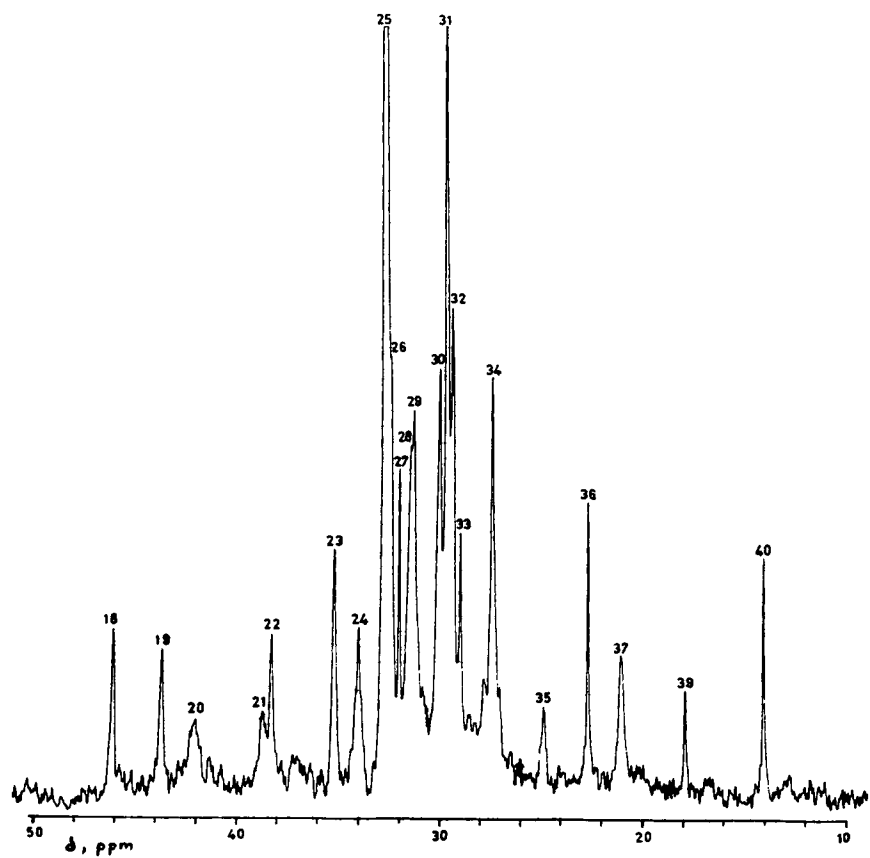
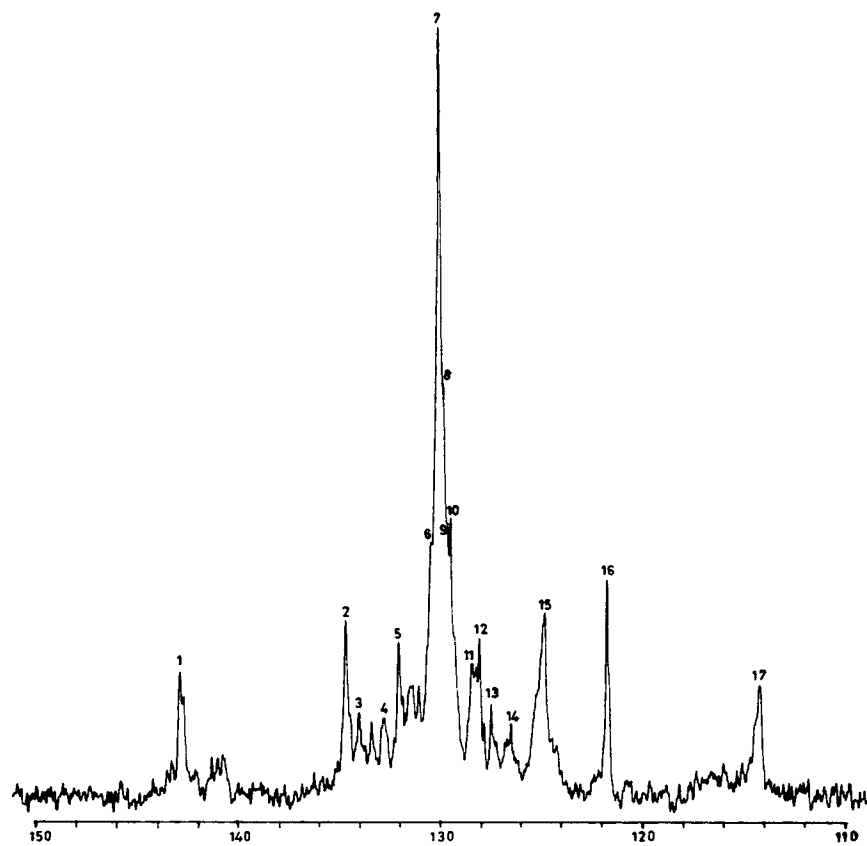


Figure 2 22.5 MHz proton noise decoupled ^{13}C -NMR spectrum of Polymer VI.

Table VI Chemical Shift Assignments of Sp³ Carbons

Peak No.	Chemical Shift (ppm)	Assignment
(i) BBB Triads		
19	43.43	1,4-v-1,4 (CH)
22	38.10	1,4-v-t (CH ₂)
24	33.84	1,4-v-1,4 (CH ₂)
25	32.62	1,4-v-c + ttt (CH ₂)
34	27.34	cc/t (CH ₂)
35	24.82	cv (CH ₂)
(ii) Triads involving B and A		
23	35.04	Carbon D ^a
28	31.30	Carbon (B + E)
30	29.91	Carbon A
(iii) Triads involving B and M		
18	45.79	C _α (MBB/BMB)
20	41.78	BMB (CH ₂ of B)
21	38.50	C _β (M)
37	21.06	CH ₃ (M)
38	18.90	CH ₃ (M)
(iv) RS Absorptions		
27	31.87	—SCH ₂ R
30	29.91	} CH ₂
31	29.59	
32	29.29	
33	28.89	
36	22.66	
40	14.10	CH ₃
(v) Miscellaneous		
39	17.91	CH ₃ (terminal)

^a Carbon designation as given in Scheme 2.

Their data, after correction as indicated earlier, was used to assign the chemical shift of the triads in the terpolymer and the results are shown in Table VI. However, the intensities of the methylene groups cannot be treated quantitatively owing to considerable overlap of triads (e.g., D = BAB, ABB, ABA).

Methacrylic Acid Absorptions

The chemical shift assignments of the Sp³ carbon of methacrylic acid in the terpolymer are arrived at by a comparison of the spectra of polymers I and VI (Figs. 1 and 2) and are based on the data of Ebdon and Kandil⁸ for copolymers of methylmethacrylate and butadiene. The results are shown in Table VI. The assignment of the methyl signal at $\delta = 21.06$ ppm is further confirmed by the absence of this signal in the spectrum of polymer VII, a butadiene-acrylonitrile-acrylic acid (PBAN) terpolymer. In addition, polymer I shows a signal at $\delta = 18.9$ ppm

which is tentatively assigned to the α -methyl group of M in BMA/AMB triad based on the assignment of $\delta = 18.6$ ppm for BMM/MMB triads in methyl methacrylate-butadiene copolymers.

Quantitative treatment of the data on triads involving M unit is not attempted due to the low concentration of the acid in the polymers I-V. However, relative differences in the distribution of the M units were evaluated considering the ratio of the intensity of peaks due to tertiary carbon of 1,2-butadiene unit ($\delta = 43.43$ ppm) and due to quarternary carbon of M unit in MBB triad ($\delta = 45.79$ ppm). The vinyl carbon of butadiene is taken as a reference, since the microstructure of the B units is same in all the polymers. It is realized that comparison of intensities of two different types of carbon may not be accurate owing to differing T₁ and NOE effects. However, it was observed by Sato et al.¹² that Sp³ carbons in polybutadiene have the same T₁ and NOE values

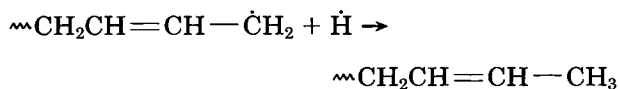
and the intensity differences between signals is less than 5%. Since the spectra were recorded under identical instrumental settings and the differences in T_1 and NOE effects among various butadiene carbons are minimal as evidenced by the microstructure data evaluated from olefinic and methylene carbon resonances (Table III), it may be reasonable to assume that the intensity ratios will at least reflect differences among the various polymers. The calculated ratios of $[BB^vB]/[MBB]$ are shown in Table V. The results clearly indicate that the population of MBB triads increases from polymer I to V and is consistent with the observation, made from the analysis of olefinic carbon resonances, that MBB triad population also increases in the same way.

1-Dodecane Thiyl Absorptions

1-Dodecane thiol was used as a chain modifier to obtain low molecular weight liquid polymers. The ^{13}C -NMR spectra of the terpolymers show a number of absorptions which can be assigned to the carbons in 1-dodecanethiyl ($\text{C}_{12}\text{H}_{25}\text{S}$) moiety as given in Table VI and comprise about 20–25% in intensity of the total Sp^3 carbon absorptions in the spectrum. The absence of unreacted dodecanethiol in the polymer is confirmed from the absence of signals at $\delta = 24.58, 28.35,$ and 34.03 ppm which correspond to $\text{C}_1, \text{C}_3,$ and C_2 carbons, respectively. This shows that incorporation of the $\text{C}_{12}\text{H}_{25}\text{S}$ moiety is quite considerable for all the polymers. This was further confirmed by estimating sulfur content of one of the polymers. The sulfur content of polymer I was found to be 1.37%, indicating the presence of about two $\text{C}_{12}\text{H}_{25}\text{S}$ units per polymer chain. These observations indicate the important role of the thiol in the polymerization reaction and are discussed later.

Terminal Methyl Absorption

The resonance observed at $\delta = 17.91$ ppm is assigned to the methyl group formed by abstraction of a H radical by a terminal butadiene radical.



The hydrogen radical may be provided by either the chain modifier or the chain stopper. That this signal is not due to the methyl group of the methacrylic acid unit is confirmed by its presence in the spectrum of PBAN whereas the methyl signal of the acid at $\delta = 21.06$ ppm is absent.

Since the concentration of a terminal group is a measure of the concentration of the propagating radicals in the system, it is interesting to compare the different polymers in this regard. Neglecting T_1 and NOE effects for the limited objective of arriving at differences only, the intensity of the vinyl BB^vB triad ($\delta = 43.43$ ppm) is taken as a reference and the ratio $[BB^vB]/[t\text{-CH}_3]$ is evaluated for all the polymers. The results are shown in Table V. The conclusions that can be drawn from these results are: (i) the ratio decreases with decrease in \bar{M}_n of the polymer confirming terminal nature of the resonance and (ii) the concentration of the propagating radicals in the system increases with increasing initial concentration of methacrylic acid, demonstrating the preferential involvement of the acid in the initiation reactions. These observations are consistent with the inferences made from the analysis of Sp^2 and Sp^3 carbon absorptions that MBB triad population increases from polymer I to V, and M is preferentially involved in the initiation reactions. Internal consistency of the data thus lends support to the method of analysis of the data.

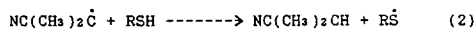
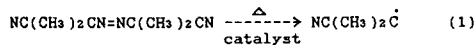
Microstructure of Terpolymers

The main conclusions that can be drawn from the ^{13}C -NMR studies of the terpolymers can be summarized as follows:

- (i) The average configuration of the butadiene units is essentially same in all the polymers.
- (ii) The incorporation of 1-dodecyl thiyl moiety into the polymer chain is quite considerable for all the polymers.
- (iii) The number of butadiene units connected to methacrylic acid unit is not commensurate with the concentration of the acid when compared to the number of butadiene units connected to acrylonitrile units. The former increases from polymer I to V.
- (iv) Polymer I contains triads of the type ABM or BMA.
- (v) The fractional population of the triads ABA increases from polymer I to V.
- (vi) The concentration of the terminal methyl groups varies from polymer I to V.

All these observations can be rationalized by assuming the mechanism of polymerization to be similar to free radical addition of thiols to olefins¹³ as outlined in Scheme 3:

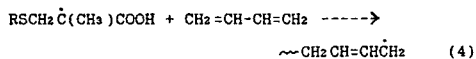
Initiation:



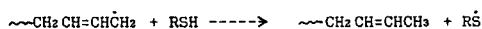
Addition:



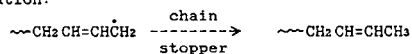
Propagation:



Chain transfer:



Termination:



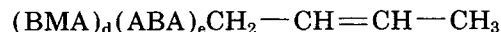
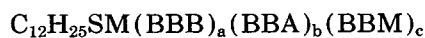
The cyanoisopropyl radical initially formed [eq. (1)] is quite unreactive and gives rise to thiyl radical [eq. (2)] by hydrogen abstraction from 1-dodecane thiol added at the beginning of the polymerization reaction itself. In fact, this is one of the methods of generating thiyl radicals.¹³ The thiyl radical preferentially attacks methacrylic acid monomer [eq. (3)] because of greater resonance stabilization of the resulting radical due to delocalization over a heteroatom compared to the allylic radical obtained by addition to butadiene monomer. Therefore, the higher the initial concentration of methacrylic acid, the greater will be the number of propagating radicals and hence greater will be the number of butadiene units connected to M units [eq. (4)]. Since polymers I-V were prepared with increasing initial concentration of the acid, observations (ii), (iii), and (vi) are readily understandable. On the other hand, when acid is added continuously, the acid can add on to a growing radical resulting in higher probability for AMB or BMA triads as was found to be the case with polymer I (observation iv). Further, the variation of the concentration of the terminal methyl groups with the initial acid concentration (obs. vi) is in accordance with this mechanism and is supported by the \bar{M}_n data from GPC.

It was observed, in the copolymerization of butadiene and acrylonitrile, that the concentration of ABA triads increases with increase in concentration of A.⁷ Therefore, the increasing population of ABA triads from polymer I to polymer V can be rationalized as follows: as the number of propagating chain increases from polymer I to V (as discussed earlier), the rate of consumption of B relative to A increases because B prefers to react with itself rather than A and also A adds on to B preferentially. In

the final phases of the reaction, the relative concentration of B and A is such that more ABA triads are formed.

The observation that the average configuration of B units in all the terpolymers is essentially the same is quite expected since B constitutes nearly 85 mol % of the monomers. The formation of branched chains is not expected to be significant at lower conversions (< 60%)¹⁴ as is the case in the synthesis of the terpolymers studied here.

In summary, the average microstructure of the terpolymers can be represented as



The essential differences between the structures of polymers I and V are: (i) the number of BBA units between two methacrylic acid units decreases from polymer I to V, as indicated by the decrease in the population ratio of (ABB + BBA) and ABA triads (Table V); and (ii) the fraction of MBB triads increases and consequently the fraction of AMB or BMA triads decreases from polymer I to V as reflected by the decrease in the ratio of BB'B and MBB sequences (Table V).

Binder Properties

The liquid polymers were cured with an epoxy resin to give crosslinked polymer networks called binders. The mechanical properties of the binders obtained from polymers I to V are given in Table VII. The values given are the averages of three measurements and they are found to vary appreciably from polymer I to V. Tensile strength varies from 4.3 to 0.6 kg/cm² and elongation changes from 130 to 450% at

Table VII Mechanical Properties of Binders

Binder from Polymer	Tensile Strength (kg/cm ²)	Elongation (%)
I	4.3	130
II	2.8	300
III	1.8	420
IV	1.4	380
V	0.6	450
VII	2.1	300

break. The important factors which affect these properties are functionality, molecular weight, and their distribution in the polymers. However, \bar{M}_n and dispersity of polymers I-V are in a narrow range and cannot account for the observed variations. The functionality of the polymer I is nearly 3 and that of polymer V is 1.5. Correspondingly, polymer I shows the highest tensile strength and lowest elongation whereas polymer V shows the least tensile strength and highest elongation as expected. Polymers II, III, and IV have almost the same \bar{M}_n and \bar{F}_n values, yet their mechanical properties differ considerably, suggesting that the microstructure of the polymers may be contributing to the observed variations. These observations can be rationalized as follows:

The mechanical properties of a crosslinked polymer network depend on the characteristic property of the polymer chain between crosslinks. Introduction of polar monomers (like acrylonitrile) into an elastomeric polymer chain (like PBD) is expected to increase the strength of the polymer.¹⁵ ^{13}C -NMR studies show that (i) the number of acrylonitrile units between methacrylic acid crosslinks decrease from polymer I to V as reflected in the ratio $[\text{BBA} + \text{ABB}]/[\text{ABA}]$ and (ii) the probability of acrylonitrile unit being connected to a methacrylic acid unit decreases from polymer I to V as reflected in the ratio $[\text{BB}^{\vee}\text{B}]/[\text{MBB}]$ (Table V). Both these factors favor an increase in tensile strength and consequently a decrease in elongation of the binders, as observed experimentally. Thus a plot of triad population ratio $[\text{ABB} + \text{BBA}][\text{BB}^{\vee}\text{B}]/[\text{ABA}][\text{MBB}]$ versus the tensile strength and elongation

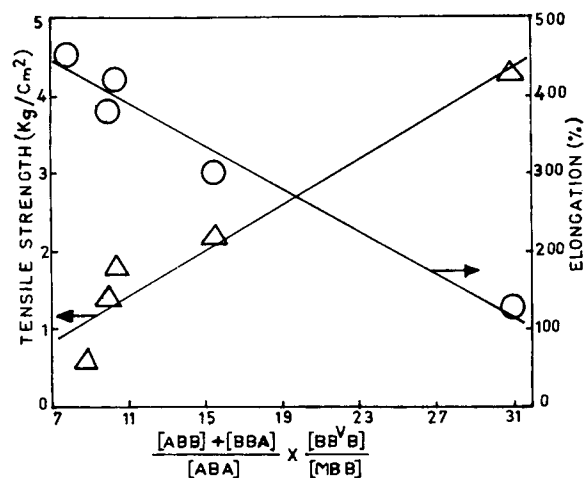


Figure 3 Plots of triad intensity ratios vs. binder mechanical properties.

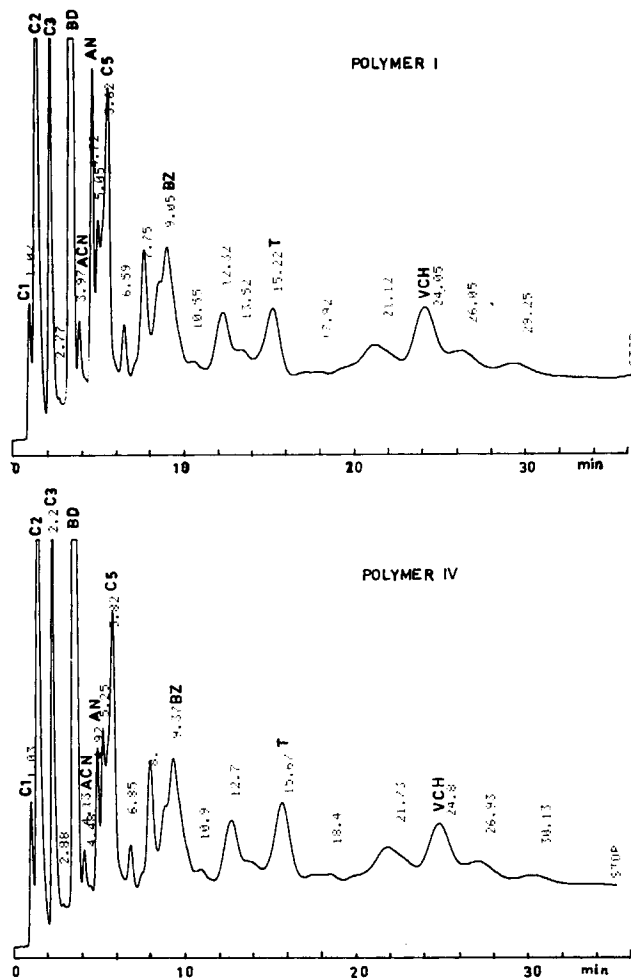


Figure 4 Pyrograms of Polymers I and V at 550°C.

of the binders (Fig. 3) is reasonably linear, demonstrating the dependence of the mechanical properties of the binders on microstructure of the polymers.

Pyrolysis-GC

The terpolymer samples (0.6–0.7 mg) were pyrolyzed at 550 and 600°C and typical pyrograms of polymers I and V are shown in Figure 4. The nature and composition of the pyrolyzates were arrived at as described earlier by us for PBD polymers,¹⁶ and the results are given in Table VIII. The major products of pyrolysis were found to be ethylene (C_2), propylene (C_3), butadiene (BD), benzene (BZ), toluene (T), and vinyl cyclohexene (VCH) from the butadiene part and acrylonitrile (AN) and acetonitrile (ACN) from the acrylonitrile part of the polymers.

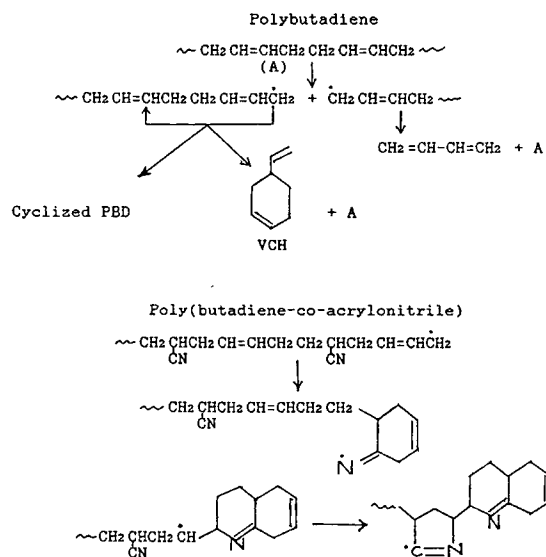
Table VIII Composition of Major Pyrolyzates

Polymer	Wt % ^a										Mol %	
	C ₁ (1.0)	C ₂ (1.3)	C ₃ (2.2)	BD (3.5)	ACN (4.0)	AN (4.7)	C ₅ (5.6)	BZ (9.1)	T (15.2)	VCH (24.1)	BD/AN	BD/VCH
Pyrolysis Temperature: 550°C												
I	1.3	7.5	4.7	24.3	0.4	3.6	7.3	9.3	5.4	6.7	6.6 ± .2	7.2 ± .2
II	1.4	7.3	4.5	23.2	1.1	2.2	7.4	8.5	5.4	5.7	10.3 ± .3	8.1 ± .2
III	1.4	7.7	4.5	26.2	1.2	2.1	7.4	9.7	5.3	6.2	12.3 ± .4	8.5 ± .3
IV	1.5	7.4	4.4	25.9	1.2	2.1	7.1	8.6	5.2	6.4	12.1 ± .3	8.1 ± .2
V	1.5	7.9	5.0	26.5	0.8	1.8	7.1	9.0	6.2	5.8	14.4 ± .4	9.1 ± .3
VII	1.4	7.4	4.5	25.7	1.1	2.0	7.7	10.3	6.3	6.7	12.6 ± .4	7.7 ± .2
Pyrolysis Temperature: 600°C												
I	2.4	8.8	5.4	20.9	1.3	3.6	8.1	7.6	6.8	3.5	5.7 ± .2	11.9 ± .3
II	2.4	8.6	5.6	20.9	1.4	2.6	7.9	7.5	6.9	3.4	7.9 ± .2	12.3 ± .3
III	2.3	8.2	5.1	20.8	1.1	2.3	7.9	7.3	6.8	3.7	8.9 ± .3	11.2 ± .3
IV	2.2	8.2	5.2	22.0	1.2	2.5	7.5	7.6	7.0	3.5	8.6 ± .3	12.6 ± .4
V	2.4	8.6	5.5	23.1	1.0	2.3	7.4	7.3	7.0	3.5	9.9 ± .3	13.2 ± .4
VII	2.2	7.8	4.8	21.4	1.5	2.5	8.0	8.1	7.2	4.1	8.4 ± .2	10.4 ± .3

^a Values in brackets are the retention times in minutes.

The composition of the products of pyrolysis at 550°C (Table VIII) shows that mole ratios of BD/VCH and BD/AN increases from polymer I to V, although the change in BD/VCH ratio is only marginal. Similar trends are observed at the pyrolysis temperature of 600°C also (Table VIII), although the differences narrow down considerably. These ratios are sensitive to the sequence distribution of butadiene and acrylonitrile units in the polymer chain. It is recognized that the formation of VCH, a dimer of butadiene, requires the presence of two butadiene moieties adjacent to each other and, consequently, in copolymers of butadiene. The VCH/BD ratio is dependent on the distribution of comonomer and becomes almost zero for an alternating copolymer.^{17,18} Hence, the marginal increase in BD/VCH ratio from polymer I to V reflects the increasing alternating nature of the placement of acrylonitrile units in the chain. This is consistent with the observation from ¹³C-NMR studies that the population of ABA triads increase from polymer I to V.

The mechanism of degradation of PBD, as suggested by Golub and Gargiulo,¹⁹ involves main chain scission to give radical ends, which can undergo depolymerization (to yield mainly BD and VCH)²⁰ or cyclization to give cyclized PBD as shown in Scheme 4:



In the case of copolymers of butadiene and acrylonitrile, the cyclization will be more facile due to the pendant nitrile group as in the case with polyacrylonitrile (PAN) polymers.^{21,22} The likely cyclization reactions are shown in Scheme 4, and this mechanism of decomposition suggests that the greater the alternating nature of the polymers, the greater will be the extent of cyclization reactions. The cyclized polymers would undergo further thermal degrada-

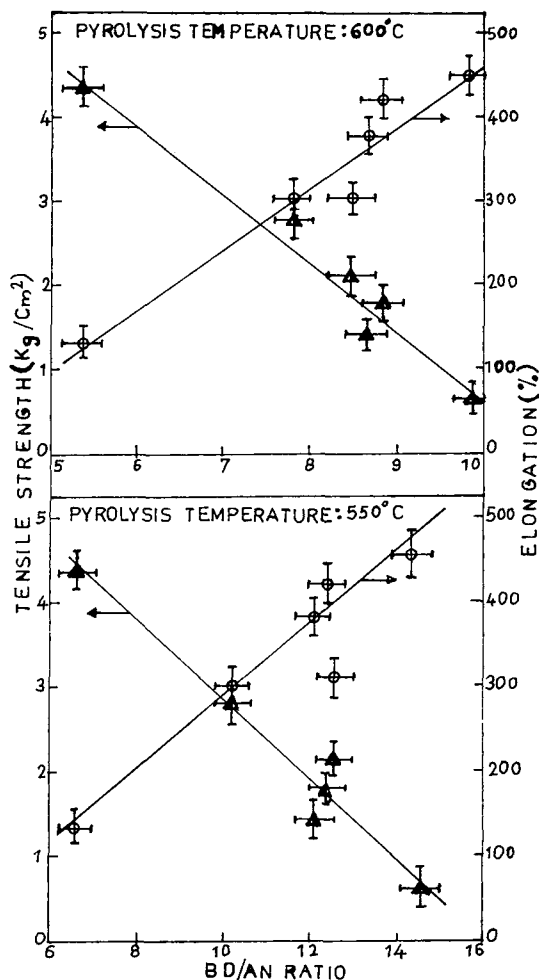


Figure 5 Plots of BD/AN ratios vs. binder mechanical properties.

tion to give various products. Consequently, the concentration of acrylonitrile decreases with an increase in the population of ABA triads and therefore BD/AN ratio increases from polymer I to V.

Similarly, for the reasons discussed earlier, the mechanical properties of the binder also show reasonable correlation with BD/AN ratio as shown in Figure 5. Thus, the results from ^{13}C -NMR studies and pyrolysis-GC are self-consistent and demonstrate correlation between the microstructure of the terpolymers and the mechanical properties of the binders obtained by curing the terpolymers.

CONCLUSIONS

The important conclusions that can be drawn from the present study are: (i) in the emulsion polymer-

ization of butadiene, acrylonitrile, and methacrylic acid terpolymer, methacrylic acid is preferentially involved in initiation reactions; (ii) the binders, prepared from the terpolymers by curing with an epoxy resin, show an increase in tensile strength and a decrease in elongation with an increase in the number of acrylonitrile units between the methacrylic acid crosslinks; (iii) this number of acrylonitrile units can be controlled by the mode of addition of the acid during polymerization; and (iv) ^{13}C -NMR and pyrolysis-GC techniques can provide a quick means of testing the suitability of the terpolymer to give desired binder properties.

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