

# Pyrolysis and Thermo-Oxidative Degradation of Polycyclopentadiene

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**ABSTRACT:** Thermal degradation of polycyclopentadiene polymer (PCPD) was investigated by pyrolysis gas chromatography (PGC) in the temperature range of 500–950°C. The nature and composition of the pyrolyzates at various temperatures are presented, and the mechanism of degradation is explained. The activation energy of decomposition ( $E_a$ ) was obtained from an Arrhenius-type plot using the concentration of the product ethylene ( $C_2$ ) at different pyrolysis temperatures and the value was found to be 138 kJ mol<sup>-1</sup>. Thermo-oxidative degradation of PCPD in the presence of ammonium perchlorate (AP), the most commonly used oxidizer for polymeric fuel binders, was studied at a pyrolysis temperature of 700°C. The compositions of the products with varying amounts of AP are given, and the exothermicity of oxidative decomposition reactions is evaluated. The energetics of the degradation processes are compared with those of polybutadiene type polymers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 635–641, 2000

**Key words:** pyrolysis-GC; thermal degradation; polycyclopentadiene

## INTRODUCTION

Hydrocarbon polymers are widely used as fuel binders in composite solid propellants, and ammonium perchlorate is the main oxidizer used. Combustion of these solid propellants proceeds through a series of complex reactions,<sup>1–4</sup> and is significantly affected by the nature of the polymeric binder.<sup>5</sup> Steady-state combustion models consider the combustion reactions to occur in the vapor phase between the pyrolysis products of the binder and the oxidizer.<sup>1,2,6</sup> The chemistry and the energetics of the combustion reactions greatly depend on the nature and composition of the pyrolysis products of the binder.

The energetics of pyrolysis of several propellant binders have been studied by various methods, and were reviewed recently.<sup>7</sup> But there are practically no studies reported on PCPD, which is

a possible candidate for solid ramjet fuel, as it possesses high volumetric heat of combustion and high density in conjunction with good compatibility with an hydroxyl-terminated polybutadiene binder.<sup>8</sup> Pyrolysis mechanisms and kinetics of decomposition strongly depend on the heating rate. Data obtained using conventional thermoanalytical methods like TGA, DTA, and DSC may not be useful for these studies, as the heating rates used are far less than the real heat fluxes in the actual systems. Pyrolysis GC is a very powerful tool for these studies, as the rate of heating under flash pyrolysis conditions is very high. Hence, we have undertaken a systematic study of pyrolysis and thermo-oxidative degradation of polymeric fuel binders using PGC, and have reported on pyrolysis of polybutadienes,<sup>9</sup> functionally terminated polybutadienes,<sup>10</sup> and thermo-oxidative degradation of hydroxyl terminated polybutadiene (HTPB) and poly(butadiene–acrylonitrile–acrylic acid) terpolymer (PBAN).<sup>11</sup> In this article the pyrolysis and thermo-oxidative degradation of polycyclopentadiene polymer are reported. The ener-

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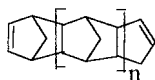
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getics of the decomposition processes are evaluated and compared with those of the HTPB polymer.

## EXPERIMENTAL

### Materials

The polycyclopentadiene polymer (PCPD) used in this study was prepared by thermal Diels-Alder polymerization of cyclopentadiene generated *in situ* by thermal cracking of commercially available dicyclopentadiene.<sup>8,12</sup> The low viscous or waxy monocyclic linear polymer was removed in toluene solvent, and the white powdery bicyclic PCPD was purified by repeated washing with toluene and methanol. The density of the polymer, determined using specific gravity bottle, is 1.15 g/cc. The elemental composition was determined by using a Perkin-Elmer 2400 CHN analyzer, and the values are C = 89.6% and H<sub>2</sub> = 8.9%. The bicyclic PCPD polymer is represented as:



### Pyrolysis Gas Chromatography (PGC)

Pyrolysis was done using a furnace pyrolyzer, Shimadzu PYR-2A, directly coupled to a Shimadzu GC-5A. A stainless steel column (3 mm i.d. × 2 m) packed with 80/100 Carbopack C/0.2% picric acid was used for separation of the products. 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 computation of peak areas, and quantitative data were obtained by area summation method.

## RESULTS AND DISCUSSION

### Pyrolysis Studies

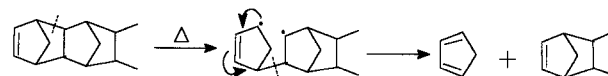
Pyrolysis was carried out at different temperatures from 500 to 950°C using about 0.6–0.7 mg of samples, and the products were analyzed by gas chromatography. A typical pyrogram is shown in Figure 1. The nature and composition of the products were arrived at as reported earlier.<sup>10,11</sup> The major products were identified by comparison with the pyrograms of polybutadiene

and hydroxyl-terminated polybutadiene polymers under identical experimental conditions. The major products identified were ethylene (C<sub>2</sub>), propylene (C<sub>3</sub>), C<sub>4</sub> hydrocarbons, cyclopentadiene (CPD), C<sub>6</sub> and C<sub>7</sub> hydrocarbons. The monomer, cyclopentadiene, was identified using standard samples. The composition of the major pyrolyzates at various temperatures is given in Table I, and the following conclusions can be derived from these results:

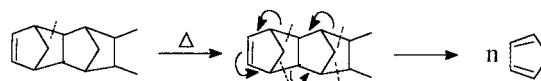
(a) at lower pyrolysis temperatures the polymer is almost completely depolymerized to yield the monomer, cyclopentadiene (~ 99% at 500°C). (b) As the pyrolysis temperature is increased, the amount of ethylene produced increased continuously, while concentration of the monomer, CPD, in the products decreased continuously. This is similar to the pyrolysis behavior of polybutadiene type polymers.<sup>9,10</sup> (c) A considerable amount of the monomer is produced even at the very high pyrolysis temperature (~ 14% at 950°C) indicating the depolymerization reaction is still operating at the high temperature, competing with random degradation.

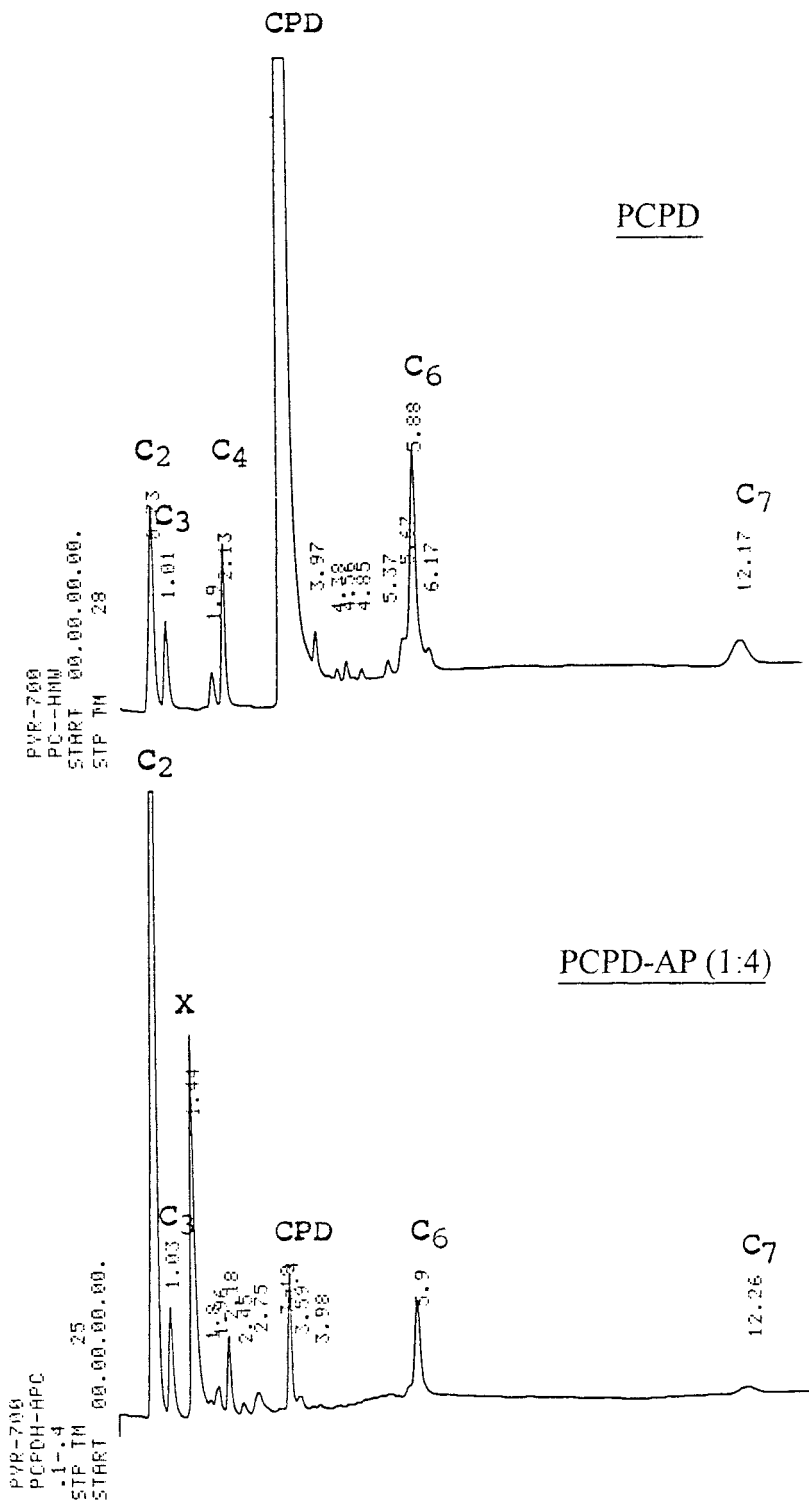
### Mechanism of Thermal Degradation

At lower pyrolysis temperatures (< 600°C) the polymer decomposes completely into the monomer, suggesting a decomposition mechanism of initial radical cleavage followed by depolymerization by chain unzipping facilitated by a retro Diels-Alder reaction. The chain-unzipping depolymerization is the major route of decomposition, even at higher temperatures, as reflected by the high concentrations of the monomer yield (~ 80% at 800°C and ~ 70% at 850°C). At the highest temperature studied (950°C), degradation becomes more random, resulting in a rapid decrease in the production of the monomer and a considerable increase in the yield of C<sub>2</sub> hydrocarbons. The mechanism of depolymerization by the retro Diels-Alder reaction leading to the formation of the monomer can be shown as follows.



Alternatively, it may be represented as a concerted process as shown below.





**Figure 1** Pyrograms of PCPD and PCPD-AP (1 : 4) at pyrolysis temperature 700°C.

This mechanism of decomposition explains the nearly 100% yield of the monomer at lower pyrolysis temperatures and the high yields even at very high temperatures.

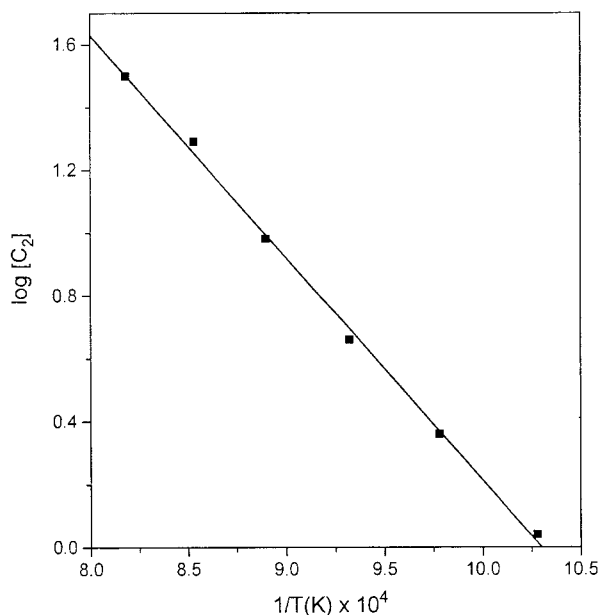
**Activation Energy of Decomposition**

A greater insight into the mechanism of decomposition can be obtained by providing an Arrhe-

**Table I** Composition of the Major Pyrolysis Products from Polycyclopentadiene Polymer at Various Temperatures

Pyrolysis Temperature, (°C)	wt % of Products					
	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	CPD	C <sub>6</sub>	C <sub>7</sub>
500	—	—	—	99.6	—	—
600	0.3	0.2	0.3	98.4	0.2	0.1
700	1.1	0.4	0.7	94.3	2.0	0.5
750	2.3	0.8	1.0	88.5	3.7	1.6
800	4.6	1.5	1.3	81.3	6.7	1.8
850	9.6	2.1	1.6	69.5	12.7	3.4
900	19.3	3.2	1.6	45.7	24.0	5.4
950	31.3	1.7	0.6	14.1	41.1	7.5

nius-type plot of the log of concentration of the products vs.  $1/T$ , as we have shown in our earlier studies.<sup>9,11</sup> Such a plot of  $\log [C_2]$  vs.  $1/T$  is shown in Figure 2. The straight line plot shows that the product C<sub>2</sub> is formed by a single mechanism throughout the temperature range studied. Under flash pyrolysis conditions the concentration of the products may be taken as a measure of the overall rates for their formation. Then, activation energy,  $E_a$ , of decomposition can be obtained from the Arrhenius-type plot of  $\log [C_2]$  vs.  $1/T$ , as we have shown in the case of HTPB and PBAN polymers.<sup>11</sup> The  $E_a$  obtained from the plot was 138 kJ mol<sup>-1</sup>.

**Figure 2** Arrhenius-type plots of  $\log [C_2]$  vs.  $1/T$  (K) for PCPD.

### Thermo-oxidative Degradation

To study the effect of ammonium perchlorate (AP) on decomposition, the polymer sample was mixed thoroughly with varying amounts of AP and pyrolyzed at 700°C. A flame ionization detector was used to detect organic products only, avoiding overlapping peaks of end oxidation products like CO, CO<sub>2</sub>, H<sub>2</sub>O, and decomposition products of ammonium perchlorate, because the aim was to study the relative changes of pyrolysis products. The pyrogram of the polymer mixed with 80% AP is shown in Figure 1, and the composition of the major products is given in Table II. The inferences drawn from these results are the following: (a) the pyrogram of PCPD with AP closely resembles that without AP except for the change in the composition of the products and the appearance of an oxidation product, X (not identified). The close similarity of the pyrograms indicates that the effect of AP on decomposition is similar to the effect of increasing pyrolysis temperature. (b) With increasing amounts of AP, the lower hydrocarbons, especially C<sub>2</sub>, are preferentially formed, while the amount of CPD continuously decreased. (c) The concentration of the oxidation product, X, increases from 0.3 to ~ 18% with increasing amounts of AP (cf. Table II). This may have been formed by the oxidation of C<sub>6</sub> hydrocarbon by the oxidizer, as explained below.

The close similarity of the effects of oxidizer and pyrolysis temperature on decomposition suggests that (1) the mechanism of decomposition of the polymer is not altered in the presence of AP. (2) Initially, the polymer and AP decompose separately, and the products react in the vapor phase, resulting in the formation of CO, CO<sub>2</sub>, H<sub>2</sub>O, etc., and the oxidation product, X. This is in agreement with the combustion models that the

**Table II** Composition of the Major Pyrolysis Products from Polycyclopentadiene (PCPD) Mixed with Various Amounts of Ammonium Perchlorate (AP) at Pyrolysis Temperature 700°C

Sample PCPD : AP (Weight Ratio)	wt % of Products						
	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	CPD	C <sub>6</sub>	C <sub>7</sub>	X
1 : 0.2	3.1	0.8	1.1	89.7	2.9	0.8	0.3
1 : 0.5	8.0	1.5	1.5	80.1	4.7	1.4	0.8
1 : 1	28.3	2.7	2.3	47.5	9.7	2.0	3.4
1 : 2	44.8	1.8	1.0	23.9	5.9	1.1	7.3
1 : 3	53.2	2.0	1.2	10.7	4.4	0.8	13.5
1 : 4	57.1	4.8	2.9	4.8	6.2	0.9	18.8

polymer thermally pyrolyzes to gaseous fuels for reactions with the decomposition products of the oxidizer.<sup>1,2,6</sup> (3) The heat generated in the exothermic vapor phase reactions is fed back to the polymer, resulting in a further breakdown of the polymer, leading to increased formation of lower hydrocarbons.

Thus, the addition of AP increases the effective pyrolysis temperature, and hence, the amount of C<sub>6</sub>, in addition to C<sub>2</sub>, in the products is expected to increase very much (cf. Table I). However, with the increase in the amount of AP the increase in the amount of C<sub>6</sub> in the products is marginal only, whereas the oxidation product, X, increases significantly (cf. Table II). Hence, it is inferred that the product X is formed by the oxidation of pyrolyzate C<sub>6</sub> by the decomposition products of AP.

### Estimation of Exothermicity

As the effects of the oxidizer and temperature are similar as discussed above, the exothermicity of oxidative degradation processes can be estimated from the variation in the product composition with the amount of oxidizer present. Thus, an equivalent temperature,  $T_e$ , for decomposition in the presence of AP can readily be obtained from the amount of the C<sub>2</sub> hydrocarbon produced and the  $E_a$  obtained earlier from the Arrhenius-type plot, as we have shown in the thermo-oxidative degradation of HTPB and PBAN polymers.<sup>11</sup> The values of  $T_e$  thus obtained, for the decomposition of PCPD with various amounts of AP at pyrolysis temperature 700°C, are given in Table III. The difference ( $\Delta T$ ) between the set pyrolysis temperature (700°C) and the equivalent temperature ( $T_e$ ), which is a measure of exothermicity of the oxidative degradation reactions of PCPD with AP, for different concentrations of AP, are also shown in Table III. With 80% AP, the value of  $\Delta T$  is ~ 300°C.

### Comparison with Polybutadiene-Type Polymers

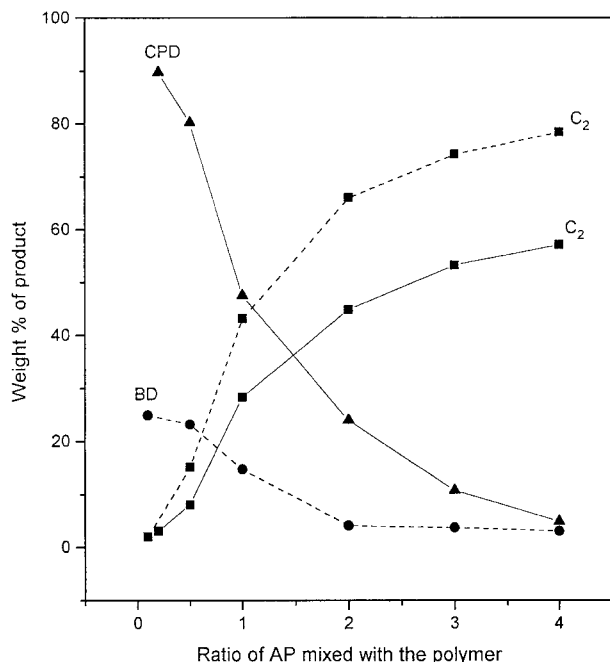
Because the pyrolysis and thermo-oxidative degradation behavior of PCPD is similar to that of HTPB and PBAN polymers reported by us earlier,<sup>11</sup> the energetics of the decomposition processes for these polymers may be compared along the following lines.

The behavior of both polymers, HTPB and PCPD, with respect to pyrolysis temperature and concentration of AP is similar. The amount of C<sub>2</sub> produced increases, and the concentration of the monomer in the products decreases with an increase in temperature as well as AP concentration. However, the amount of C<sub>2</sub> produced from HTPB is much higher compared to that from PCPD with respect to pyrolysis temperature and concentration of AP, while the monomer produced from PCPD is much more compared to that from HTPB. Thus, at a pyrolysis temperature of 850°C HTPB<sup>11</sup> produced 44% C<sub>2</sub> and only 2% of the monomer, butadiene (BD), whereas even at 950°C, PCPD produced only 31% C<sub>2</sub> and a considerable amount of the monomer, cyclopentadiene (~ 14%). With 80% AP, HTPB yielded ~ 78% C<sub>2</sub> and only 3% of the monomer at a pyrolysis temperature of 500°C, whereas even at a higher pyrolysis temperature of 700°C PCPD with 80% AP

**Table III** Calculated Values of "Equivalent Temperature" ( $T_e$ ) and the Difference ( $\Delta T$ ) between Set Pyrolysis Temperature (700°C) and  $T_e$  for PCPD Binder

Binder : AP (Weight Ratio)	$T_e$ (°C)	$\Delta T$
1 : 1	937	237
1 : 2	979	279
1 : 3	997	297
1 : 4	1003	303





**Figure 3** Concentration of C<sub>2</sub> and monomer produced from PCPD and HTPB with varying amounts of AP : PCPD (—), at pyrolysis temperature 700°C; HTPB (---), at pyrolysis temperature 500°C (data from ref. 11 is used for the plots for HTPB).

yielded only 57% C<sub>2</sub> and nearly 8% monomer. Thus, the average molecular weight of the decomposition products from HTPB is much less compared to that from PCPD. The variation of C<sub>2</sub> and the monomer produced from HTPB and PCPD with varying amounts of AP is shown in Figure 3. (The data from ref. 11 is used for the plots for HTPB).

The activation energy,  $E_a$ , of decomposition obtained from Arrhenius-type plots of  $\log [C_2]$  vs.  $1/T$  is 53 kJ mol<sup>-1</sup> for HTPB,<sup>11</sup> whereas the corresponding value for PCPD is 138 kJ mol<sup>-1</sup>.

The difference  $\Delta T$  between the set pyrolysis temperature and the equivalent temperature  $T_e$ , which reflects the exothermicity of the combustion reactions with varying amounts of AP, is much higher in the case of HTPB compared to the corresponding values for PCPD. With 80% AP,  $\Delta T$  for HTPB<sup>11</sup> at a pyrolysis temperature of 500°C was 430°C, while the corresponding value for PCPD even at a higher pyrolysis temperature of 700°C was  $\sim 300^\circ\text{C}$  only.

From the above results it is inferred that HTPB, with a lesser activation energy,  $E_a$ , of decomposition, greater exothermicity of combustion reactions, and lower mean molecular weight of the decomposition products, may be energeti-

cally a favored polymer compared to PCPD in primary combustion reactions. Theoretical evaluation of performance of HTPB and PCPD-based propellants<sup>13</sup> using the NASA-SP-273 program showed a lower primary specific impulse ( $I_{sp}$ ) value for the latter, and was in agreement with the experimental results obtained,<sup>14</sup> substantiating the above inference drawn from the PGC results.

The peak decomposition temperature for PCPD ( $\sim 275^\circ\text{C}$ ) is much lower than the corresponding value ( $\sim 475^\circ\text{C}$ ) for HTPB, as observed from thermogravimetric analysis (TGA). This can be attributed to the ease of depolymerization of PCPD by retro Diels-Alder reaction. The ease of depolymerization yielding nearly 100% monomer at a lower pyrolysis temperature favors PCPD as a fuel for secondary combustion reactions, for example, ramjet fuel for air-breathing propulsion.

## CONCLUSIONS

The important conclusions drawn from the present study are: (1) polycyclopentadiene decomposes by chain unzipping by retro Diels-Alder reaction at lower pyrolysis temperatures, and at elevated temperatures random degradation also becomes important. (2) The activation energy for thermal degradation of PCPD is about 138 kJ mol<sup>-1</sup> at high heating rates. (3) The effect of AP on decomposition is similar to the effect of increasing the pyrolysis temperature. (4) The polymer and AP decompose separately, and the products react in the vapor phase yielding the end products. (5) The data obtained from pyrolysis GC studies of polymer fuels are useful for extrapolation to combustion studies.

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