

Thermal Degradation of Functionally Terminated Polybutadienes: Pyrolysis Gas Chromatography and Thermogravimetric Studies

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Synopsis

Thermal degradation of functionally terminated liquid polybutadiene polymers, carboxy-terminated polybutadiene (CTPB), hydroxy-terminated polybutadiene (HTPB), and poly(butadiene-acrylonitrile-acrylic acid) terpolymer (PBAN) and their cured analogues were studied by pyrolysis gas chromatography in the temperature range 500–850°C. It was found that CTPB, HTPB, and PBAN could be distinguished from one another by the variation in the composition of their pyrolyzates. The differences in the product composition were rationalized by the relative importance of unzipping and hydrogen transfer reactions in the mechanisms of their degradation. The presence of the OH group was found to favor hydrogen transfer reactions whereas the COOH group has only marginal effect. The cyclization reactions were found to predominate in the thermal degradation of cured PBAN and the pyrolysis results were substantiated by thermogravimetric studies at several heating rates. The activation energy for the decomposition of cured PBAN was estimated to be $259 \pm 16 \text{ kJ mol}^{-1}$ by Ozawa's method.

INTRODUCTION

Composite solid propellants contain essentially an organic fuel binder matrix in which an inorganic solid oxidizer, high energy metal additives, burning rate modifiers, plasticizers, and other ingredients are uniformly distributed. Combustion of these solid propellants proceeds through a series of complex physicochemical processes¹⁻⁴ and is significantly affected by the nature of the polymeric fuel binder.⁵ Steady state combustion models consider that the polymer thermally pyrolyzes to gaseous fuels for reactions with the decomposition products of the oxidizer.^{1,2,6} Since the products of pyrolysis of the fuel binders are simpler molecules, combustion chemistry of solid propellants can be considered to be reactions between gaseous species. Decomposition of the binder and the oxidizer is also affected by the heat feedback from the combustion zone.⁷ Therefore, analytical modeling of combustion requires an understanding of the gaseous product distribution, mechanisms, and kinetics of decomposition of the polymeric binders.

Binders obtained by curing functionally terminated liquid polybutadiene prepolymers are widely used in solid propellant technology.^{8,9} Carboxy-terminated polybutadiene (CTPB), hydroxy-terminated polybutadiene (HTPB), and poly(butadiene-acrylonitrile-acrylic acid) (PBAN) are the liquid prepoly-

mers commonly employed. Considerable work has been reported on the thermal decomposition of nonfunctional, high molecular weight polybutadienes concerning the volatile products and residues,¹⁰⁻¹² microstructure changes accompanying degradation,¹³⁻¹⁶ and correlation of pyrolysis products with microstructure.¹⁷⁻²³ However, studies on the pyrolysis behavior of the liquid prepolymers are limited.^{24,25} Therefore, in this communication, we report on the thermal decomposition studies on CTPB, HTPB, and PBAN and the binders derived therefrom. Relative differences in the composition of their pyrolyzates are studied using pyrolysis GC and the mechanisms of decomposition are suggested to rationalize these differences. Kinetic parameters for the decomposition of cured PBAN binder are evaluated from thermogravimetric studies.

EXPERIMENTAL

Materials

The functionally terminated liquid polybutadienes, CTPB, HTPB and PBAN, used in this study are samples available commercially and their details are shown in Table I.

Curing of Liquid Polymers

One hundred grams of CTPB was mixed with 5.2 g of methylaziridinylphosphineoxide (MAPO). One hundred grams of HTPB was mixed with 8 g of toluene diisocyanate (TDI) and 1.7 g of trimethylol propane (TMP) as crosslinking agent. One hundred grams of PBAN was mixed with 8.2 g of MAPO. Curing of all the samples was carried out at 100°C for 48 h.

Pyrolysis Gas Chromatography (PGC)

A furnace pyrolyzer, Shimadzu PYR-2A, was directly coupled to a Shimadzu GC 5A gas chromatograph. Samples of about 0.6–0.8 mg were taken in a platinum boat and introduced into the furnace by means of a sample introduction rod, the thermocouple of which measured the furnace temperature. A stainless steel column (3 mm i.d. × 2 m) packed with 80/100 Carbowax C/0.2% picric

TABLE I
Details of the Liquid Polybutadiene Samples Used

Sample	Source	Mol wt ^a	Microstructure ^b (%)			Functional group (meq/100 g)
			<i>Trans</i>	<i>Cis</i>	Vinyl	
CTPB	Hycar, USA	6470	50.9	29.3	19.8	COOH, 40
HTPB	Arco, USA	3200	53.2	27.2	19.6	OH, 85
PBAN	Thiokol, USA	3412	66.2	22.5	11.6	COOH, 64
PBD	Polyscience, USA	2760	53.8	41.9	4.4	—

^a By VPO using toluene solvent.

^b From ¹³C NMR analysis.

acid was used. The experimental conditions were: column temperature 50–130°C programmed at a linear rate of 20°C/min; injection port 250°C; carrier gas (helium) flow rate 80 mL/min; detector, FID. A Shimadzu data processor C-R1A was used for calculation of peak areas.

Thermogravimetric Studies

Dynamic thermogravimetric studies were carried out using a DuPont 990 thermal analyzer in dry nitrogen atmosphere at a flow rate of 50 mL/min. Thermograms were recorded at different heating rates (β) of 2, 5, 10, 20, and 50°C/min.

RESULTS AND DISCUSSION

Effect of Functional Group

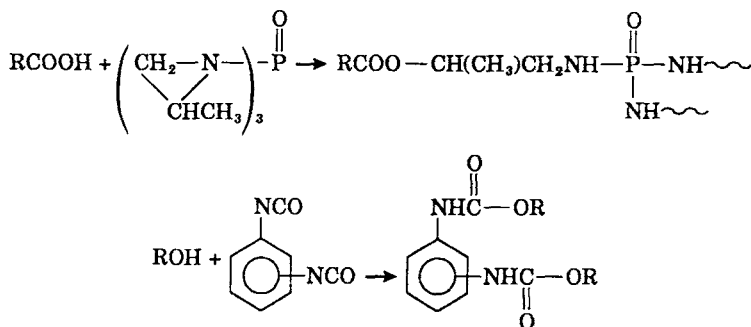
Hydroxy-terminated polybutadiene (HTPB), carboxy-terminated polybutadiene (CTPB), and poly(butadiene-acrylonitrile-acrylic acid) terpolymer (PBAN) are the liquid prepolymers widely used in rocket technology. Consequently, it is of considerable interest to study the nature and composition of products of pyrolysis of these polymers. With this in view, 0.6–0.8 mg of HTPB, CTPB, and PBAN and a nonfunctional polybutadiene (PBD) samples were pyrolyzed at different temperatures from 500–850°C. Typical pyrograms are shown in Figure 1. The nature and composition of the pyrolyzates were arrived at as reported by us earlier²³ for high molecular weight polybutadiene. The major products identified were: ethylene (C_2), propylene (C_3), butadiene (BD), benzene (B), toluene (T), and vinyl cyclohexene (VCH). The variation of the composition of these products with the temperature of pyrolysis is given in Table II. The important conclusions that can be drawn from these results are:

- (i) At a pyrolysis temperature of 500 or 550°C, the polymers HTPB, CTPB, and PBAN can be distinguished from one another by the variation in the product composition. At higher temperatures of pyrolysis, the degradation becomes more random and the polymers behave similarly.
- (ii) The product composition of the pyrolyzates from CTPB is very similar to that from nonfunctional PBD.
- (iii) HTPB can be differentiated from CTPB and PBD by the considerably lower yields of butadiene. The amount of VCH produced is also lower for HTPB. Further, HTPB yields a characteristic product, ethanol, which was identified using a Porapac Q column;
- (iv) PBAN is characterized by the lower amount of VCH produced compared to CTPB and HTPB. Also, the BD/VCH ratio is higher for PBAN than that for CTPB and HTPB. PBAN is further characterized by the presence of acetonitrile, acrylonitrile, and propionitrile components among the products of pyrolysis. A Porapac Q column separated these components well from C_5 and C_6 hydrocarbons. and
- (v) Amount of VCH produced decreases in the order PBD > CTPB

> HTPB > PBAN and butadiene decreases in the order PBD ~ CTPB
> HTPB ~ PBAN.

Effect of Curing

For propellant formulations, the functionally terminated polybutadienes are cured with appropriate curing agents to develop a network to hold the oxidizer particles and also to impart dimensional stability. CTPB and PBAN are cured by reacting with methylaziridinylphosphineoxide (MAPO) and HTPB is cured with toluene diisocyanate (TDI) using trimethylol propane (TMP) as crosslinking agent. The cure reactions may be represented as



The effect of curing on the nature and composition of the products of pyrolysis was studied by pyrolyzing the cured polymer samples at 500°C and the results are shown in Table II. These results indicate that: (i) the nature and composition of the products from cured and uncured HTPB are very similar; (ii) cured and uncured CTPB differ in their product composition, BD and propylene (C₃), are present in higher concentrations in the case of cured CTPB; and (iii) cured PBAN shows considerable increase in C₃ hydrocarbons and a decrease in butadiene concentration.

Thus, cured PBAN shows considerable difference in its behavior on pyrolysis compared to the uncured resin. To confirm this, PBAN was cured with different amounts of MAPO (0.5–1.7 eq) and the cured samples were pyrolyzed at 500°C. The product composition of the pyrolyzates is shown in Table III. It is quite clear from the results that the concentration of C₃ hydrocarbon increases and that of butadiene decreases with the amount of the curing agent. This demonstrates convincingly the dependence of the product composition on the extent of curing.

Mechanism of Thermal Degradation

The differences observed in the product composition of the different functionally terminated polybutadienes as well as their cured analogues can be satisfactorily explained on the basis of the postulated mechanisms for thermal degradation of higher molecular weight nonfunctional polybutadienes. Two types of mechanisms are considered to explain the free radical decomposition of PBD.^{10,11,23} In type I mechanism, a free radical is formed by a β-cleav-

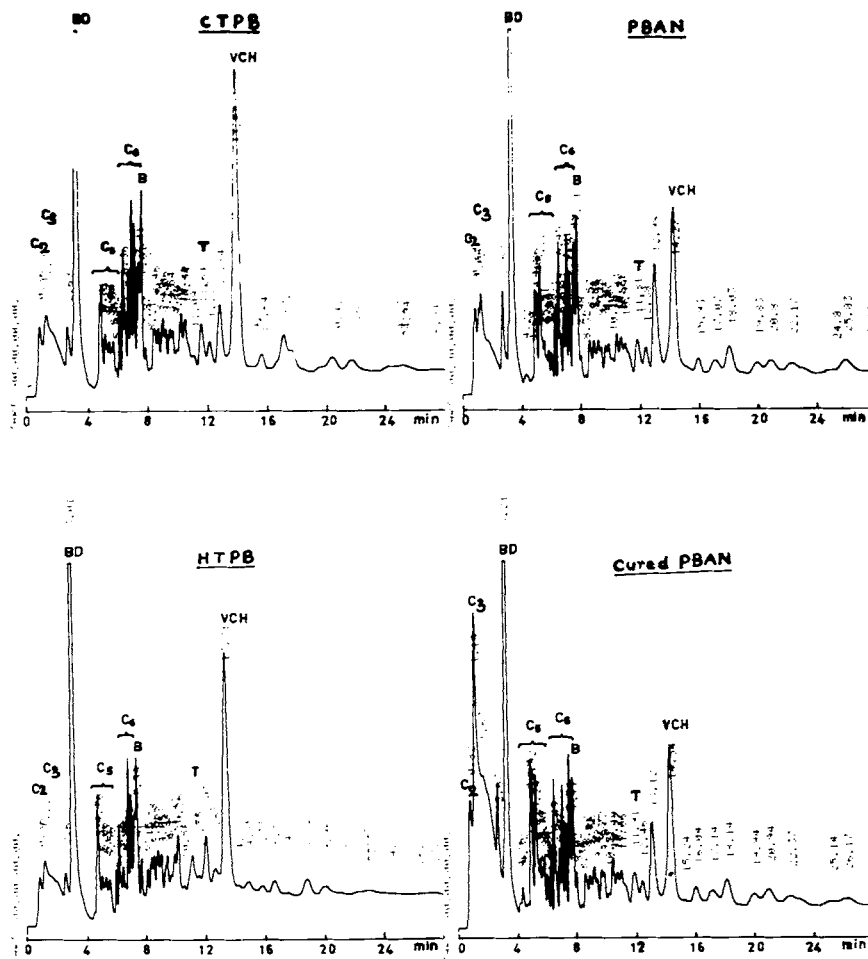
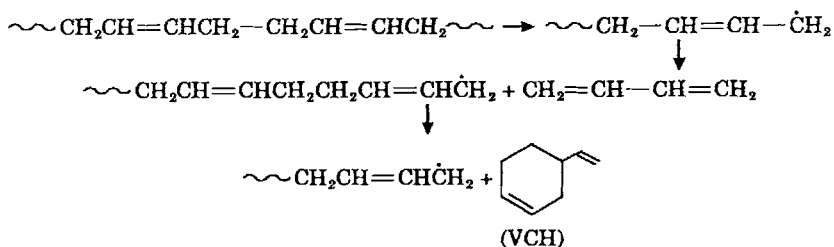


Fig. 1. Pyrograms of CTPB, HTPB, PBAN, and cured PBAN at 500°C with 80/100 Carbowax C/0.2% picric acid column; column temp 50–130°C, 20°C/min; flow rate 80 mL/min.

age which then unzips to yield mainly BD and VCH as the products of pyrolysis:



Type I mechanism

In type II mechanism, a hydrogen transfer to an allylic carbon in a “1,5-sigmatropic” manner results in the formation of one saturated and one unsat-

TABLE II
Composition of the Major Pyrolyzates from the Liquid and the Cured Polymers

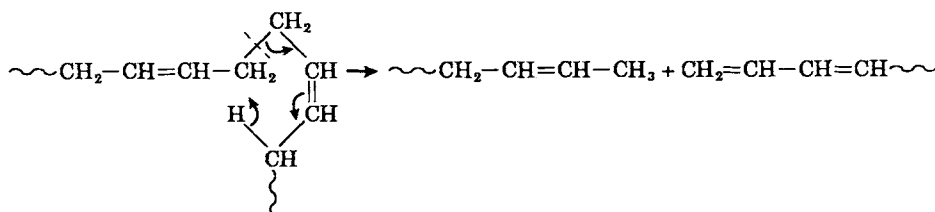
Sample	C ₂	C ₃	BD	C ₅	C ₆	B	T	VCH	BD/VCH
Pyrolysis temperature: 500°C									
PBD	1.4	5.7	35.4	4.6	7.0	2.2	2.8	15.8	2.24
CTPB	1.7	7.1	34.1	4.1	6.4	4.8	3.2	14.6	2.34
HTPB	1.8	8.4	27.6	6.5	6.9	4.7	3.3	13.1	2.11
PBAN	2.4	8.4	27.5	6.4	9.6	4.2	4.7	9.1	3.02
Cured CTPB	1.6	9.8	38.7	3.2	6.2	3.9	3.7	12.4	3.12
Cured HTPB	1.5	5.6	28.9	6.2	6.7	6.9	4.7	12.8	2.26
Cured PBAN	3.1	18.7	21.9	8.0	8.2	3.1	3.7	7.8	2.80
Pyrolysis temperature: 550°C									
PBD	4.4	4.8	31.8	5.3	8.3	3.7	3.1	12.9	2.47
CTPB	6.1	5.5	30.5	5.6	8.4	4.0	3.4	12.4	2.46
HTPB	5.9	5.4	24.1	6.8	8.2	3.6	4.0	10.4	2.32
PBAN	6.7	5.8	24.2	7.4	8.5	4.6	5.1	6.5	3.72
Pyrolysis temperature: 650°C									
PBD	12.2	5.9	23.1	8.4	8.1	11.2	6.3	2.4	9.6
CTPB	15.2	6.2	21.6	8.6	8.8	12.5	6.8	2.1	10.3
HTPB	14.4	5.8	17.0	9.2	9.3	13.1	6.4	1.8	9.4
PBAN	17.7	7.3	16.4	8.1	8.0	15.4	6.6	0.9	18.2
Pyrolysis temperature: 750°C									
PBD	25.8	10.4	13.8	7.1	2.7	21.7	12.2	0.2	
CTPB	25.9	9.5	12.4	7.6	3.4	22.7	10.9	0.1	
HTPB	29.7	11.5	10.3	7.0	2.2	21.0	10.9	0.1	
PBAN	30.0	11.5	10.4	8.1	3.0	19.5	9.6	0.1	
Pyrolysis temperature: 850°C									
PBD	41.7	7.4	5.4	2.7	0.5	28.5	10.1	—	
CTPB	43.5	6.9	4.3	2.3	0.5	28.0	10.1	—	
HTPB	44.2	6.9	3.6	1.8	0.3	27.9	10.2	—	
PBAN	45.5	7.4	3.9	3.6	0.8	25.1	8.7	—	

TABLE III
Composition of the Major Pyrolyzates from PBAN Cured with Different Amounts of MAPO

Sample	C ₂	C ₃	BD	C ₅	C ₆	B	T	VCH
Pyrolysis temperature: 500°C								
PBAN	2.4	8.4	27.5	6.4	9.6	4.2	4.7	9.1
PBAN + MAPO								
0.5 eq ^a	2.7	10.6	25.3	8.1	9.2	3.8	4.3	8.9
1.0 eq	2.9	14.8	23.7	7.7	8.5	3.6	4.1	8.4
1.5 eq	2.9	17.9	22.4	8.2	8.1	3.5	4.1	8.4
1.7 eq	3.1	18.7	21.9	8.0	8.2	3.1	3.7	7.4

^a eq = equivalents.

urated end. We have shown earlier²³ that type II mechanism is favored at higher temperatures and is probably due to increased chain mobility which favors hydrogen transfer through a cyclic transition state:



Type II mechanism

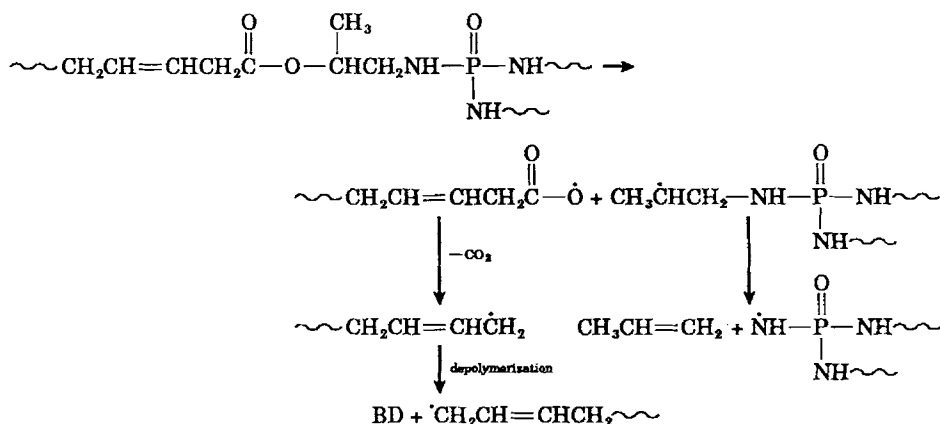
These two basic pathways of degradation can satisfactorily explain the pyrolysis behavior of the functionally terminated polybutadienes also as outlined below.

Carboxy-Terminated Polybutadiene (CTPB). Since carboxylic acids readily undergo decarboxylation at higher temperatures, the first step in the thermal degradation of CTPB can be represented as



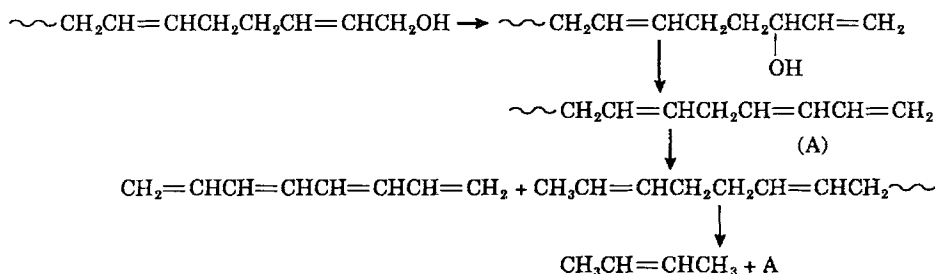
and results in the formation of a nonfunctional polymer. Therefore, it is not surprising that the composition of the products of pyrolysis of CTPB closely resembles that of a nonfunctional polymer as observed experimentally. In addition, butadiene and VCH comprise about 51% of the products formed on pyrolysis at 500°C. Hence, it is quite reasonable to postulate that type I mechanism predominates in the thermal degradation of CTPB. It is to be pointed out that an ionic mechanism involving addition of H^+ ion to double bond was invoked to explain the thermal degradation of CTPB.²⁵ However, the fact that CTPB behaves like a nonfunctional PBD suggests that the ionic mechanism is not significant under the present conditions of flash pyrolysis.

In the case of cured CTPB, the decarboxylation step is no longer facile and the first step in the degradation of the cured analogue may be considered to be cleavage of the ester bond, followed by loss of carbon dioxide and unzipping reactions as shown below:



This satisfactorily explains the higher amounts of C_3 observed in the products of cured CTPB compared to the uncured resin and the increase can be attributed to the contribution from the curing agent MAPO. The slightly higher amount of BD observed may result from the facile end initiated depolymerization. Thus, the thermal degradation of cured CTPB may be considered to consist of the initial cleavage of the ester crosslinks followed by type I degradation mechanism.

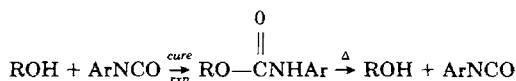
Hydroxy-Terminated Polybutadiene (HTPB). The observation that HTPB on pyrolysis gives a lesser amount of butadiene compared to CTPB and nonfunctional PBD suggests that in addition to type I mechanism HTPB undergoes degradation by other pathways as well. A probable mechanism is shown in Scheme 1:



Scheme 1

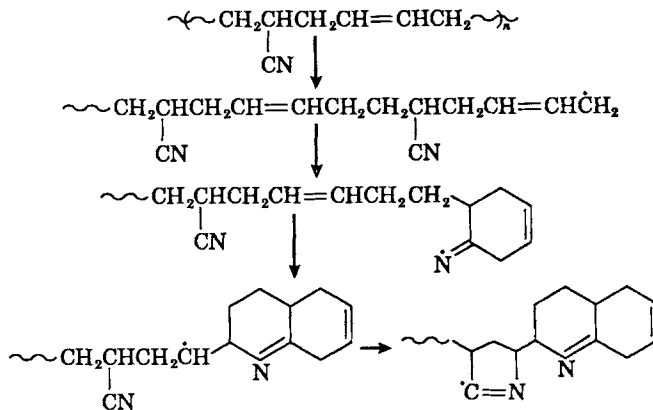
The initial step is an allylic rearrangement and is followed by degradation to give polymer A. Extended conjugation of the resulting product favors the decomposition of polymer A by hydrogen transfer reactions as in type II mechanism. Consequently, HTPB gives on pyrolysis significantly lesser amount of BD. Therefore, type I as well as type II mechanisms occurring simultaneously satisfactorily explains the thermal degradation of HTPB. The effect of the presence of hydroxyl group in polybutadiene favors hydrogen transfer reactions.

The cured analogue of HTPB behaves very similar to uncured polymer. This can be rationalized by the observation that urethane linkage undergoes reversible cleavage at higher temperatures to give the alcohol and isocyanate back^{26,27}:



Poly (butadiene–Acrylonitrile–Acrylic Acid) (PBAN). The strikingly low yield of VCH produced on pyrolysis of PBAN can be understood on the basis of pyrolysis behavior of copolymers of butadiene. It is suggested that formation of VCH requires the presence of two successive units of butadiene in the copolymer chain. The presence of comonomers in the chain acts as impediments to depolymerization and consequently VCH produced will decrease. Thus, in the alternating copolymers of butadiene and other vinyl comonomers the VCH/BD molar ratio tends almost to zero.²⁸ Therefore, PBAN polymer, which contains acrylonitrile and acrylic acid as comonomers to the extent of about 15% (w/w), yields on thermal decomposition a much lower amount of VCH compared to CTPB or HTPB polymers. Further, the presence of pendant nitrile groups favors cyclization

reactions as was observed for polyacrylonitrile homopolymers.²⁹ The likely cyclization reactions involving nitrile groups are outlined in Scheme 2. Similar cyclization reactions were invoked to explain the thermal degradation of poly(butadiene-acrylonitrile-methacrylic acid) polymer³⁰:



As discussed earlier, the composition of the products of pyrolysis from cured PBAN is considerably different from the uncured polymer. The increase in the amount of C₃ hydrocarbon is greater than what could be accounted from MAPO in comparison with cured CTPB. Butadiene also shows a decrease. These factors can be rationalized by invoking the cleavage of the ester link followed by decarboxylation as the first step in the degradation. The resulting radical leads to the formation of conjugated and cyclized products by hydrogen transfer

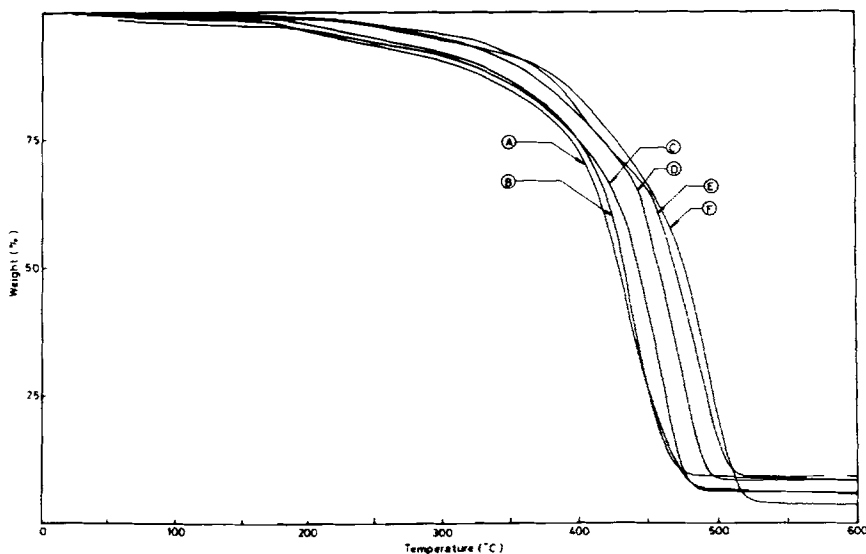
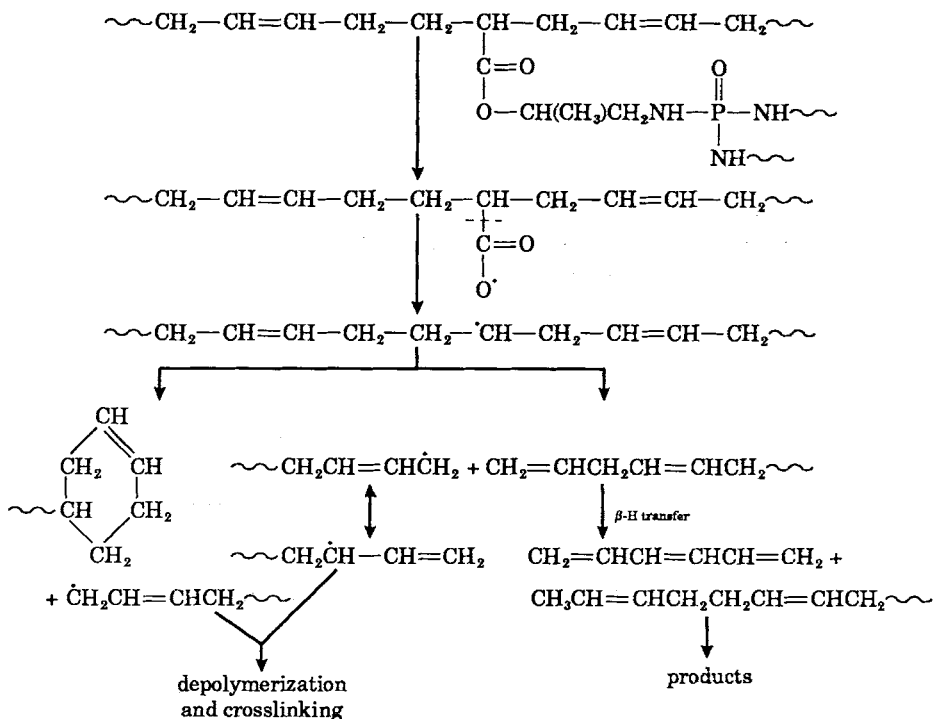


Fig. 2. TG curves of cured PBAN at different heating rates ($^{\circ}\text{C}/\text{min}$): (A) 2; (B) 5; (C) 10; (D) 20; (E) 50; (F) PBAN at heating rate $50^{\circ}\text{C}/\text{min}$.

reactions as shown in Scheme 3 and results in a decrease in the formation of BD and VCH and an increase in the concentration of lower hydrocarbons. This is in contrast to the decomposition of cured CTPB where the radical resulting from the decarboxylation is terminal and can undergo facile depolymerization to yield BD and VCH.



Scheme 3

Thus, the thermal decomposition of functionally terminated liquid polybutadienes, HTPB, CTPB, and PBAN, can be satisfactorily explained based on the mechanisms proposed for higher molecular weight nonfunctional polybutadienes.

Thermogravimetric Studies

The kinetic parameters for the thermal decomposition of CTPB^{25,31-33} and HTPB³³ have been reported by others. Moreover, the product composition of the pyrolyzates of PBAN and its cured analogues are considerably different compared to the corresponding differences for HTPB and CTPB. Therefore, thermogravimetric studies of PBAN and its cured polymer were undertaken to evaluate the kinetic parameters for their thermal decomposition.

Thermograms were recorded on 5 mg of the samples at heating rates (β) of 2, 5, 10, 20, and 50°C/min in nitrogen atmosphere. PBAN resin was studied only at $\beta = 50^\circ\text{C}/\text{min}$. The thermograms are shown in Figure 2. The kinetic parameters were evaluated by Ozawa's method.

Ozawa's Method.³⁴ In this method, the activation energy for decomposition is calculated from a plot of $\log \beta$ against T^{-1} for a fixed degree of conversion (α). Several of these isoconversional plots are shown in Figure 3 for the cured PBAN resin. Clearly, the plots are linear except for the heating rate $\beta = 2^\circ\text{C}/\text{min}$, suggesting a different mechanism of decomposition at the lowest heating rate studied. The slope of such a line is given by $-0.4567 E/R$ and the calculated values of E are given in Table IV. The values for $\beta = 2^\circ\text{C}/\text{min}$ are omitted for calculation of activation energies for $\alpha > 0.2$. It is seen from the results that values of E increase with extent of degradation and remain more or less constant above $\alpha = 0.35$. This suggests that the degradation is taking place in the initial stages by more than one mechanism and above $\alpha = 0.35$ a single mechanism operates. The value of 259 ± 16 kJ/mol for the activation energy for the main stage ($\alpha > 0.35$) is closer to that found experimentally for main chain scission of saturated polymers such as polyethylene¹¹ than that of 179 kJ/mol calculated³⁵ for unsaturated polymers such as polybutadiene and polyisoprene. This value is also in good agreement with 259 kJ/mol reported from isothermal studies of polybutadienes.¹²

Thus, thermogravimetric results suggest that PBAN and its cured analogue undergo extensive cyclization reactions in the initial stages of degradation. The occurrence of cyclization reactions would be more favored in the case of PBAN compared to PBD due to the presence of pendent nitrile groups. These results are consistent with and support the mechanism of degradation proposed from pyrolysis studies. Further, polybutadiene was found to undergo decomposition in two stages.³⁶ In the first stage, depolymerization and crosslinking reactions

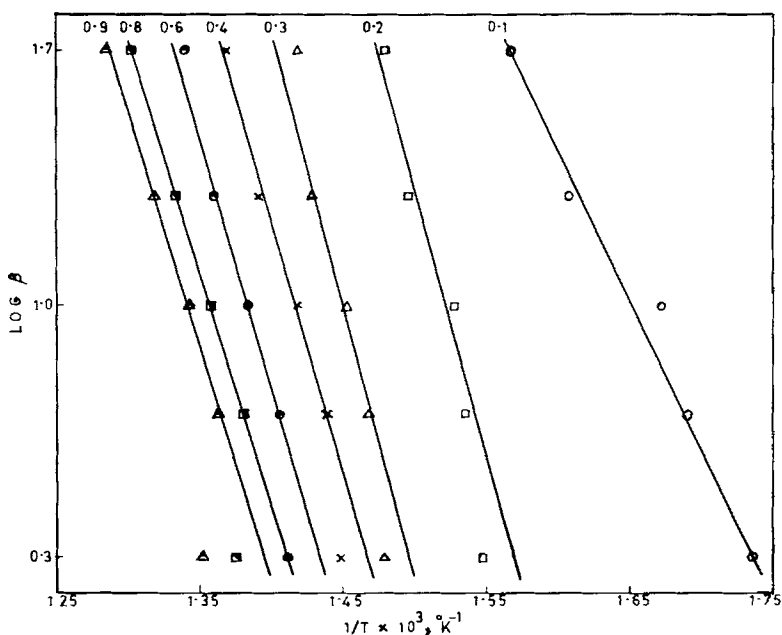


Fig. 3. Ozawa's plots of $\log \beta$ vs. $1/T$ at constant values of conversions (α) for the degradation of cured PBAN.

TABLE IV
Activation Energies Determined by Ozawa's Method for Cured PBAN

Fractional weight loss (α)	Temperature (K) for heating rate (β) ($^{\circ}\text{C}/\text{min}$)					Activation energy E (kJ/mol)	Correlation coefficient
	$\beta = 2$	$\beta = 5$	$\beta = 10$	$\beta = 20$	$\beta = 50$		
0.05	495	523	526	570	596	71.5	0.9547
0.08	546	570	578	606	623	107.5	0.9844
0.10	573	594	598	622	636	150.3	0.9871
0.15	619	629	635	649	661	252.3	0.9931
0.20	646	652	655	669	675	312.6	0.9688
0.25	665	669	673	686	689	368.2	0.9584
0.30	677	680	686	700	705	323.2	0.9745
0.35	685	690	697	713	722	275.7	0.9851
0.40	691	696	705	720	731	266.0	0.9934
0.60	708	709	723	736	746	269.9	0.9875
0.80	727	724	737	750	768	239.7	0.9988
0.90	740	734	744	758	778	244.5	0.9971
Average ($\alpha = 0.35\text{--}0.90$)						259 \pm 16	

are predominant and, in the second stage, the decomposition of the crosslinked polymer formed in the first stage is the dominant process, supporting the conclusions drawn from pyrolysis GC and thermogravimetric studies of cured PBAN.

CONCLUSIONS

The important conclusions that can be drawn from the present study are (i) HTPB, CTPB, and PBAN polymers can be distinguished from one another from the composition of their pyrolyzates; (ii) the presence of hydroxyl functional group favors hydrogen transfer reactions in the thermal degradation of polybutadienes whereas carboxyl functional group has little effect; and (iii) thermal degradation of PBAN and cured PBAN involves extensive cyclization reactions in the initial stages and has an activation energy of 259 ± 16 kJ/mol for the main stage decomposition.

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