

9-30-1988

High-energy, curable polycyclopentadiene binder for solid rocket propellants

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ABSTRACT

**Title of Thesis: High-energy, Curable Polycyclopentadiene
Binder for Solid Rocket Propellants**

Jian guo NING, Master of Engineering Science, 1988

Thesis directed by : Associate Prof. Dr. George Lei

Diels Alder polymerization of cyclopentadiene (CPD) has been carried out at 170°C under inert atmosphere. The resulted polymer has a low bulk viscosity, 7.4 cps, and a number average molecular weight M_n up to 3000. This liquid Prepolymer is curable with maleic anhydride. With ammonium perchlorate, aluminum, and maleic anhydride, a high energy solid propellant has been formulated with this polymer. Via bomb calorimeter, Instron, and density measurement, it was found that this propellant has a better heat of combustion, tensile strength, and solid loading than that of the commercial rocket propellant based on hydroxyl terminated polybutadiene.

**HIGH-ENERGY, CURABLE POLYCYCLOPENTADIENE
BINDER FOR SOLID ROCKET PROPELLANTS**

by

Jian guo NING

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment
of the requirements of the degree of
Master of Science in Chemistry Division of Chemical Engineering
1988

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Binder for solid Rocket Propellants

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DEDICATION

This thesis is dedicated to my wife, Xijie Ni, without whose sacrifice and unending support, this project would not have been completed.

ACKNOWLEDGMENT

I would like to express my appreciation and gratitude to Dr. George Lei for his patience, encouragement and guidance during my graduate research. I am deeply indebted to him for the knowledge and experience I have acquired as a result of his expertise in the field of polymer chemistry.

I am grateful to Dr. Richard Parker for permitting me to use oxygen bomb calorimeter which was essential for the experimentation conducted in this work.

I would also like to thank Dr. Richard Parker and Dr. C.C. Lin as member of my graduate committee for their input, encouragement, and the time to review the thesis.

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GLOSSARY

AP	: ammonium perchlorate
BL	: 1,4-butanediol
CPD	: cyclopentadiene
DMF	: N,N-dimethylformamide
GL	: glycerol
HTPB	: hydroxyl terminated polybutadiene
MA	: maleic anhydride
PA	: phathelic anhydride
PB	: polybutadiene
PCPD	: polycyclopentadiene
THF	: tetrahydrofuran
TTR	: total temperature rise

INTRODUCTION

A solid propellant is a gas-producing combustible dense material which is stable at room temperature and allows a controlled release of energy to drive a rocket motor without dependence on the atmosphere. Modern solid composite propellants are heterogeneous and consist of three components: an organic polymer (10 - 20 % by weight) which serves as both a binder and gas-forming, combustible fuel, a solid oxidizer (60 - 70 % by weight) which may also contribute to gas formation, and a combustible metal additive (10 - 20 % by weight) which provides the primary source of thermal energy. The most energetic solid propellants result when the oxidizing and reducing agents exist in discrete molecules. Thus from the standpoint of energy potential, the best binders are hydrocarbons and the best fillers are inorganic oxidizer, such as ammonium perchlorate, and the fuel, such as aluminum metal.

The polymer material as a binder in a solid propellant must meet a multitude of requirements. It represents a reducing agent and must be easily oxidized to serve as source of gas, it must also be sufficiently resistant to interaction

with the oxidizer to prevent degradation during aging and storage. The polymer provides the continuous matrix around each solid filler particles and is responsible for providing mechanical properties adequate to the stresses and strains imposed during use. The polymer must have viscosity and cure characteristics that facilitates functioning of the motor and must bond adequately to rocket-motor insulation. To be castable, a propellant must have a viscosity which will allow it to flow readily for a number of hours after mixing. A polymer which reaches its gel point before the casting is complete would lead to poor consolidation of the propellant in the motor resulting in unreliable ballistic performance. The polymer itself serves as fuel with high enthalpy or heat of combustion. Table 1 gives a summary about roles of binder in propellants.

Table 1. Basic criteria for polymer binder

-
- .reducing agent
 - .resistant to interaction with other elements in the system
 - .provide enough mechanical properties
 - .suitable viscosity and cure characteristics
 - .fuel with high heat of combustion as primary source of gas
 - .binding agent to motor insulation
-

A maximum content of hydrogen is particularly desirable because of the low molecular weight of the gas. The maximum content of hydrogen in conventional polymers occurs in saturated hydrocarbons. A considerable development of saturated hydrocarbons have been made since the late 1960's.

Most modern high-energy solid propellants contain metallic fuel such as aluminum. These metallic fuels increase the chemical energy of solid propellants not only through their highly exothermic reaction with the oxidizer but also because they exclude water vapor from the exhaust product and increase its hydrogen content. Thus, use of metallic fuels prevents energy losses due to the water-gas equilibrium and the dissociation of the water molecules into radicals at the combustion temperature.

Propellants prepared with a linear amorphous polymer have very good dimensional stability because the polymer

crystals dissolve in the plasticizer. The chemically crosslinked polymers yield propellants with the best thermal stability and do not show any abnormal behavior until chemical degradation of the binder starts. The mechanical behavior of the crosslinked binder depends on the degree of crosslinking in the network. Some crosslinking must be introduced to prevent the plastic flow which would readily occur under the influence of pressure and the heat in a purely linear polymer, but if an additional crosslink is introduced into the network, the system is no longer capable of reasonable extension. The result must be a compromise to obtain reinforcement while allowing original extension.

The organic elastomeric binder has the dual function of furnishing most of the gas producing elements and of being the continuous matrix which binds the composite mass together into a grain with useful mechanical properties for case-bonded motors. To approach the ideal elastomeric network in the binder structure is necessary to achieve the optimum mechanical properties of the highly filled solid propellants, To achieve this objective and still retain the other necessary polymer properties is difficult. Only a few of the commercially product polymers are useful as binders, because of requirements imposed by the technique of preparing and using case-bonded solid rocket motors. The polybutadiene

binders developed in the 1950's possessed a high hydrogen content in the exhaust and therefore had a high specific impulse as well as a longer shelf-life and better mechanical properties. A typical propellant consisting of polybutadiene binder, ammonium perchlorate oxidizer, and aluminum metal additive burns with an energy evolution of about 1500 cal/g [1].

The current research is expected to result in considerable improvements in the polymers available for solid propellant binders. The directions which research has taken to develop new and improved binder systems are two: the first is an attempt to improve physical properties while maintaining energetics, the second is a straight-forward attempt to increase energetics. This research on synthesis of polycyclopentadiene polymer binder is an attempt towards these two directions.

At room temperature, 1,3-cyclopentadiene is in the form of the Diels-Alder dimer, dicyclopentadiene. In thermal polymerization, 1,3-cyclopentadiene monomer is formed in situ and reacts further. Oligomerization of cyclopentadiene is believed to involve partial dissociation of the dimer to monomer, which reacts with dimer in a Diels-Alder reaction to form trimer, or the reaction of monomer with trimer to form tetramer, and so on [2]. Polymerization of cyclopentadiene

initiated by SnCl_4 , TiCl_4 , BF_3 etherate, $\text{AlCl}(\text{C}_2\text{H}_5)_2$ and $\text{AlCl}_2\text{C}_2\text{H}_5$ at -60 to -90 °C in various solvents gives polymers insoluble or partially soluble in hydrocarbons[3]. A search for a less active cationic catalyst that would give soluble high molecular weight PCPD led to the choice of $n\text{-C}_4\text{H}_9\text{OTiCl}_3$ as initiator, but the soluble polymers have very high intrinsic viscosity and do not meet the requirements of low viscosity for the prepolymer. Cyclopentadiene can be copolymerized with maleic anhydride between 80 to 200 °C in the presence of peroxides [4]. Terpolymers of ethylene, propylene, and a small amount of a diene are termed EPDM elastomers; dicyclopentadiene was one of the first diene examined for this application and is still used in commercial products[5]. Dicyclopentadiene in the presence of a metathesis catalyst forms a thermoset polymer of high modulus and impact strength for injection molding according to several patents to Hercules Inc.[6][7].

The high energy properties of PCPD have been realized for many years. The study on preparation and characterization of PCPD oligomers as solid ramjet fuel was first reported in the 1980's [8] in which, thermal polymerization of cyclopentadiene to tetracyclopentadiene and high molecular weight oligomers was investigated, and the heat of combustion was given for the mixture of PCPD as ramjet fuel.

Nevertheless, through literature search, the author has not found any report that PCPD has been used as propellant binder. Therefore, the purpose of this project is to synthesize the polymer and subsequently use it as a binder for formulating high energy solid propellant.

EXPERIMENTAL**1. Synthesis of HTPB**Chemicals

Naphthalene (fw 128.18) Purified, Mallincrodt

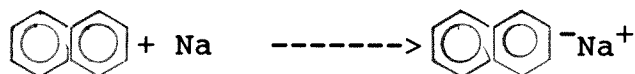
Tetrahydrofuran (fw 72.12) Baker Analyzed Reagent, J.T.Baker

Lithium (fw 6.94) 99.9 % , Aldrich

Sodium (fw 22.99) Technical grade

Lithium Aluminum Hydride (fw 37.95) 94 % , Pfaltz & Bauer

1,3 Butadiene (fw 54.09) 99 % , Matheson

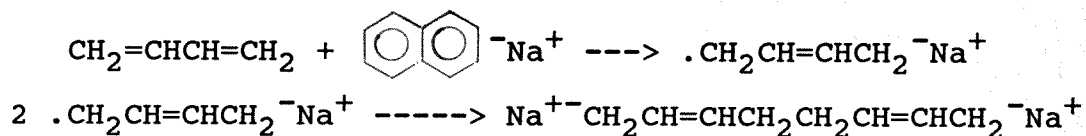
Procedure1.) Synthesis of lithium and sodium naphthalene initiators

A three-necked reaction flask of suitable size was equipped with a gas inlet, a magnetic stirrer, a stopper, an oil bubbler and a drying tube to allow the inert gas to escape. The flask was flamed under nitrogen before 50 ml of tetrahydrofuran, (purified by distillation from lithium

aluminum hydride) and 15 g lithium (in small pieces) were added. The reaction occurred almost immediately as evidenced by the formation of the dark greenish-black color of lithium naphthalene (if the lithium is not oxidized by air). The reaction was exothermic and proceeded very rapidly. Soon, the reactor became hot, an external cooling was necessary. After 2 hours of stirring, the reaction was considered complete, a 3 ml aliquot was withdrawn and whole reaction mixture was quenched in methanol. The titer was then determined with standard hydrochloric acid. Normally, the solution should contain approximately 1.6 millimole OH / ml.

Sodium naphthalene was prepared in similar manner except different concentrations were used (sodium 1.3 - 2.3 g , naphthalene 3.2 - 6.4 g and THF 65 - 110 ml).

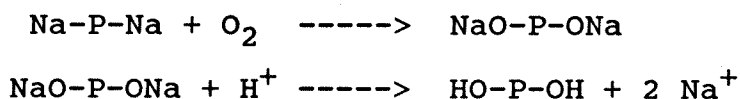
2.) Polymerization of 1,3 butadiene



A four-necked flask was equipped with a gas inlet, a magnetic stirrer, a septum stopper, a gas outlet / inlet, and a thermometer. The flask was flamed under nitrogen, before the purified dry solvent THF or cyclohexane (purified by

distillation over the lithium aluminum hydride) was charged. The reactor was then cooled in a salt-ice bath down to -10°C . After passing a predried nitrogen gas through solvent for half minute to expel the air, the gaseous monomer butadiene was introduced into the chilled solvent by a capillary tube. Initiator was added through the septum by syringe. The reaction was effected in a nitrogen atmosphere for 1 - 2 hours. The polymerization temperature varied from -10 to 20°C .

3.) Conversion of polybutadiene to hydroxyl terminated polybutadiene



The unquenched polymer solution was then treated with oxygen by passing it through the solution at room temperature and acidified with HCl. The organic layer was washed with water and the polymer was precipitated in isopropanol. The precipitate was filtered and dried at 50°C over night in vacuum oven.

2. Synthesis of PCPD

Chemical

Dicyclopentadiene (fw 132) Technical, Pfaltz & Bauer

Procedures

1.) Purification of monomer

A fractional distillation flask was equipped with a thermometer, a condenser, a receiver, and a heating mantle. The raw monomer, which exists mainly as dicyclopentadiene, was charged into the flask. Two boiling chips were added to the flask to bring about a smooth boiling of the monomer. The flask was gently heated up to the boiling point, 40°C , the fraction between 40 to 130°C was collected, which was then subjected to a second fractional distillation and the fraction between 40 to 60°C was finally collected and stored in the refrigerator. Freshly distilled fraction was preferred to be used in polymerization.

2.) Polymerization of cyclopentadiene

A three-necked flask of suitable size was equipped with a refluxing condenser, a stirrer, a thermometer, an inlet and

outlet of nitrogen. The freshly distilled monomer was charged to the flask under nitrogen, and was gently heated up to refluxing between 150 to 170 °C for 4 to 8 hours. Low molecular weight molecules could be separated by further distillation after polymerization.

3. Formulation and Curing of Propellant

Chemicals

PCPD (\bar{M}_n range 100 - 3000) , made in this project
Maleic anhydride (fw 98.06) , Pfaltz & Bauer
Antifoam CO-52, Hodag
Lecithin, Pfaltz & Bauer
N,N dimethyl aniline, (fw 137.18) Technical , Du pont
N,N dipropylamino methylamine (fw 145.25) , Aldrich
Pyridine (fw 79.10) Spectranalyzed, Fisher
Phenol (fw 94.11), aldrich
Polyethylene glycol (fw 300 - 400) , Aldrich
Ethylene glycol (fw 62.07) Aldrich
Glycerol (fw 92.10) Aldrich
2,4 Hexanediol (fw 118.17) Aldrich
1,4 Butanediol anhydrous (fw 90.12) GAF Corp.
Phathelic anhydride (fw 148.12) Reagent, Fisher

Pentaerythritol (fw 136) , Aldrich
 Epoxy resin DER 324, Dow
 DEH 24 Dow
 Potassium chloride (fw 74.56) Matheson Coleman
 Ammonium perchlorate (fw 117.49) Pfaltz & Bauer
 Al powder (fw 27) J.T. Baker
 Antioxidizer 754 Ethyl Corp.
 Dioctyl apitate Pfaltz & Bauer
 Triethylamine (fw 101) 99 % , Aldrich

Procedure

1.) Premix

PCPD (M_n range 100 - 3000)	70 - 80 %
Maleic anhydride	10 - 16 %
Epoxy resin DER 324	0 - 10 %
Catalyst (glycerol, DEH 24)	1 - 5 %
Plasticizer (dioctyl apitate)	5 - 10 %
Sulfactant (antifoam CO-52)	0.05 %

2.) Propellant

Premix	15 - 25 %
Oxidizer (NH_4ClO_3)	60 - 70 %
Al	15 %
Antioxidizer 754	0.05 %

3.) Processing

With stirring the premix was well mixed to a homogeneous liquid (apply heat if necessary). Al powder, oxidizer and antioxidant were then added to the premix and mixed thoroughly (the grounded oxidizer was added last). The thick viscous mass was discharged into a small glass bottle and compressed to exclude the air entrapped during mixing . Curing of propellant was effected in the oven with temperature range between 90 to 150 °C and a time period of 24 to 72 hours.

4. Characterization of Polymers

1.) Infrared spectra

a, HTPB

The solution of HTPB in benzene was smeared evenly on a salt plate. After the evaporation of the solvent, a thin film of HTPB was left on the salt plate which was mounted and examined on Perkin Elmer IR spectrometer PE - 730. The absorption at 1660 cm^{-1} was selected to verify C=C stretch of cis CH=CH, 967 cm^{-1} for CH out of plane vibration of trans CH=CH, 1640 cm^{-1} , 1418 cm^{-1} , and 909 cm^{-1} for existence of

CH=CH₂.

b, PCPD

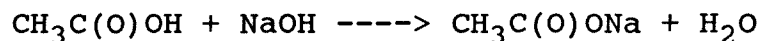
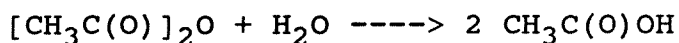
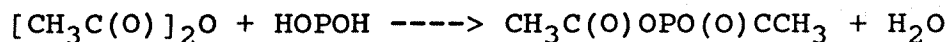
For liquid samples (monomer, prepolymer and PCPD of different molecular weights), the analysis was carried out with salt plate. For solid polymer samples (with or without crosslinking agent) KBr (1 %) pellets were made for the examination. The change of absorption ratio of olefinic CH to five carbon ring was observed during the course of polymerization. The bands selected for analysis were 1365 cm⁻¹ for olefinic CH bending vibration, 805 cm⁻¹ for cyclopentadiene ring bending, 1760 cm⁻¹ for ester, and 1150 cm⁻¹ for ether.

2.) \bar{M}_n and \bar{M}_v

Dilute solution viscosities were measured with Ubbelohde viscometer at 25.00 ± 0.05°C. Measurements were performed at 4 to 5 concentrations using toluene as solvent. The initial concentration of HTPB was less than 5 g/dl, and of PCPD 3 g/dl. The constants a and k for Mark - Houwink equation , $[\eta] = k m_v^a$, are 0.62 and 11.0*10⁻⁴ dl/g taken from literature [9]. For PCPD, both a and k were determined by the results of vapor pressure osmometry measurements as 0.86 and 0.539*10⁻⁴ dl/g.

The number average of molecular weight M_n of PCPD was determined with Wescan Vapor Pressure Osmometer at 50 °C in toluene. Measurements were performed at three to five concentrations (below 10 g/l) and M_n was calculated from the intercept of a plot of v (voltage difference between sample and reference electrodes) vs. concentration at zero concentration. The instrument calibration constant was determined with benzil.

3.) OH end group of HTPB



Hydroxyl equivalent weight of the whole polymer was determined as follows:

A 3-g sample was refluxed with 5 ml of freshly prepared 20 % acetic anhydride in pyridine for 1 hr on a steam bath. After cooling, 80 ml water and 20 ml benzene were added to the solution which was back titrated with 1.0 N standard NaOH to a phenolphthalein end point. A reagent blank was carried out through the entire procedure. The % OH was calculated as following:

$$\text{OH \%} = [(V_b - V_p) * N * 17 * 100] / (W * 1000) \quad \text{.....eq. 1}$$

where

V_b : blank consumption of alkali in ml

V_p : polymer consumption of alkali in ml

N : normality of alkali

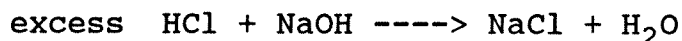
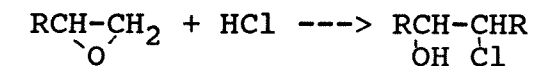
W : weight of HTPB polymer sample in gram

The equivalent weight E_w and the functionality F of HTPB were separately calculated from the equations:

$$E_w = (W * 1000) / [(V_b - V_p) * N] \quad \text{.....eq. 2}$$

$$F = M_n / E_w \quad \text{.....eq. 3}$$

4.) Epoxy functional groups of PCPD



Accurately weighed samples (0.2 - 0.5 g) of the PCPD were introduced into 250 ml Erlenmeyer flasks fitted with stoppers. Any particles of the sample on the walls of the

flasks were washed down with about 5 ml of anhydrous ether. Exactly 25.0 ml of standard 0.2 N hydrogen Chloride in anhydrous ethyl ether was pipetted to each of the flasks and two blanks containing no polymer. The flasks were stoppered, shaken, and allowed to stand at room temperature (20 - 25 °C) for 3 hours. To each flask were added 50 ml of ethanol and 1 ml phenolphthalein (1 % ethanol solution), The excess hydrogen chloride was back titrated with the standard 0.1 N sodium hydroxide solution to a faint pink end point.

$$\text{epoxide oxygen \%} = [(B-A)*N*0.016*100] / S \dots\dots\text{eq. 4}$$

where

B : ml of standard alkaline solution in the blank

A : ml of standard alkaline solution used in the back
titration

N : normality of alkaline solution

S : weight of sample in gram

The anhydrous hydrogen chloride ether solution (may be obtained from a cylinder) was generated by introducing concentrated hydrochloric acid into concentrated sulfuric acid by means of a dropping funnel fitted with a capillary tube leading to the sulfuric acid, The HCl gas was then passed through a bubbler of concentrated sulfuric acid (to remove the moisture) into the anhydrous ethyl ether.

% Sol , gel and swelling

% sol , gel swelling were determined simultaneously for cured PCPD by extracting and swelling the material in toluene, acetone, and dimethylformamide (solvent to sample ratio = 100 : 1). The total extraction time was between 60 and 90 hours. At the end of the period, the sample was taken out of the solvent, dipped rapidly into acetone, and blotted lightly on filter paper. The swollen polymer was weighed in a stoppered tared weighing bottle. % of swelling was calculated by the following equation:

$$\text{Swelling \%} = [(W_2 - W_1) * 100] / W_1 \dots\dots\dots\text{eq.5}$$

where

W_1 : weight of dry sample before swelling

W_2 : weight of swollen sample

% of sol content was determined by the ratio of the weight difference between the extractable sample to the initial weight of the sample. To determine the weight of extracted solid, the extraction solution was filtered through a filter paper. Half of the filtered extraction solution was let to evaporate to dryness. The solid weight on the filter paper was determined. The % sol and gel were calculated by the

following equations:

$$\text{Sol \%} = [200 (W_2 - W_1)] / W_2 \dots\dots\dots\text{eq. 6}$$

$$\text{Gel \%} = 1 - \% \text{ sol} \dots\dots\dots\text{eq. 7}$$

where

W_1 : weight of solids after evaporation of solvent

W_2 : weight of initial sample

Bulk Viscosity of Liquid Prepolymer

The viscosity of liquid PCPD was determined by the Brookfield Viscometer Model LV at 60 rpm, with # 1 spindle at 25 °C, 300 g of polymer was needed for the measurement. (for details see instrument manual).

Densities of Cured / Uncured polymer and propellant

A 10 ml pycnometer was employed to determine densities of liquid and solid samples at. The volume of the pycnometer was calibrated with distilled water at 25 °C (0.9970 g/cm³). The volume of the sample was the volume of the distilled water displaced by the sample in the pycnometer.

HPLC

HPLC data were obtained at ambient temperature with chloroform as eluent at a flow rate of 0.5 ml/min. The instrument, Altex, consists of a UV detector and Spectra-physics spheri-5 silica column (250 * 4.6 mm).

GC

The purity of the monomer, CPD, was analyzed with GC under the following conditions:

instrument: Varian 3300
Carrier gas: N₂
Column: chrom W - HP Capillary
Detector: FID
Injector temp.: 220 °C
Column temp.: 200 °C
Detector temp.: 250 °C
Injection vol.: 5 ul
Attenuation: 7

5. Bomb Calorimetry--Heat of Combustion for Polymer and Propellant

Heats of combustion for polymer sample of and propellant were determined by the Oxygen Bomb Calorimeter, Parr 1341. Conditions for the measurements were as follows:

Sample size : about 1 g (accurately weighed). Liquid samples were weight directly into the combustion capsule and solid samples were pressed into pellets with Pellet Press 2811.

Oxygen pressure : 30 atm.

Ni - Cr fuse : 10 cm

Absorbent : 1.0 ml distilled water

Bucket water : 2000 ± 0.5 g

The temperature was read and recorded at one-minute intervals for 5 minutes. At the start of the 6th minute the ignition button was pressed and held down for 5 seconds. For measuring the time to reach 60 per cent of total rise, the temperature was recorded to the nearest 0.02 °C at 45, 60, 75, 90 and 105 seconds interval. Among these readings interpolation method was applied to identify the 60 % total temperature rise point. During the rapid temperature rising period, the reading of was taken to one-tenth of the smallest scale division at one-minute intervals until the

difference between successive readings was constant for five minutes. (see instrument manual for details)

After the last temperature reading, the bomb was lifted out of the bucket, wiped dry, and the knurled knob opened to release the pressure, The cap was unscrewed, the interior surface of the bomb was washed and all unburned pieces of fuse wire removed. The washings were titrated with standard sodium carbonate (0.0725 N) solution, using methyl red indicator, to determine the nitric acid formed.

To calculate the heat of combustion H_C and the corrected temperature rise T the following equations were used:

$$T = t_c - t_a - r_1 (b - a) - (c - b) \dots\dots\dots\text{eq. 8}$$

$$H_C = (T * W - e_1 - e_3) \dots\dots\dots\text{eq. 9}$$

where

a = time of firing

b = time (to nearest 0.1 min.) when the temperature reaches 60 % of the total rise

c = time at beginning of period (after the temperature rise) in which the rate of temperature change has become constant

t_a = temperature at time a

t_c = temperature at time c

r_1 = rate at which the temperature was changing during the 5 min period before firing

r_2 = rate at which the temperature was rising or falling during the 5 min period after time c

W = energy equivalent of the calorimeter, determined under standardization

m = mass of sample in gram

T = temperature rise corrected

For thermochemical corrections,

e_1 = correction in calories for heat of formation of nitric acid equal c_1 if 0.0725 N alkali was used for titration

e_3 = correction in calories for heat of combustion of fuse wire equal $2.3 * c_3$

c_1 = ml of standard alkali solution used in nitric acid titration

C_3 = cm of fuse wire consumed in combustion

The heat capacity of the calorimeter was determined with the standard benzoic acid and calculated via the following equation:

$$W = (H' * m' + e_1 + e_3) / T \dots\dots\dots\text{eq. 10}$$

where

W = energy equivalent of the calorimeter in cal/°C

H' = Heat of combustion of the standard benzoic acid,
= 6318 Cal / g

m' = mass of the standard benzoic acid in grams

T = net corrected temperature rise in °C

RESULTS AND DISCUSSIONS

1. Polymerization of Hydroxyl Terminated Polybutadiene

Conditions and results of preparing naphthalene-alkali metal initiator, and polybutadiene with alkali metal ions at chain ends, are separately listed in Table 2 and 3:

Table 2. Preparation of Naphthalene-Na/-Li initiators

run #	naphthalene (g)	alkali metal	metal (g)	solvent (ml)	temp °C	time (hrs)	remarks*
1	6.51	Li	1.38	THF 133	23	1.5	n. r.
2	6.41	Li	1.38	THF 130	24	1.5	n. r.
3	6.4	Na	1.3	THF 110	24	1.5	deep gr
4	3.2	Na	1.15	THF 65	25	2.5	deep gr
5	3.2	Na	1.15	THF 65	18	2	deep gr
6	6.4	Na	2.3	THF 65	25	1.5	deep gr

Remarks:*

n.r. : No reaction occurred because metal Li was oxidized readily by air before reaction.

deep gr : Deep green color was produced by reaction.

Table 3. Preparation of Polybutadiene with alkali metal ions at chain ends

run #	butadiene (g)	solvent THF (g)	initiator # (in T.2)	amount (ml)	time (hrs)	yield (%)	M_v
7	30	220	4	19.5	4	none	
8	40	220	3	17	6	little	
9	44	220	5	39	9	24	2067
10	22	220	6	19	6	65	2100

Note:

1. All reactions proceeded at temperatures between - 5 to 5 °C. For runs 9 and 10, half the initiator was added at the start of the reaction; the other half was added dropwise during the first two hours of reaction.

2. Polymers obtained in runs 9 and 10 were used to produce hydroxyl terminated polybutadiene by treating the polymer with oxygen at room temperature for 15 min and acidified with HCl. The final organic layer was washed with water.

Data in Table 2 and 3 indicate that initiators were made successfully only with naphthalene sodium. The concentrations of initiator were rather low between 0.38 to 0.76 mole.

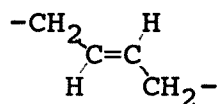
As a result, the polymer yield was affected as listed in Table 3, the highest yield is only 65 %. The low yield could

also be the cause of insufficient exclusion of water and air.

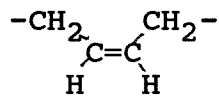
2. Characterization of HTPB

Microstructures of Polybutadiene

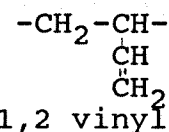
The addition polymerization of butadiene may give rise to the following configurations depending on the catalysts:



trans 1,4



cis 1,4



1,2 vinyl

The physical properties of polybutadiene depend, therefore, to a large extent on the molecular structures of the polymer. There are many methods which can be used to determine molecular structure of polybutadiene. Among them the most popular ones are infrared spectroscopy [10], two dimensional TLC [11], GPC [12], refractive index [13], NMR [14]. The infrared spectroscopy was used in the present work.

Fig. 1 shows the IR spectra of three polybutadiene samples predominated with trans-1,4, cis-1,4 and 1,2 addition configurations. Examination of these spectra one finds

that trans 1,4 has a strong absorption band at 970 cm^{-1} , 1,2 addition at 909 cm^{-1} , and cis 1,4, virtually all the region of 625 to 830 cm^{-1} . The absorption of cis 1,4 in the 625 to 830 cm^{-1} region has been studied in a large number of polymers with different unsaturation distribution. Results show that as the amount of cis 1,4 decreases, the band maximum shifts gradually to about 725 cm^{-1} , and which disappears rapidly, as the relative intensity of the 690 cm^{-1} band compared to 740 cm^{-1} increases [15]. In another literature [16], 1660 cm^{-1} was preferred to verify cis 1,4 addition. At present there is a disagreement outstanding about the proper method to identify cis 1,4 structure because the absorption band from 625 to 830 cm^{-1} is too broad.

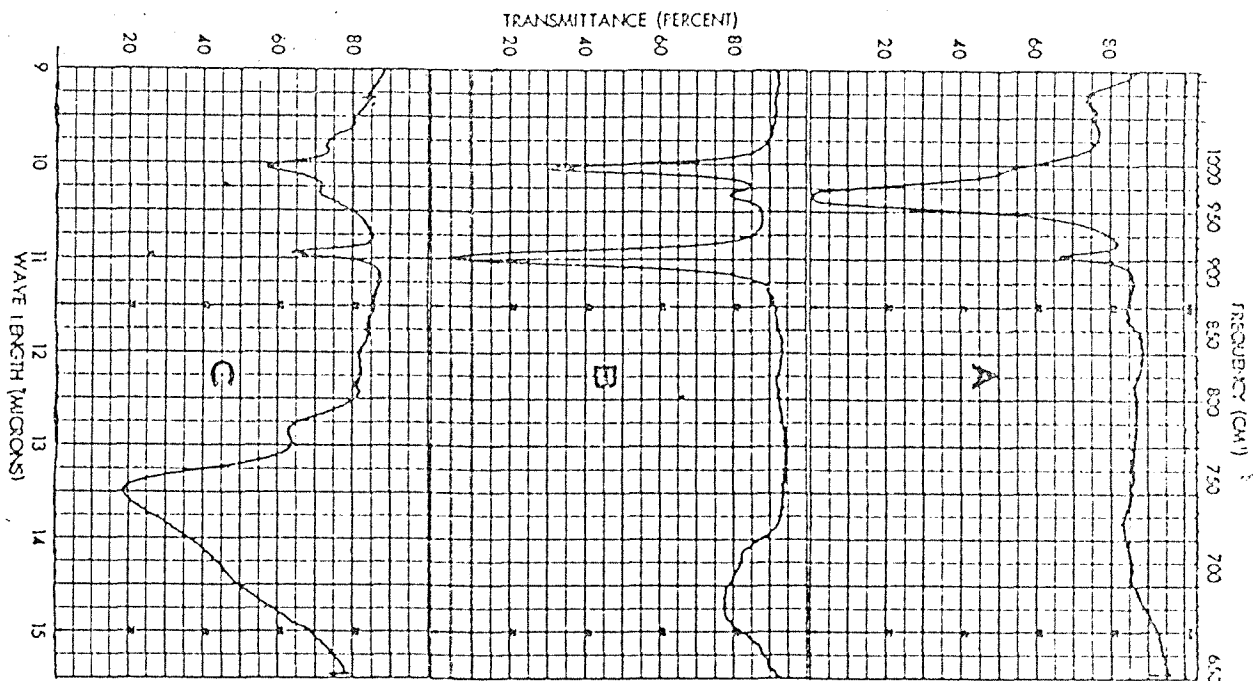


Fig. 1. IR spectra of polybutadienes showing strong absorption of trans 1,4 (A), 1,2 addition (B), and cis 1,4 (C) from literature [15]

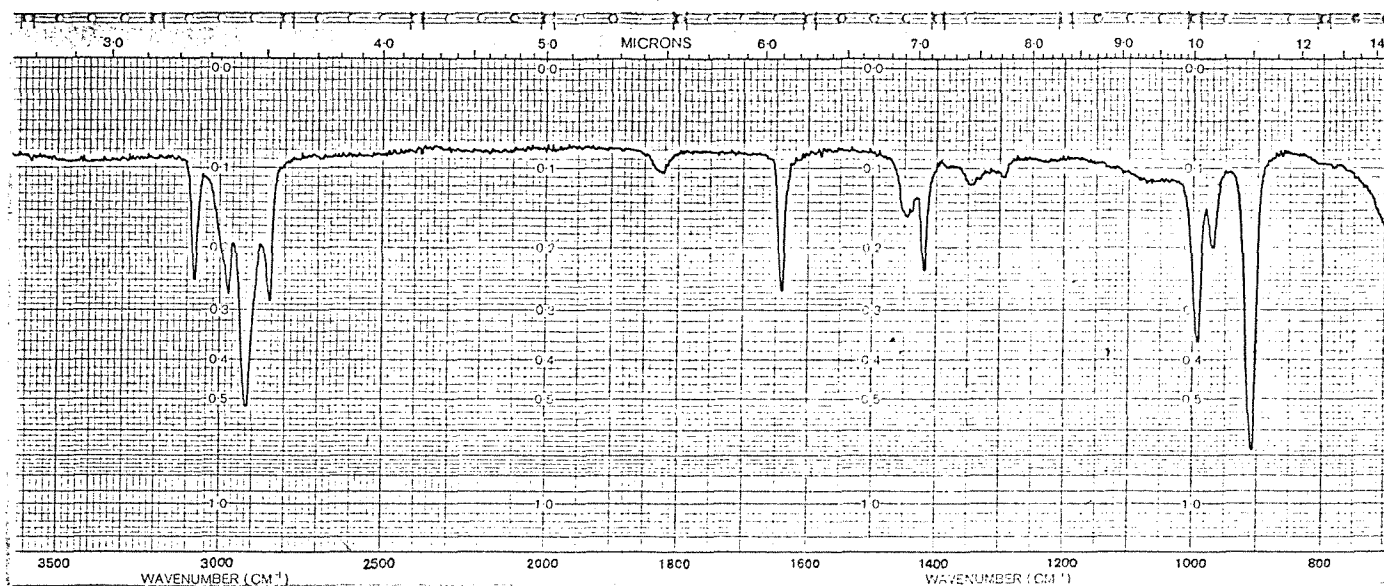


Fig 2. IR spectra of polybutadiene made in this project (film cast on salt plate from the polymer-benzene solution)

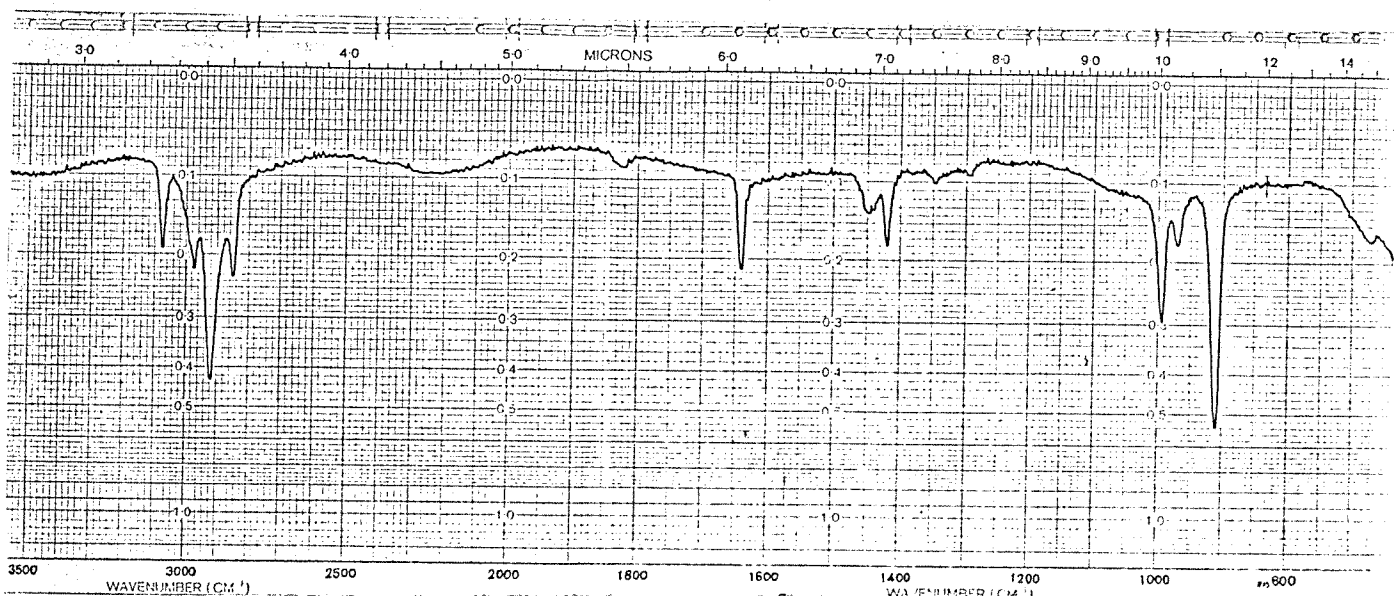


Fig 3. IR spectra of polybutadiene made in this project
(film cast on salt plate from polymer- CS_2 solution)

Comparing Fig.1 with Fig.2 and 3, it is obvious that the polybutadiene made in this project is primarily 1,2 addition plus a small amount of trans 1,4. Since there is no appreciable amount of 1,4 cis absorption, therefore, it is possible to estimate the relative amount of 1,2 and trans 1,4 in the polymer structure. The absorbances of 1,2 structure at 909 cm^{-1} and trans 1,4 at 970 cm^{-1} are separately 0.64 and 0.09. Therefore, the relative amount of 1,2 addition to trans 1,4 is about 7 : 1 or 87 to 13 %. The absorption data are summarized in Table 4.

Table 4. Summary of Microstructure of Polybutadiene Determined by IR Absorption Spectra

	1.2 addition	trans 1.4	cis 1.4
wavenumber cm^{-1}	909	970	1660
absorbance	0.64	0.09	0
%	87	13	0

Data from the measurements of diluted solution viscosity of HTPB are tabulated in Table 5. A plot of η_{sp} and $\ln \eta_r$ vs. concentration is shown in Fig 4.

Table 5. Dilute Solution viscosity of HTPB

t_0	t	$t/t_0(\eta_r)$	η_{sp}	C g/dl	η_{sp}/C	$\ln \eta_r/C$
81.44	133.54	1.6395	0.6395	3.9868	0.1604	0.1240
	116.23	1.4272	0.4272	2.8477	0.1500	0.1249
	107.49	1.3199	0.3199	2.2149	0.1444	0.1253
	102.33	1.2565	0.2565	1.8122	0.1415	0.1260
	98.88	1.2141	0.2141	1.5334	0.1396	0.1265

Note: solvent - toluene, temperature - $25.00 \pm 0.05^\circ\text{C}$

All data were averaged over triplicates.

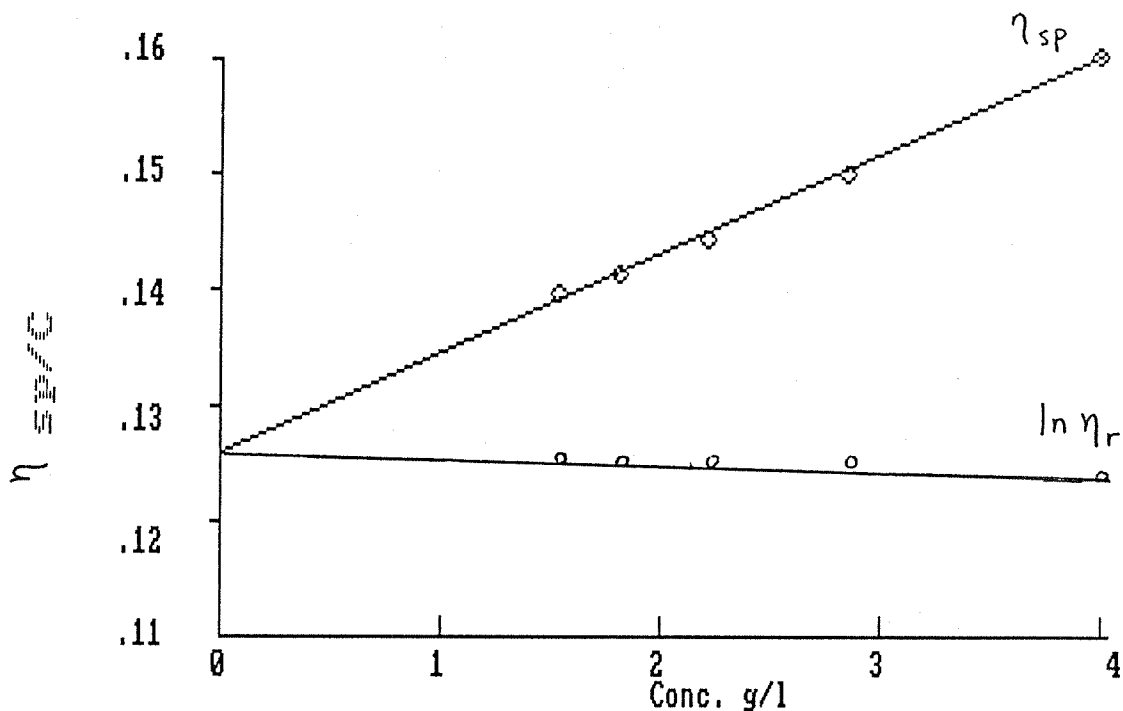


Fig 4. Plot of η_{sp} and $\ln \eta_r$ vs. Concentrations for HTPB - Toluene System

From the interception of the plot, the average molecular weight of the polymer \bar{M}_n was found to be 2100 via the Mark - Houwink equation:

$$[\eta] = k M^a$$

where the constant k and a are separately 11.0×10^{-4} dl/g and 0.62 taken from the literature [17].

The attempt for measuring of the functionality was made in an effort to determine the extent to which the polymer with OH group can be further reacted with crosslinking agent.

Table 6. Analysis of OH end group of HTPB

sample no.	weight (g)	0.1 N NaOH (ml)	OH %
9 - 1	1.6794	48.90	0.1012
9 - 2	2.5843	48.70	0.1973
average			0.1493
std. dev.			0.0680
blank		49.00	

The result (Table 6) shows negligible OH groups on # 9 HTPB. Because the standard deviation on duplicates is more than 1/3 of experimental values the result is unacceptable. In addition, the infrared spectra also show a negative result on the OH group absorption (Fig. 2 and 3).

3. Preparation of PCPD

Fig 5 shows the gas chromatograms of purified CPD (twice fractional distillations). The chromatogram of the raw monomer is shown in Fig 6. The first primary peak around retention time 0.54 min is obviously contributed by the cyclopentadiene. Peaks after 0.54 min observed in the raw material virtually disappear in the chromatogram of purified CPD except for a very small peak around 1.9 min. This could be the result from a trace of dicyclopentadiene caused by

high potential for Diels Alder reaction even at room temperature.

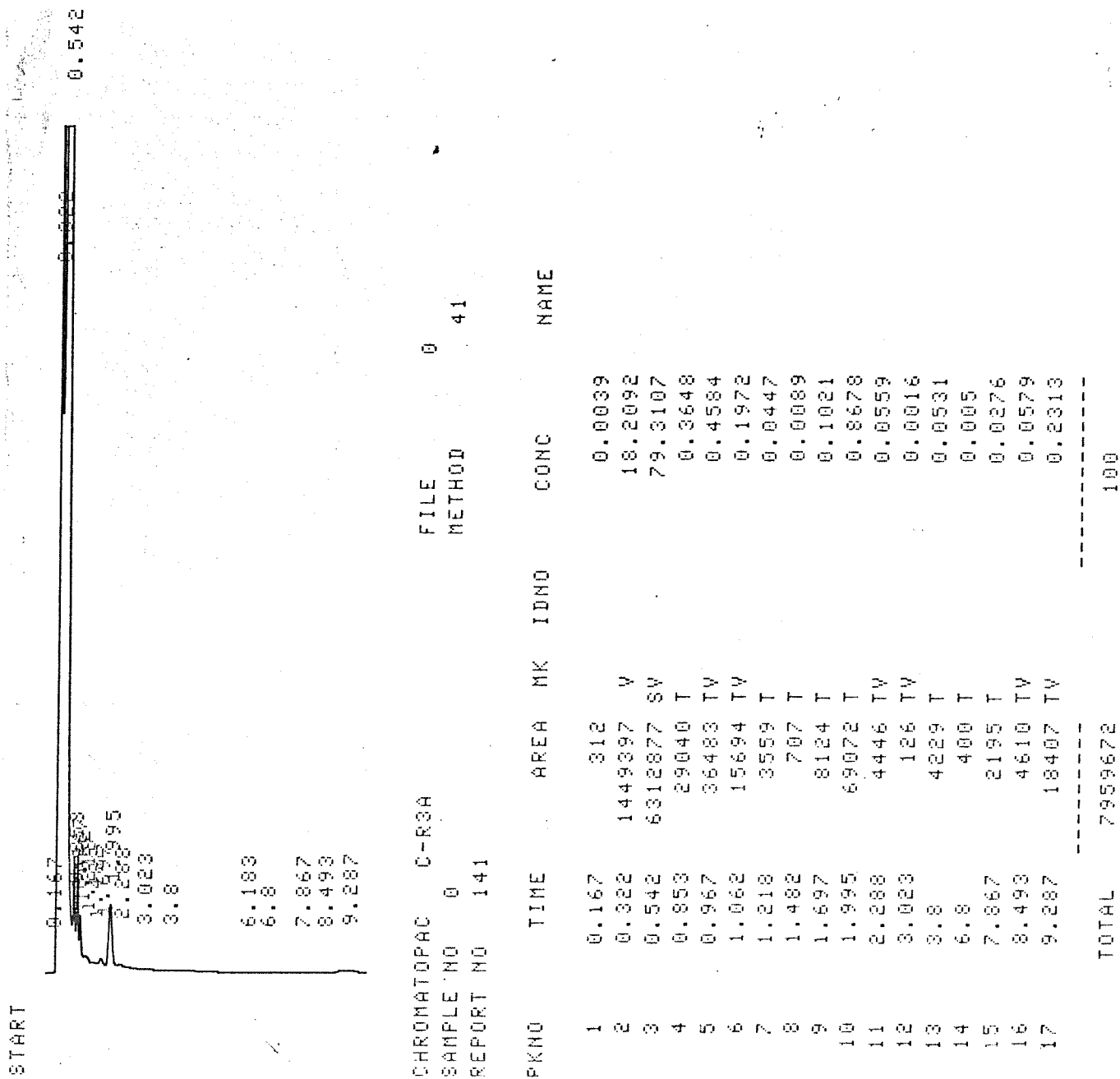
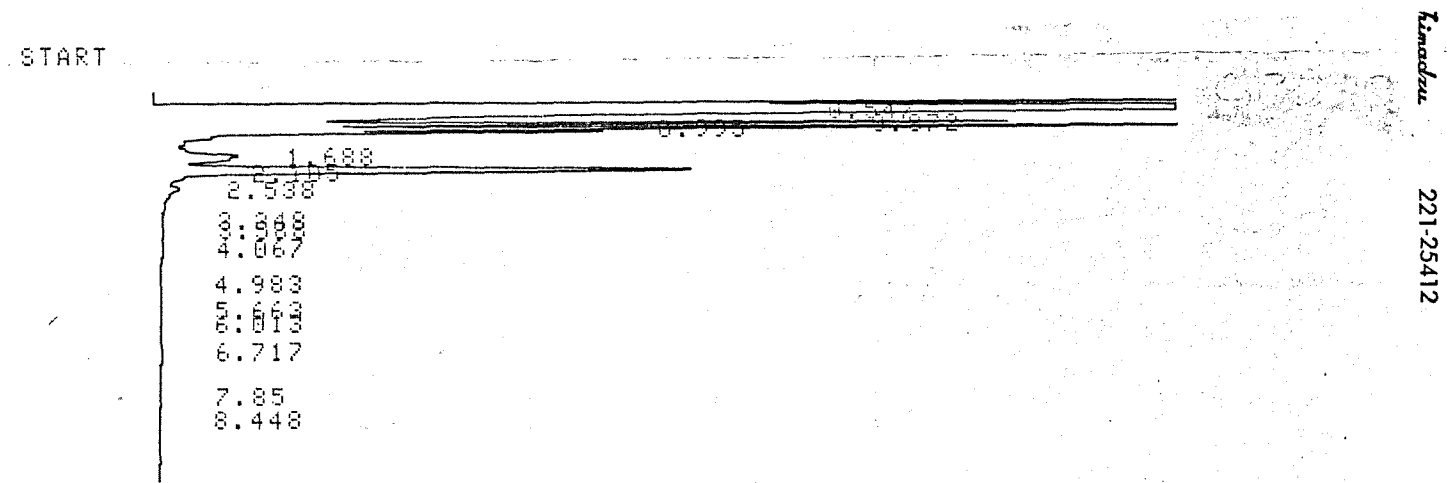


Fig 5. Gas Chromatograph of Purified CPD

Fig 6. Gas Chromatogram of Raw Monomer



CHROMATOPAC C-R3A
 SAMPLE NO 0
 REPORT NO 138

FILE 0
 METHOD 41

Kinadzu 221-25412 065

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.547	6852882			75.2137	
2	0.872	442011	V		4.8513	
3	0.995	778361	V		8.5429	
4	1.688	183987	V		2.0194	
5	2.105	625463	V		6.8648	
6	2.538	76469	V		0.8393	
7	3.348	9699	V		0.1065	
8	3.588	24874	V		0.273	
9	4.067	26870	V		0.2949	
10	4.983	16905	V		0.1855	
11	5.663	20298	V		0.2228	
12	6.013	15876	V		0.1742	
13	6.717	26314	V		0.2888	
14	7.85	6911	V		0.0758	
15	8.448	4303	V		0.0472	
TOTAL		9111217			100	

The reaction time and the refluxing temperature for polymerization of CPD are listed in Table 7 along with the molecular weight of the polymer. It can be seen that the number average molecular weight M_n of PCPD is proportional to the reaction time.

Table 7. Polymerization of CPD

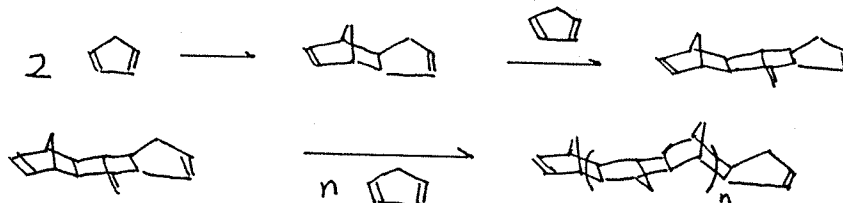
sample ID	time (hr)	temp. °C	M_n
2	2	65	
f-5-13	3	125	102
4	4	150	111
6	6	163	227
8	8	172	2236
p-6-4	8	172	2240
p-5-13	9	172	2920
p-2-9	13	172	*

* Sample p-2-9 has too high molecular weight to be dissolved in the chosen solvent toluene for VPO.

Mechanism of polymerization of CPD

Diels Alder polymerization mechanism of CPD has been proposed for a long time [18], but no detailed experimental evidence has been reported. Cyclopentadiene acts as both diene and dienophile, the mechanism can be illustrated as

follows:



Semiquantitative infrared spectroscopy with peak ratio measurement was employed in this project to support the mechanism. There were several studies on IR spectra of cyclopentadiene. The assignments of absorption bands were reported in Table 8 [19].

Table 8. IR spectrum assignment of molecular vibration

cm^{-1}	vibrational modes
1590	CH=CH stretching
1360	olefinic C-H bending
805	ring bending

Figs 7 to 11 are IR spectra of monomer and samples taken from reactor as reaction proceeded to 2, 4, 6 and 8 hrs. In Fig 7, monomer cyclopentadiene shows strong absorptions for CH=CH stretching (1590 cm^{-1}) and olefinic C-H bending (1360 cm^{-1}) and a moderate absorption for the ring bending (805 cm^{-1}). As reaction time increases the samples in Fig 8, 9, 10 and 11 show dramatically decrease of absorption intensity at

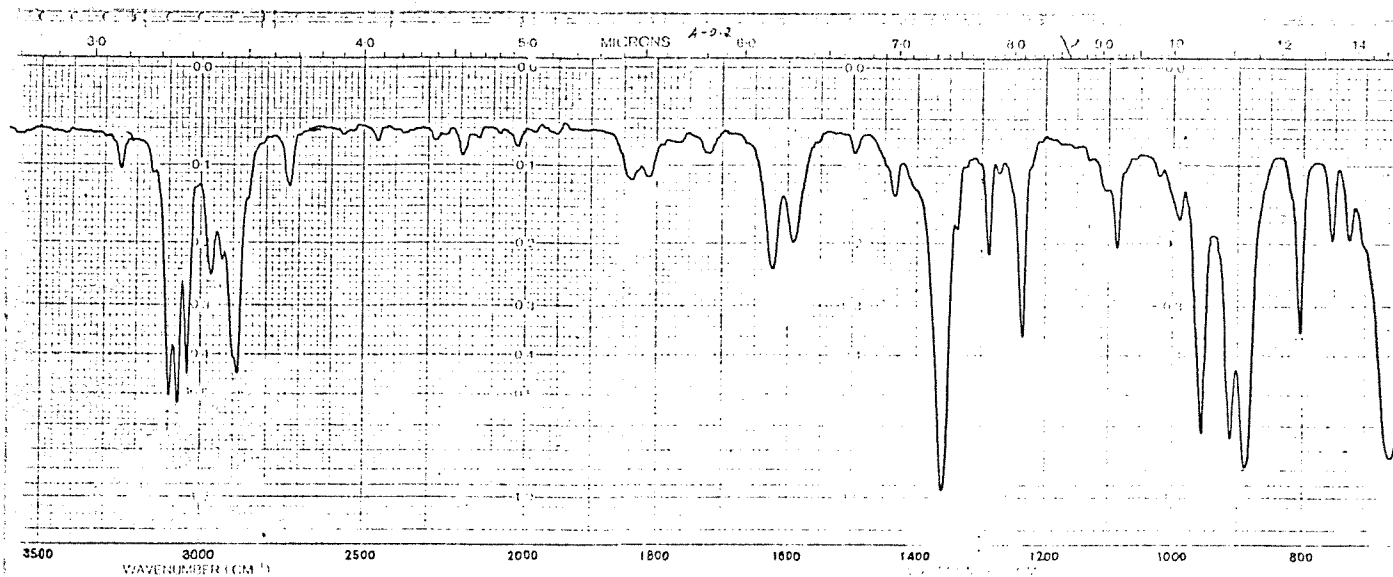


Fig 7. IR spectrum of monomer, CPD

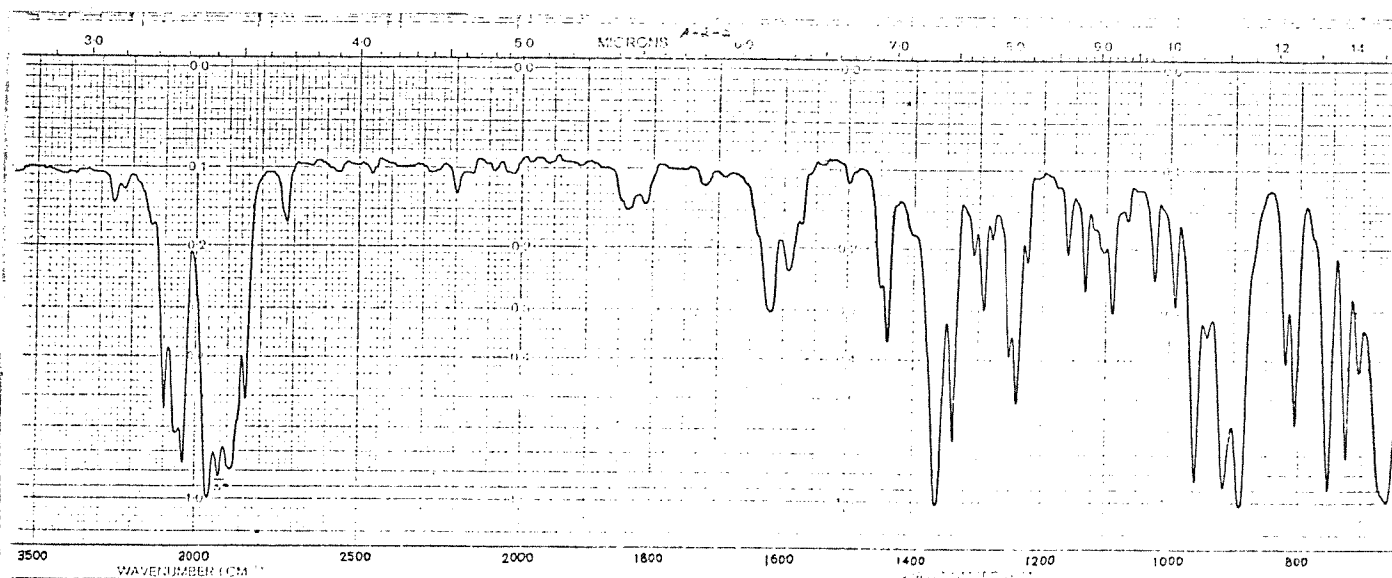


Fig 8. IR spectrum of PCPD # 2

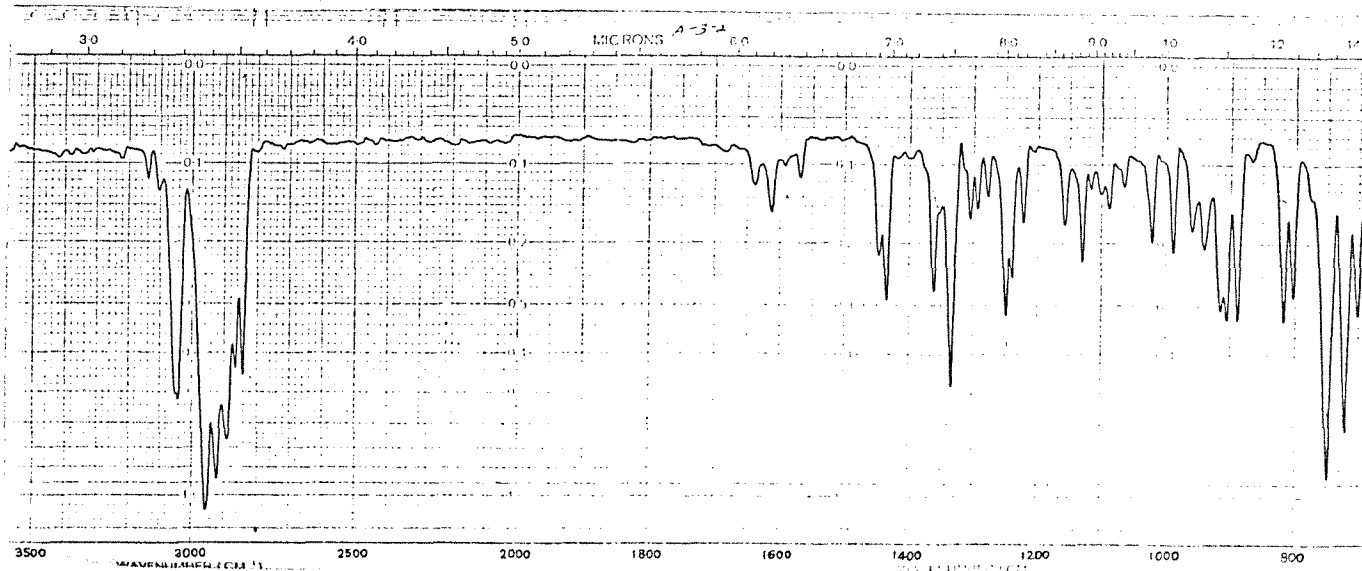


Fig 9. IR spectrum of PCPD # 4

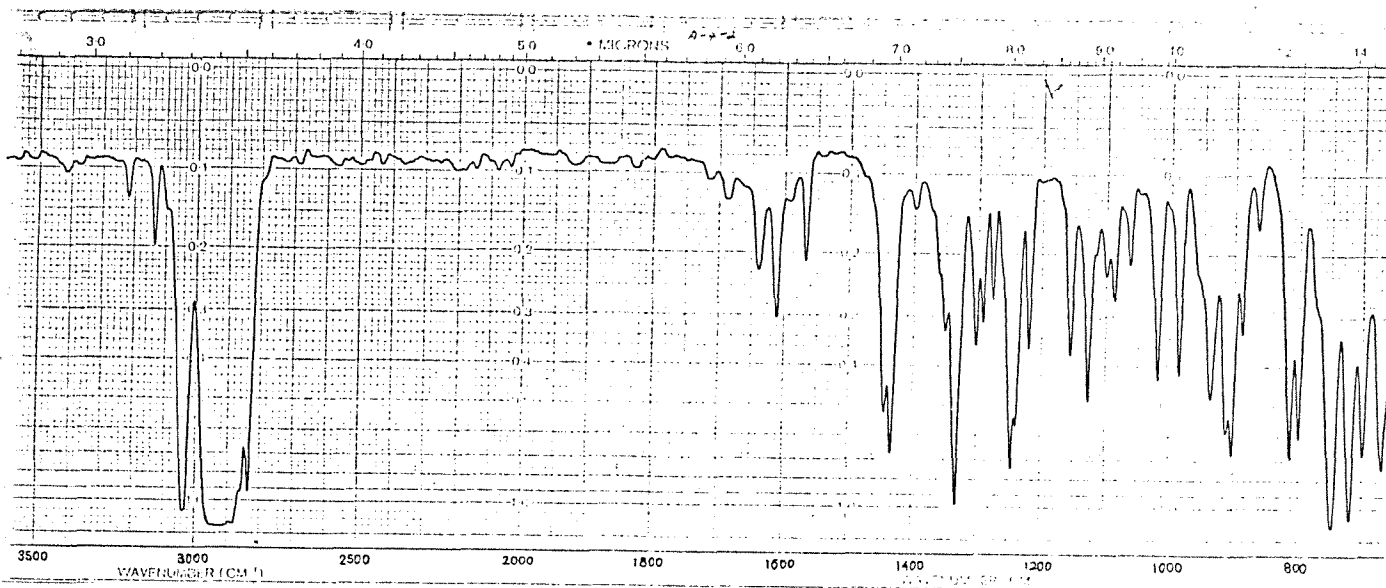


Fig 10. IR spectrum of PCPD # 6

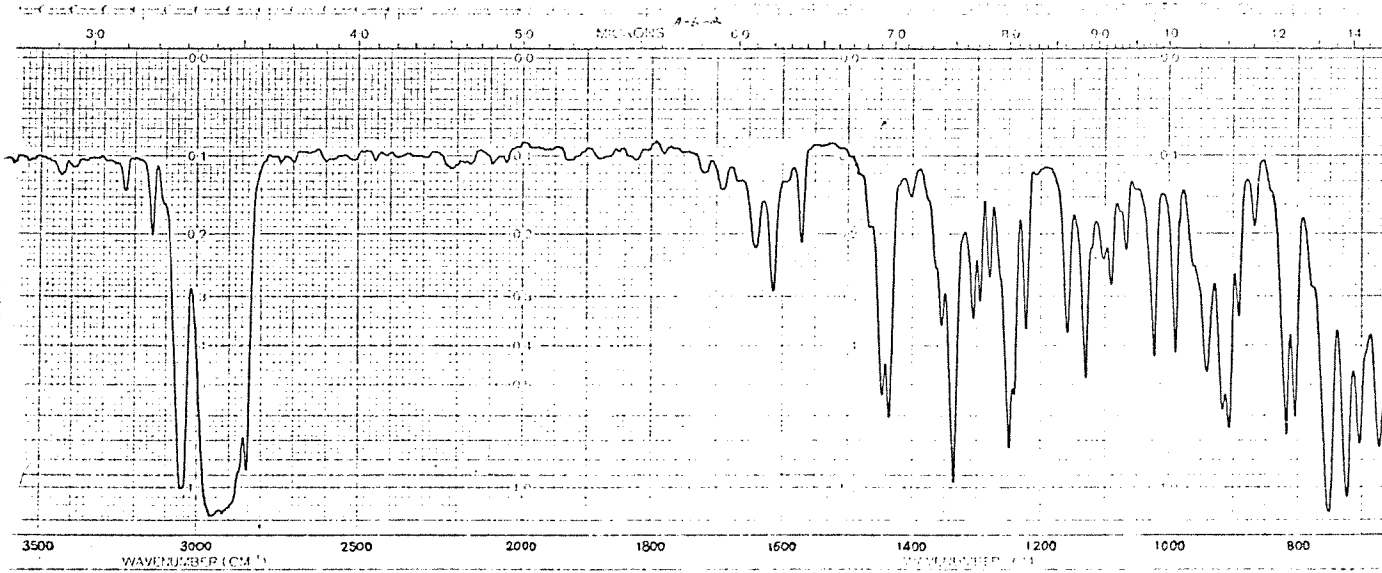


Fig 11. IR spectrum of PCPD # 8

1590 and 1360 cm^{-1} while the absorption of bending seems to remain constant. This may be contributed to the reaction mechanism. During the reaction, double bonds in cyclopentadiene are supposed to break down for each addition of another ring and as more rings add on, fewer double bonds will exist in the system. On the other hand, while ring addition is going on, the ring itself still remains intact, although the rigidity of the long chain molecule may show some restriction on the bending of the ring. In the measurement of the absorption peaks the base line method was employed. The peak heights and ratio are reported in Table 9.

Table 9. Peak height and relative ratios of PCPD at different extent of polymerization

Sample #	805 cm^{-1}	1360 cm^{-1}	1590 cm^{-1}	1360/805	1590/805
0 monomer	0.455	0.875	0.20	100	100
2 2 hrs	0.440	0.770	0.14	89	71
4 4 hrs	0.240	0.135	0.03	28	29
6 6 hrs	0.465	0.030	0.05	3	24
8 8 hrs	0.450	0.020	0.04	2	17

The change of molecular weight (Table 7) and the relative absorption intensity of olefinic C-H bending (1360 cm^{-1}) to ring bending (805 cm^{-1}) with reaction time is shown in Fig 12.

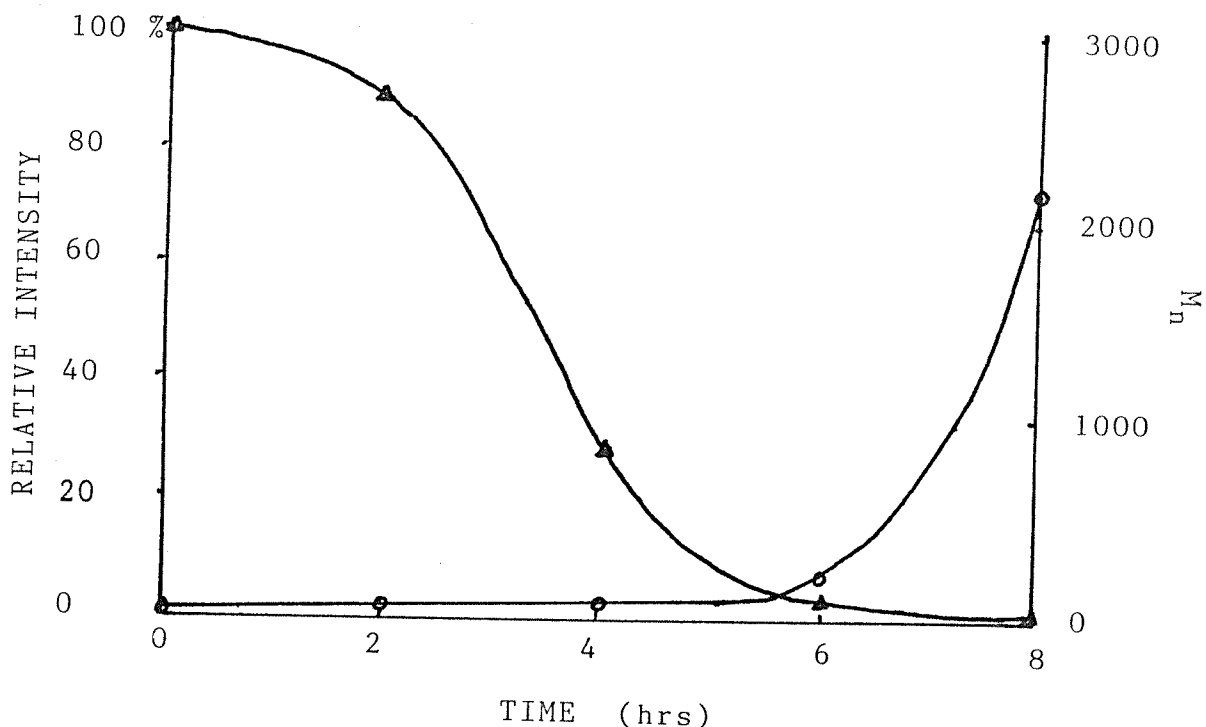


Fig 12. Change of \bar{M}_n / absorption intensity ratio with reaction time

From Fig 12 and data previously presented, some ideas about the reaction mechanism can be pictured. From the origin to 2 hrs the absorption due to double bonds is still strong and no significant polymerization has occurred. When reaction proceeded for 4 hrs, the system has consumed about 70 % of the double bonds but the average molecular weight was still very low, probably dimers. When the reaction ran for 6 hrs. the number of double bonds dropped almost to negligible level, and the molecules grew to 227 , averaging 3 - 4 rings oligomers. From 6 to 8 hrs, molecular weight increased almost 10 times, averaging a 30 - 40 ring polymer; double

bonds remain at a negligible level. Table 10 lists the increase in degree of polymerization and the decrease in double bonds.

Table 10. Degree of polymerization and number of double bonds

#	\bar{M}_n	n	1360/805	1590/805
0	66	1	100	100
2			89	71
4	111	1.7	28	29
6	227	3.4	3	24
8	2336	35	2	17

It is evidenced by the data in Table 10 that in Diels Alder polymerization of cyclopentadiene, low molecular weight species such as dimers and trimers are formed first before the higher molecular weight oligomers are formed. The sharp rise in molecular weight between the reaction time 6 - 8 hrs may have been a result of combination of higher molecular weight oligomers.

The results also show there is no significant increase in molecular weight until double bonds are almost consumed. The relative intensity may be calculated from the number of double bonds D and the degree of polymerization n in the macromolecule:

$$\text{relative intensity \%} = D / (n * 2) \dots\dots\dots\text{eq. 11}$$

Values calculated from the equation are listed in Table 11.

Table 11. Calculated relative intensity of double bond as a function of degree of polymerization, n

n	D	relative intensity %
1	2	100
2	2	50
3	2	33
4	2	25
5	2	20
10	2	10
20	2	5
35	2	2.8

At the beginning, each monomer has two double bonds which will react with other monomer molecules to form dimer. After the reaction, the number of double bonds decreases from 100 to 50 % which is a 50 % reduction in absorption intensity. With further addition of one more ring to the dimer, trimer forms and double bonds decrease from 50 to 33 % which is 34 % deduction. However, molecular weights do not increase accordingly with the big drop in number of double bonds or relative intensity. With more rings adding on the

double bond has decreased to the extent where no further significant change could be followed by the method employed, and the molecular weight starts to increase significantly.

It is surprising to notice how closely the molecular weight of sample # 8 corresponds to the result of the IR analysis, although other samples hardly coincide (see Table 12).

Table 12. Comparison of theoretical and experimental relative intensity for # 8 PCPD

	\bar{M}_n	n	relative intensity %
VPO	2336	35.4	2.82
IR			2.0
theoretical (from Table 11)			2.8

The important meaning of the result lies in the relationship between the more involved molecular weight determination method by VPO, and a simple method of IR in order to find out a quick and easy way for quality control.

The C=C stretching band at 1590 cm^{-1} has almost the same absorption intensities as that of 1360 cm^{-1} except for high molecular weight samples. The reason for that could be inherent different vibration modes between CH=CH stretching and C-H bending when molecules grow larger, or simply from

nonexact measurement of peak height because the band 1590 cm^{-1} was masked by neighboring peaks to such an extent that the base line method becomes unreliable.

To verify the result from IR analysis, spectra of monomer and polymer were measured on the UV spectrometer. 0.1 % THF solutions were used. It can be seen from Fig 13, that the monomer has stronger absorption in the UV region than that of the polymer. However, the reason for the polymer still showing an intensity absorption and a shift toward short wavelength is unclear.

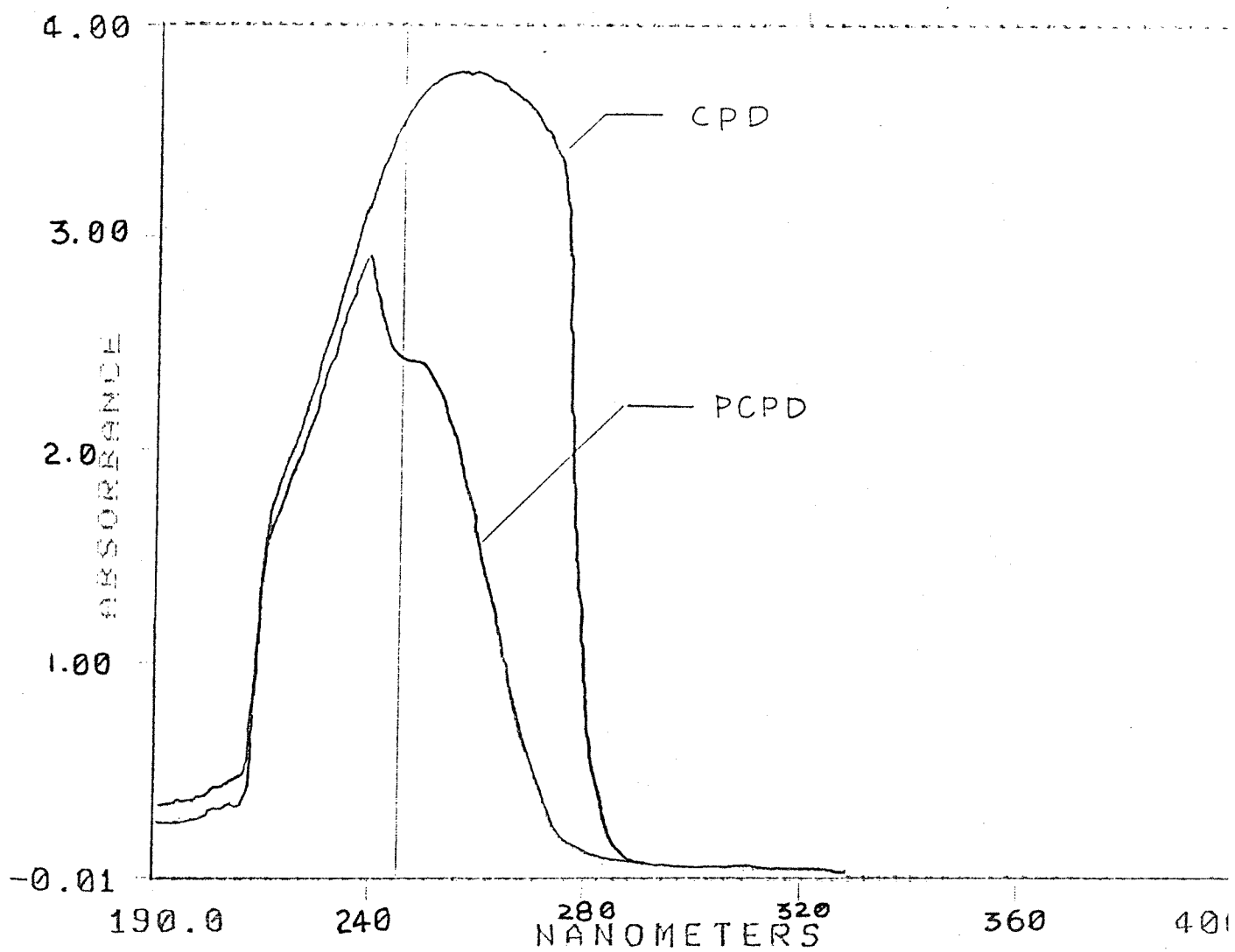


Fig 13. UV spectra of PCPD and CPD

4. Characterization of PCPD

1.) \bar{M}_n and \bar{M}_v of Polymer

Wescan vapor pressure osmometer can be applied to measure the vapor pressure lowering of a polymer dilute solution. The measured data of vapor pressure lowering (actually, measured voltage difference between the solvent and sample solution thermistors) can be applied to evaluate the number average molecular weight of the sample via a plot of the data against the concentration of the sample based on the following equation:

$$\Delta v / C = K / M_n + A_2 C K \dots\dots\dots \text{eq.12}$$

where Δv : signal response in volt or milivolt

C : concentration in g/l

K : solvent calibration constant (in this curve

K = 3360 determined with solvent toluene and standard benzil, fw 210.23)

A_2 : second viral constant

Example plots for the calibration and the polymer sample are separately shown in Fig 14 and 15. The molecular weights thus evaluated for polymers of different extents of reaction are listed in Table 13.

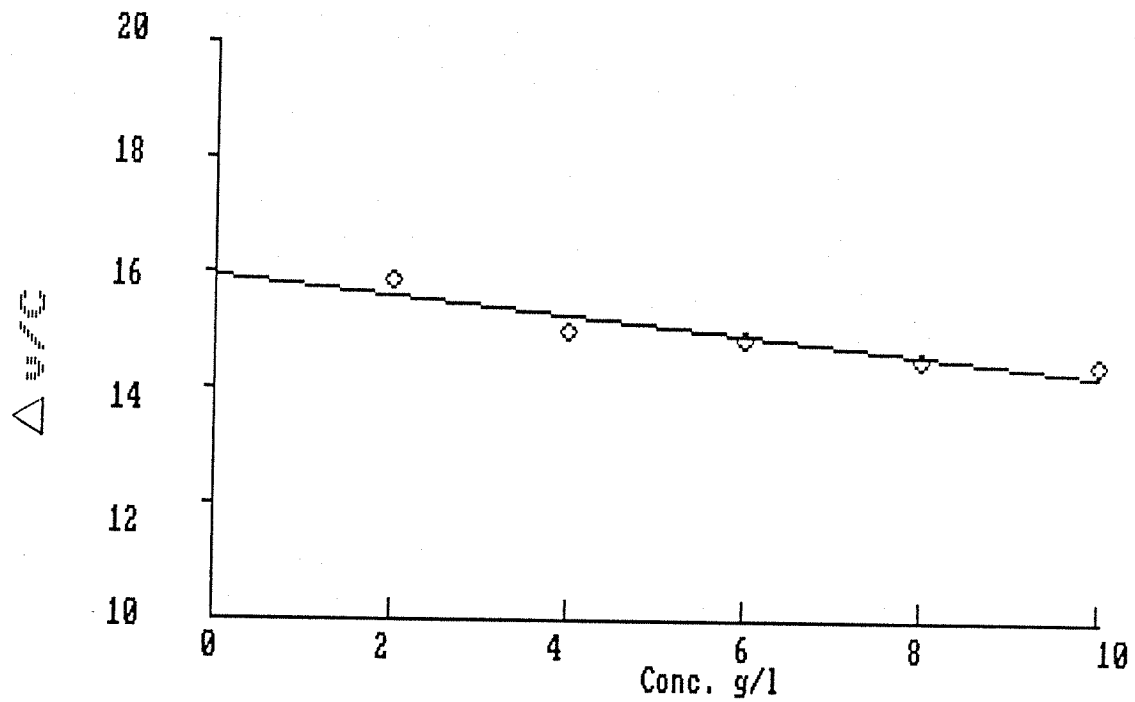


Fig. 14. Calibration of solvent by benzil standard

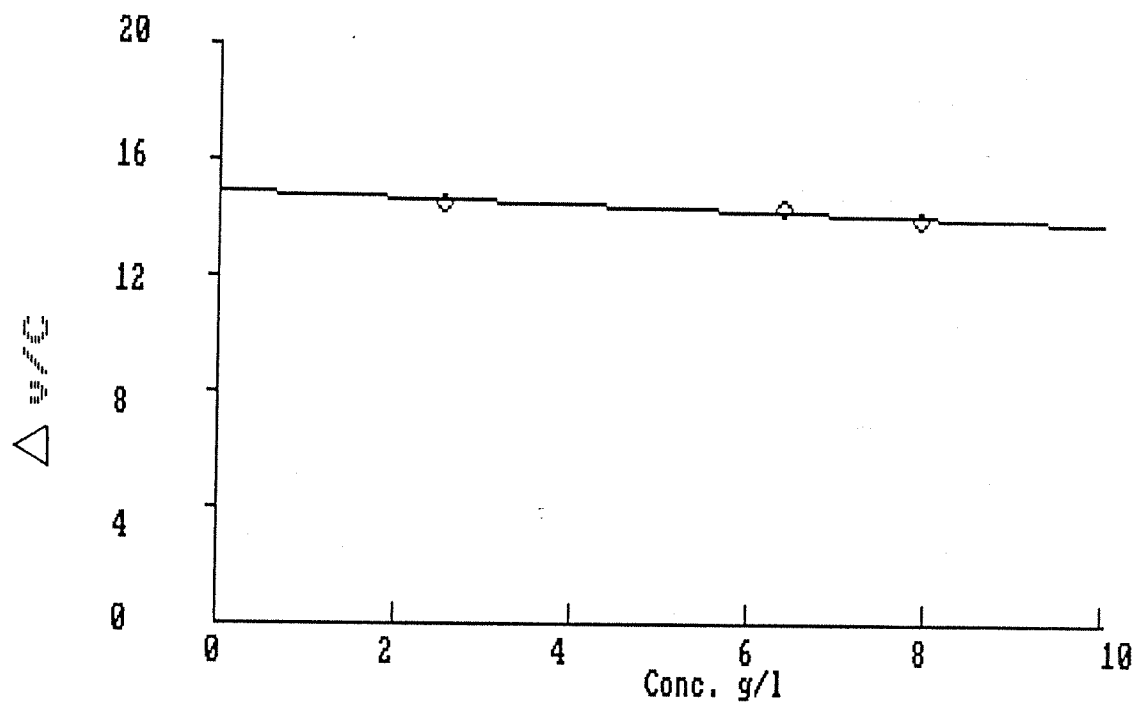


Fig 15. VPO measurement of PCPD sample # 6

Table 13 lists the results of molecular weights of PCPD.

Table 13. Number average molecular weight of PCPD

Sample NO	$[\Delta v / C]_{c=0}$	K	\bar{M}_n
F-5-13	33.0	3360	102
4	30.3	3360	111
6	14.8	3360	227
8	1.50	3360	2236
P-5-13	1.15	3360	2920

In order to calculate the viscosity average molecular weight, \bar{M}_v , we must know the values of constants K and a in Mark - Houwink equation. These are not available in literature for PCPD. The present work tried to determine k and a by correlating intrinsic viscosity of the sample to the number average molecular weights of the sample. Fig 16 illustrates a typical viscometric plot, and Table 14 gives a list of intrinsic viscosities for several PCPD samples.

Table 14. Intrinsic viscosities of PCPD

Sample No.	initial conc. g/dl	$[\eta]$
8	2.300	0.0404
6	1.5868	0.00819
4	1.9380	0.00243

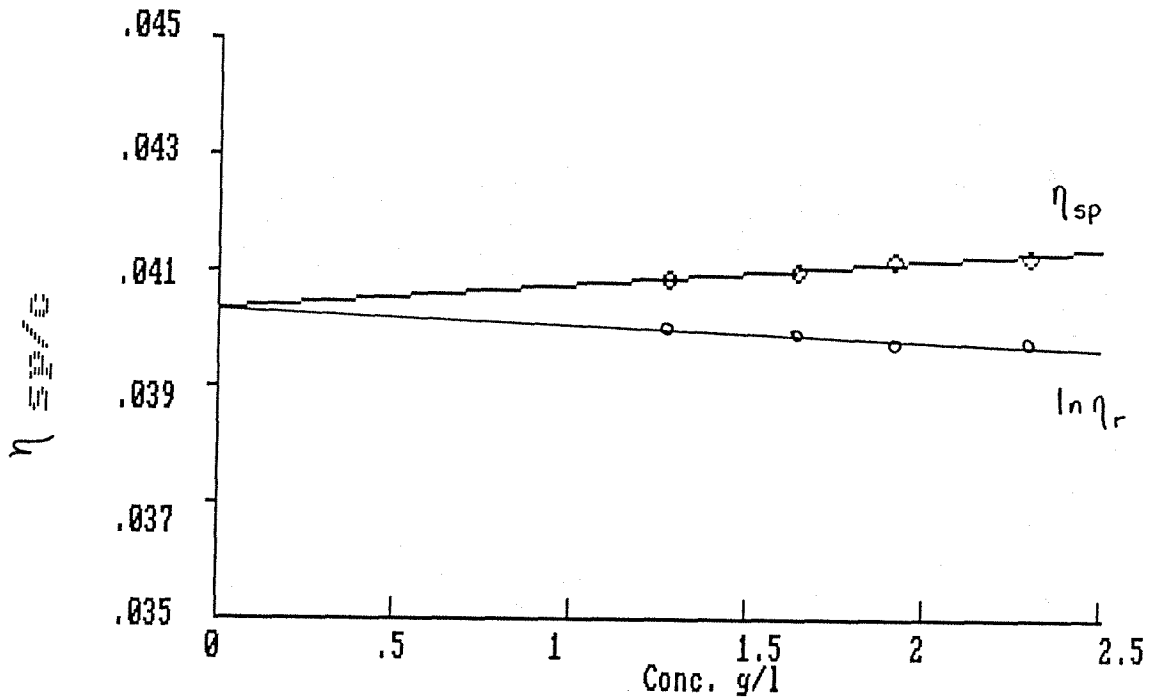


Fig 16. Typical viscometry plot of PCPD # 8

By using data from Table 13 and 14, k and a can be calculated from the following,

$$[\eta] = k \bar{M}_v^a$$

or

$$\ln [\eta] = \ln k + a \ln \bar{M}_v \dots\dots\dots \text{eq.13}$$

Data used for calculation are listed in Table 15. A plot of $\ln [\eta]$ vs $\ln \bar{M}_n$ is shown in Fig 17. From the plot the following information are thus obtained:

$$\begin{aligned} \text{Interception} &= -9.829 & k &= 5.39 \times 10^{-5} \text{ dl/g} \\ \text{slope} &= 0.86 & a &= 0.86 \end{aligned}$$

Table 15. Calculation of k and a

sample no	\bar{M}_n	$\ln \bar{M}_n$	$[\eta]$	$\ln [\eta]$
4	111	4.7095	0.00243	-6.0199
6	227	5.4250	0.00819	-4.8048
8	2336	7.7562	0.0404	-3.2089

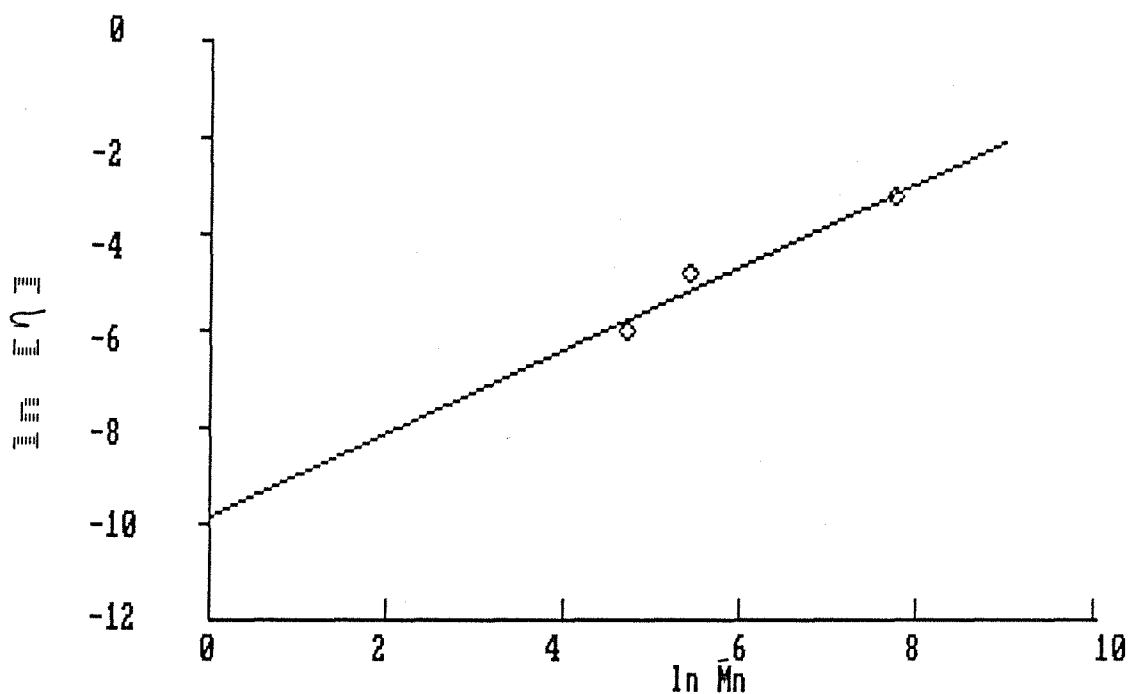


Fig. 17. Plot of $\ln \bar{M}_n$ vs $\ln [\eta]$

With the value of k and a known, The viscosity average molecular weights of the polymers, \bar{M}_v , are calculated from eq. 4 and tabulated in Table 16 and with \bar{M}_n .

Table 16. \bar{M}_n and \bar{M}_v of PCPD

sample No	\bar{M}_n	\bar{M}_v
4	111	84
6	227	344
8	2336	2202

It is well known that normally, \bar{M}_v is greater than \bar{M}_n of the polymer, but in this work because k and a which are averaged over only 3 sets of data can not perfectly fit back to individual points, sample # 4 and # 8 have lower values of \bar{M}_v .

2.) Analysis of epoxy end group

It will be shown later that PCPD made in this project is curable with maleic anhydride. The reason for this is that PCPD may have a small amount of epoxy group ends. Maleic anhydride is known for its reactivity to epoxy resin. The following wet analysis was carried out in order to verify this idea.

To examine the reliability of the analysis method epoxy resin DER 324 made by Dow Chemicals was first analyzed with sample P-5-13. Table 17 gives the analysis results.

Table 17. Analysis of epoxy groups

Sample	weight (g)	0.1000 N NaOH (ml)	epoxide oxygen %
DER 324*	0.5085	10.82	8.35
P-5-13	0.8179	36.78	0.11
blank	0	37.35	0

* DER 324 was first titrated with 0.4 ml of 0.1000 N NaOH to neutralization before adding 25.00 ml of 0.15 N hydrogen chloride in ether.

The percentage of epoxide oxygen of the sample is calculated as follows:

a, For DER 324

$$\begin{aligned} \text{epoxide oxygen \%} &= [(37.35 - 10.82) * 0.1000 * 0.016 * 100] / 0.5085 \\ &= 8.35 \% \end{aligned}$$

b, For PCPD P-5-13

$$\begin{aligned} \text{epoxide oxygen \%} &= [(37.35 - 36.78) * 0.1000 * 0.016 * 100] / 0.8179 \\ &= 0.11 \% \end{aligned}$$

By substituting the known molecular weight, the mole of epoxide group per mole of sample is:

$$M_O = W M / 16 \dots \dots \dots \text{eq.14}$$

where M_O : moles of epoxide oxygen per mole of resin

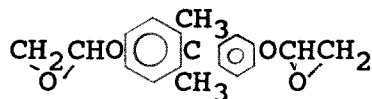
W: weight of epoxide oxygen per gram of sample

M: molecular weight of sample

For DER 324, $M = 340$,

$$M_O = 0.0835 * 340 / 16 = 1.77 \text{ mole}$$

The result is close to the chemical formula of DER, that is, diglycidyl ether of bisphenol-A,



For P-5-13 PCPD, $M = 2920$,

$$M_O = 0.0011 * 2920 / 16 = 0.2 \text{ mole}$$

Further analysis of other PCPD samples are listed in Table 18.

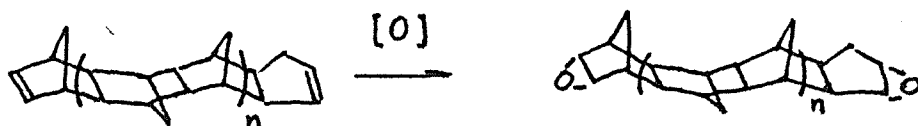
It is noted that the analysis method has good reproducibility, the standard deviation of duplicates of P-5-13 is only 0.007 % and relative standard deviation is 0.067 %. Therefore the results of epoxide group analysis by this method is acceptable.

Table 18. Analysis of epoxy groups of PCPD

Sample	weight (g)	0.1 N NaOH (ml)	% O	\bar{M}_n	M_o
P-2-9	0.2329	49.40	0.55		
P-5-13	0.4679	49.90	0.10	2920	0.18
F-5-13	0.5520	49.60	0.17	102	0.01
blank		50.20			

Note: 20.00 ml of 0.29 N HCl/ether was added to analyze samples. Molecular weight of sample P-2-9 was not measurable because its molecular weight is too large to dissolve in the chosen solvent toluene.

The further conclusion may be drawn that PCPD polymer with high molecular weight (2920) has 20 mole % of epoxide group which comes from oxidization of double bonds at ends of polymer chain as illustrated below. However, PCPD polymer with low molecular weight (102) hardly has any epoxide groups. It is, however, necessary to verify the result of the wet analysis by other methods such as elementary analysis because of the limitation of the quantitative analysis.



HPLC

The HPLC graphs of PCPD are shown in Fig 18. Three samples were injected in the instrument concomitantly at the same instrumental conditions. The three single peaks indicate that these polymer samples are purely single component systems. Table 19 lists the retention time, concentration and molecular weight of the sample.

Table 19. HPLC data of PCPD

sample	\bar{M}_n	conc. (%)	R_t (min)	peak height (cm)	relative response (cm/% conc)
monomer	66	0.1	5.0	5	50
F-5-13	102	0.2	5.4	8	40
P-6-4	2240	9.2	5.6	6.5	0.7
P-5-13	2920	10.9	5.7	3	0.3

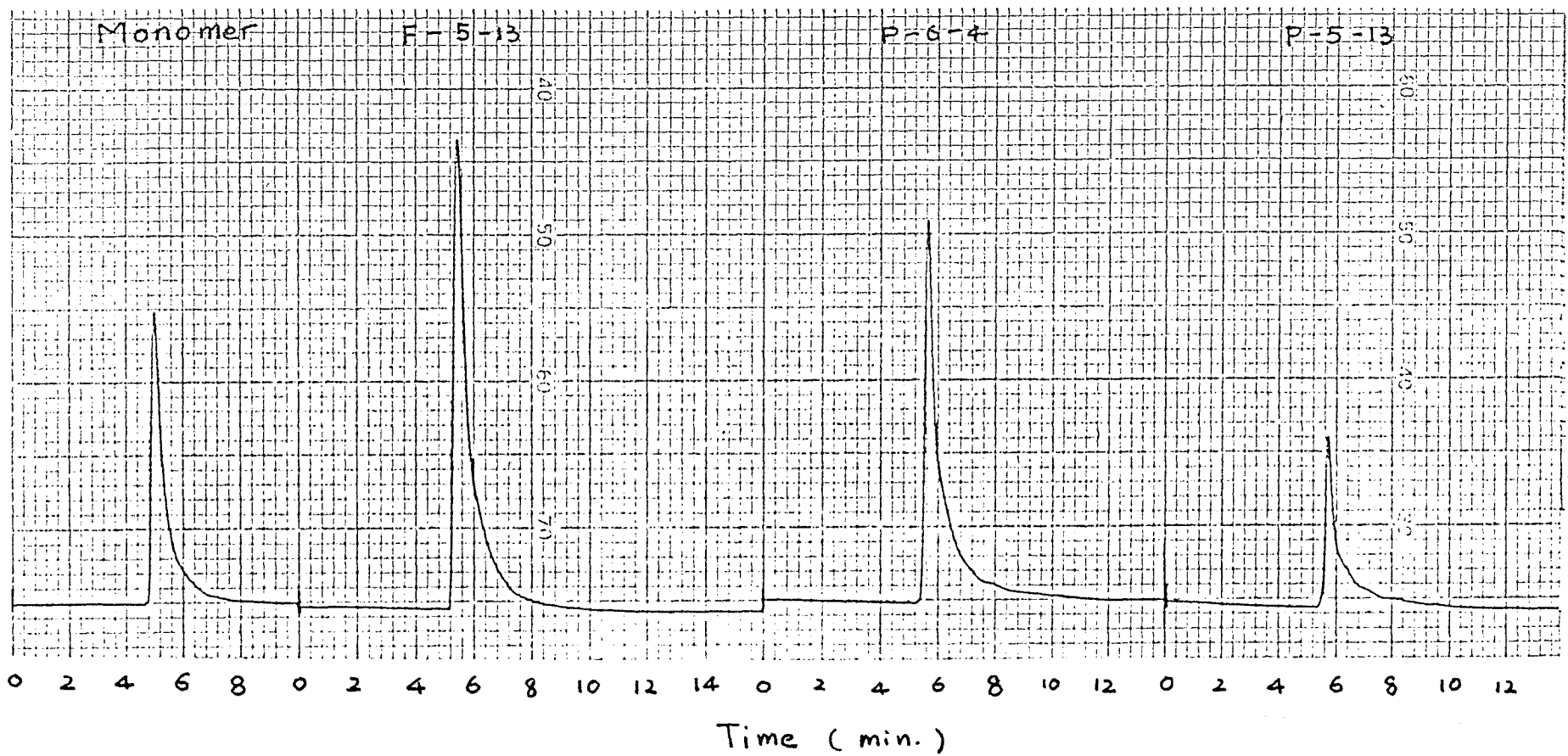


Fig. 18 HPLC Graph of CPD and PCPD

The plot of the retention time vs. the molecular weight and the relative response is shown in Fig 19.

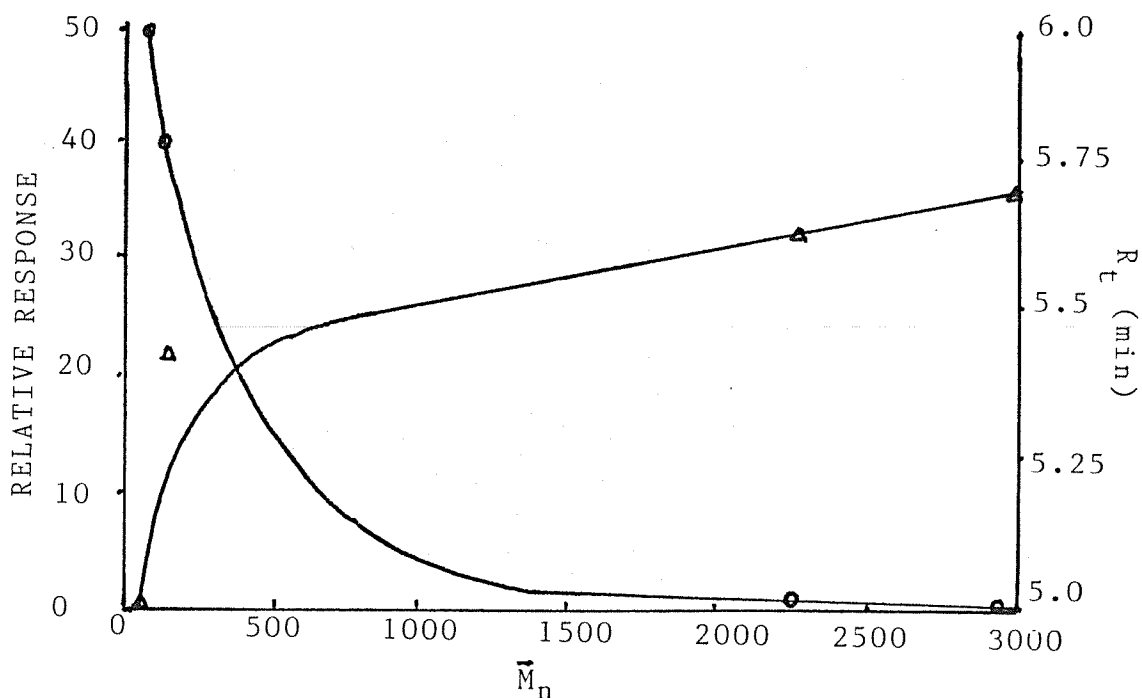


Fig 19. HPLC data vs molecular weight of PCPD

The HPLC has a mercury light source as detector. As compared with that of the monomer, the sharp drop in response of the polymer to UV absorption implies much fewer double bonds associated with the polymer than that of monomer. The spectra of the monomer and the polymer in Fig. 13 also confirm this. It is understandable that the retention time of the polymer should be longer than that of monomer. However, the molecular weight does not bear any relationship with the retention time in a normal polar phase HPLC with chloroform as

eluent. The relatively large tailing for both monomer and polymer chromatographs can not be contributed to the molecular weight distribution. Because the constant of absorption and desorption of the absorbed molecules in the silica column are not a simple matter. It may also involve the number of the theoretical plates in the column, the concentration of the sample and the poor response of the detector.

5. Formulation and Curing of PCPD Propellant

1.) Curing of PCPD prepolymer

a. Screening of potential curing agents

Attempts of curing the liquid prepolymer were made with several potential curing agents. The results are listed in Table 20, along with the curing conditions.

Table 20. Results of Curing of PCPD

formulation #	0-3	24	8	55	63
chemical(g)					
PCPD	10	2	2.7	2	2
MA		1	0.1	0.5	0.5
PA					0.5
DER 324	1	0.2	0.3		
DEH 24	1	0.1			
GL				0.4	
curing °C/hrs	120/24 160/14	120/12 160/6	110/14 160/10	145/38	145/38
result *	-	+	+	+	-

* + : cured ; - : uncured

As shown in above Table PCPD polymer can be cured by a combination of maleic anhydride, DER 324 and DEH 24. Formulation # 55 also raises the possibility of curing PCPD with maleic anhydride alone. Phathelic anhydride is not a curing agent in this case.

b, Selection of catalysts

It is a well known fact that the reaction of MA with unsaturated and epoxy compounds can be accelerated by a hydrogen donor or amino compound. The effectiveness of several catalysts to accelerate the reaction of PCPD - MA system is shown in the next table.

Table 21. Catalysts for curing PCPD with MA

formulation	19	28	26	46	67	86	35	36	37	38	139
chemicals(g)											
amine 1									.1		
amine 2										.1	
pyridine								.1			
phenol							.1				
BL	.2	.1	.1		.2	.2					
GL				.1	.1	.1	.1	.1	.1	.1	
MA	1	.5	1	.5	.5	.2	.5	.5	.5	.5	.5
PCPD	2	2	2	2	2	2	2	2	2	2	2
Curing °C/hrs	120/62	I 120/14	I 140/6	I 150/18	I 150/18	I 150/18	I 150/18	I 120/15	I 150/48	I 130/24	I 110/24
		I 160/13	I 160/13				I 150/17				
Result	+	-	+	+	+	+	+	+	+	+	-
Note: amine 1	: $\text{CH}_3(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2$										
amine 2	: N,N dimethyl aniline										

It is of interest to note formulations 28 and 46, with 5 % glycerol (GL) PCPD can be cured with 25 % MA. Whereas butanediol (BL) can not. The experimental results show that pyridine can decrease the curing temperature to some extent (addition of pyridine caused polymer to become partially solidified even at room temperature). The amino compounds in formulations 37 and 38 result in the cured polymer more tough, and phenol was found having good compatibility with PCPD. Formulation 139 shows a negative result. Thus, without proper catalyst, curing of PCPD with MA is rather ineffective. Formulations 67 and 86 show low molecular weight PCPD F-5-13 (\bar{M}_n 102) can also be cured by MA at the same curing conditions. Among the 11 fomulations listed, fomulation 86 illustrates the least amount of the curing agent needed to achieve a cured polymer.

c, IR spectra of cured and uncured PCPD

As mentioned earlier in this section, the epoxy groups formed in the polymer are suggested responsible for the curing reaction. To examine this further, IR spectra of the cured polymer were taken and shown in Fig 20 to 24.

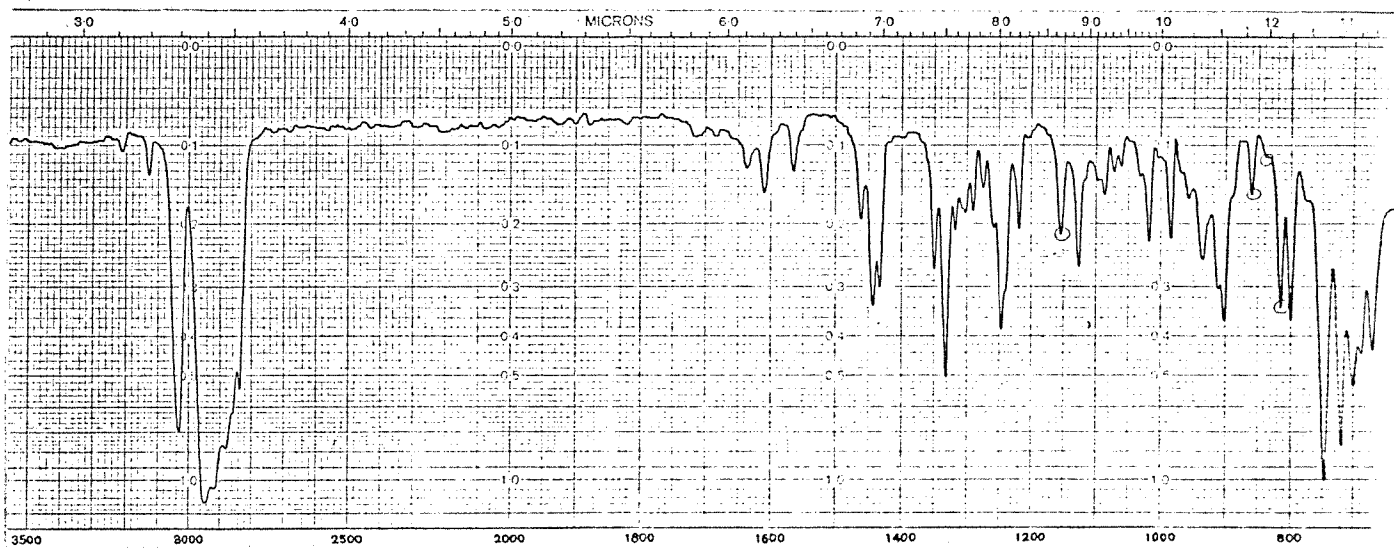


Fig 20. IR spectrum of PCPD P-5-13

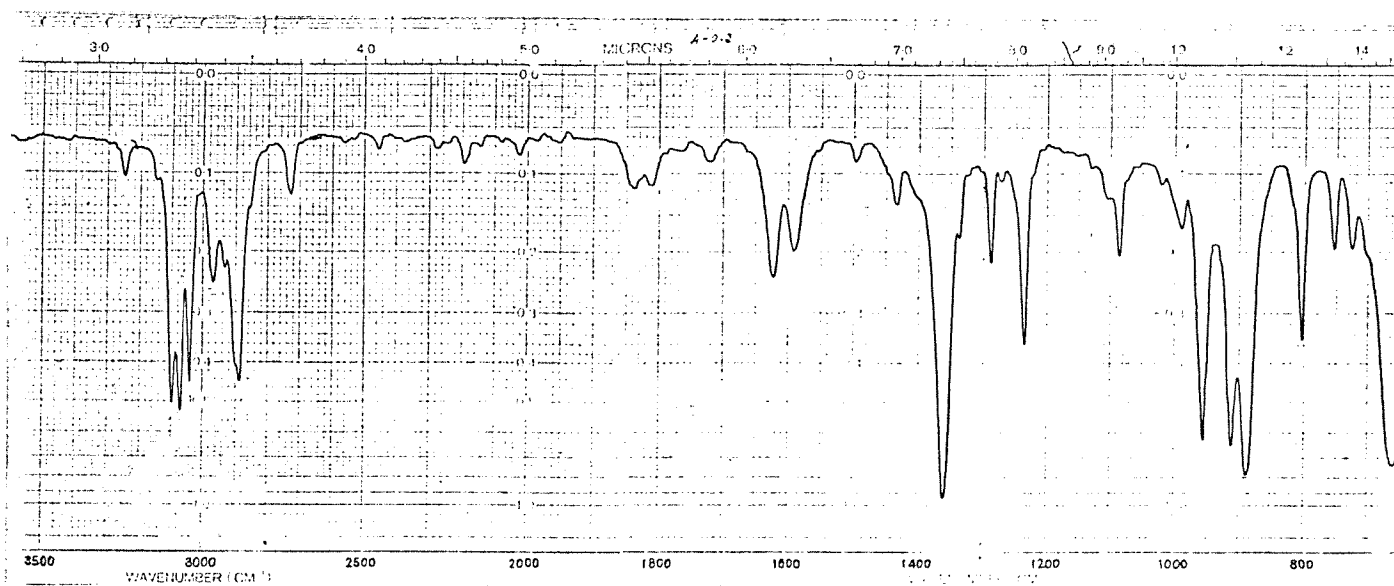


Fig 21. IR spectrum of monomer

Fig 20 is the IR spectrum of PCPD P-5-13 with M_n of 2920; wet analysis of epoxy groups showed 20 mole % epoxy oxygen. Comparing with the IR spectrum of monomer in Fig 21, the new peak at 1150 cm^{-1} in Fig. 20 is an evidence of ether groups. Absorptions at 820 , 840 and 860 cm^{-1} may have come from epoxy groups as the result of air oxidization of chain end double bonds during the long hours of reaction at high temperatures. Comparing these spectra with that of in Fig. 22 for the solid polymer, PCPD P-2-9 (which was made in the same way as other PCPD polymers except it has a longer reaction time and is practically insoluble in toluene).

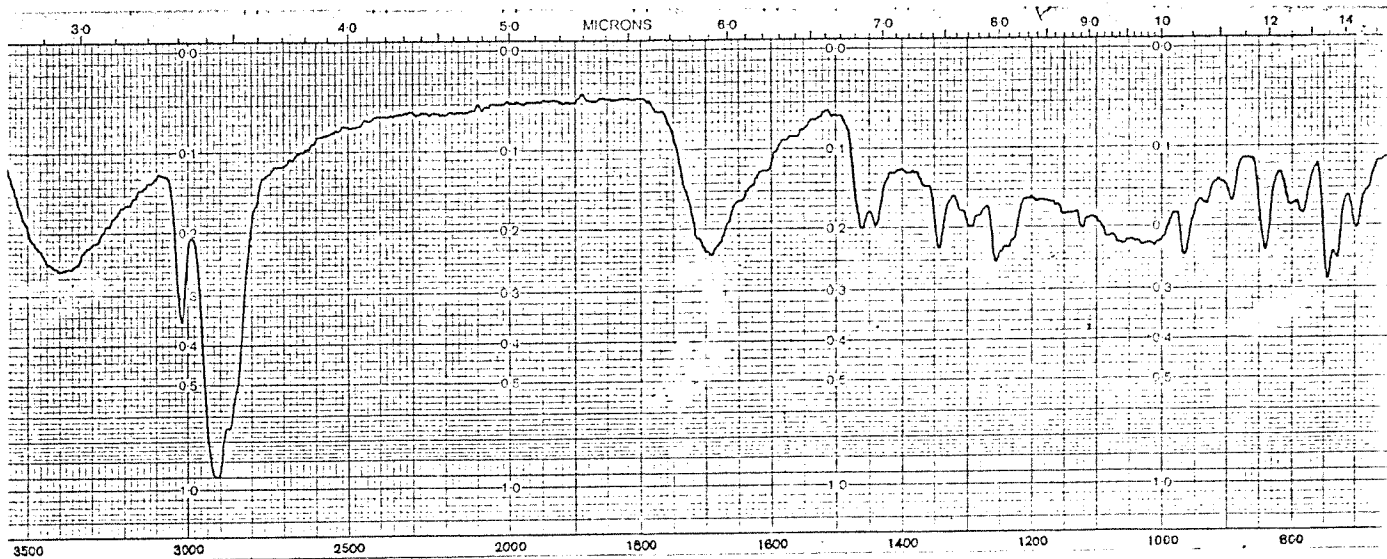


Fig 22. IR spectrum of PCPD P-2-9

One finds the polymer has an enhanced absorption at 840 cm^{-1} which may be caused by the extra ether groups that are formed by the extended oxidization occurred on the chain end double bonds during the long reaction period. The strong absorptions at 1700 cm^{-1} and 3400 cm^{-1} show clearly, the existences of carbonyl and OH groups. The OH absorption comes mainly from the chemical structure of the polymer and partially from the air moisture absorbed by the sample (due to the oxygen atoms in the polymer during the measurement period). The wet analysis confirms that the polymer has the highest epoxy content among all PCPD samples examined (see Table 18).

Figs 23, and 24 are the IR spectra of cured PCPD from the Formulation 16 and 18 as tabulated in Table 22.

Table 22. Formulation of curing PCPD

formulation	16	18
chemical(g)		
PCPD	2	2
MA	1	1
DER 324		0.2
DEH 24		0.1
BL	0.2	0.2

The cure condition was 120°C /62 hrs and 160°C /14 hrs.

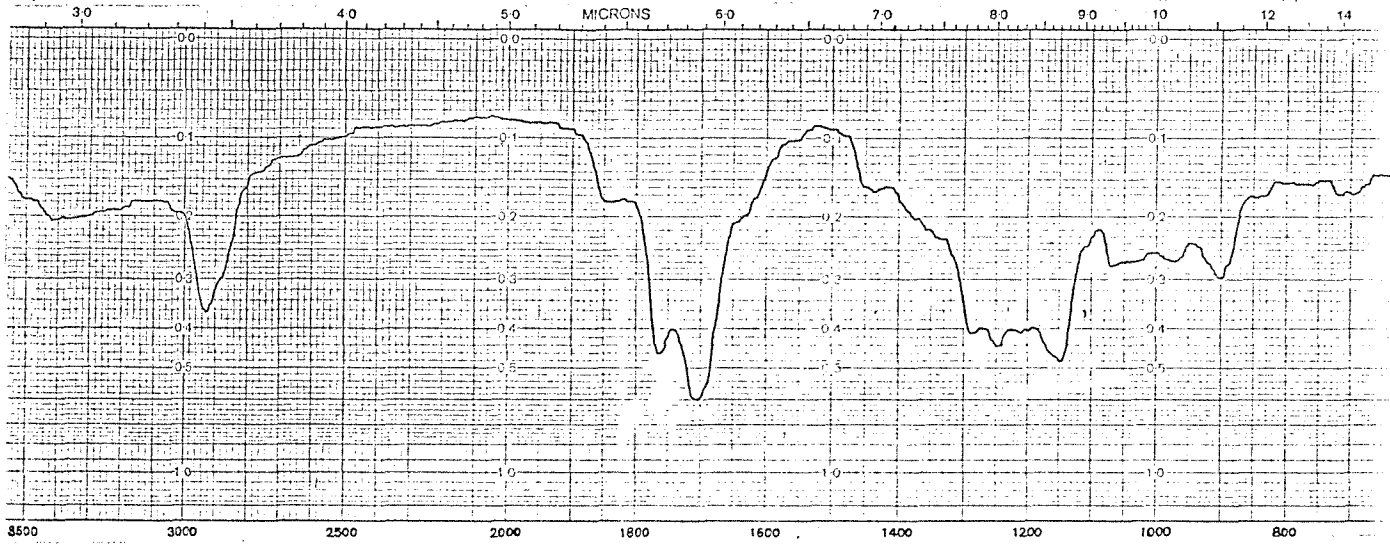


Fig 23. IR spectrum of PCPD (formulation # 16)

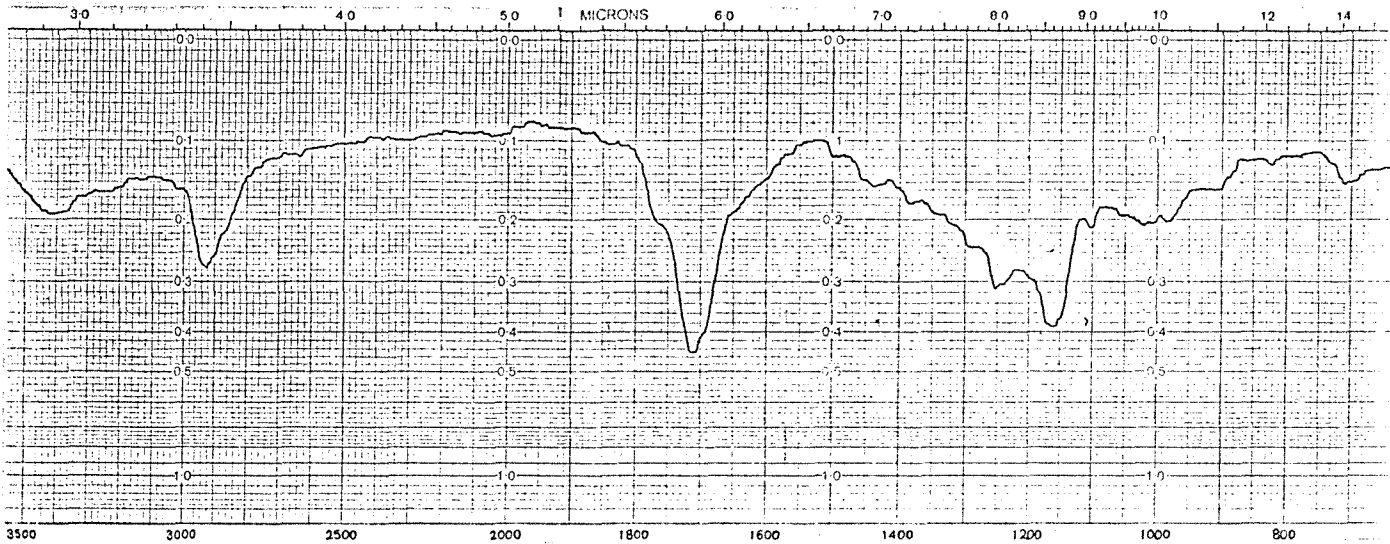
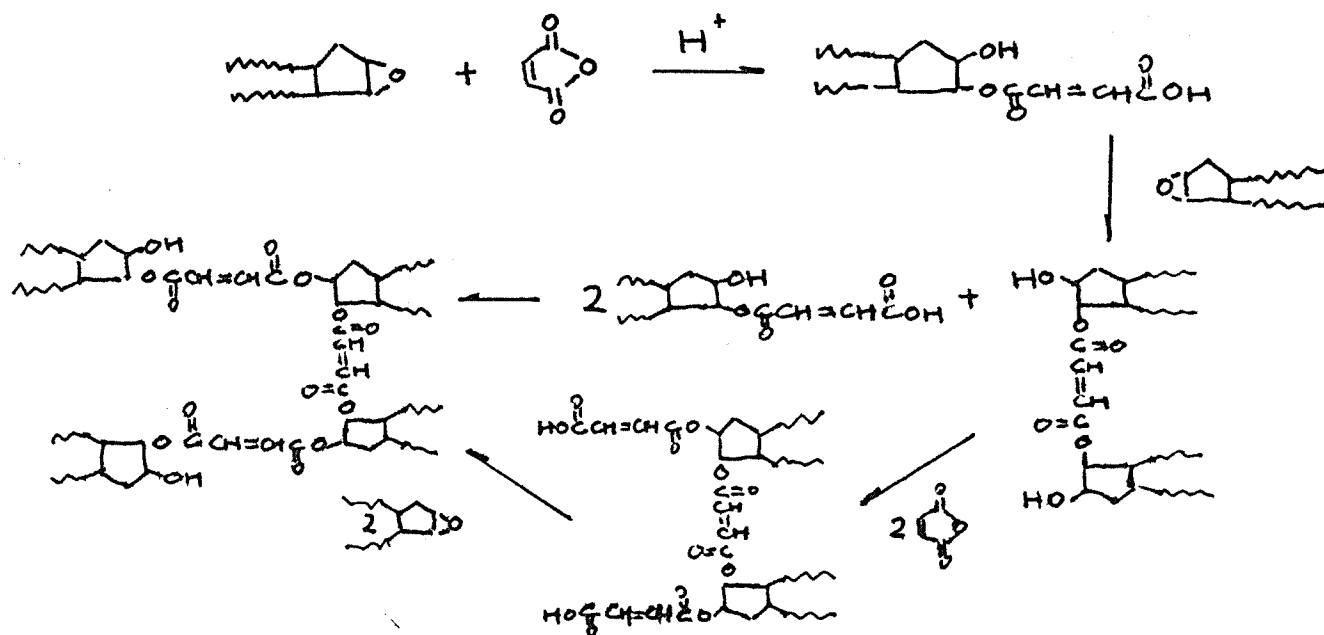


Fig 24. IR spectrum of PCPC (formulation # 18)

Both spectra are relatively Broad and lack of fine

details. This is probably, due to the higher rigidity of the crosslinked polymers on molecular vibrations. For MA cured PCPD, the most important structural changes are indicated by the stronger absorptions of ester groups at 1750 and 1700 cm^{-1} . These ester groups are parts of maleates and fumarates formed as a result of curing. Comparing IR spectrum in Fig. 23 with that of in Fig. 24, one finds that PCPD cured with DER 324 and MA has relative weaker ester group absorption at 1700 and 1750 cm^{-1} than that of cured with MA alone. From the IR spectra and the wet analysis of epoxy groups, the curing of PCPD with MA may be through the following reactions:

1) via epoxy ends of the chain

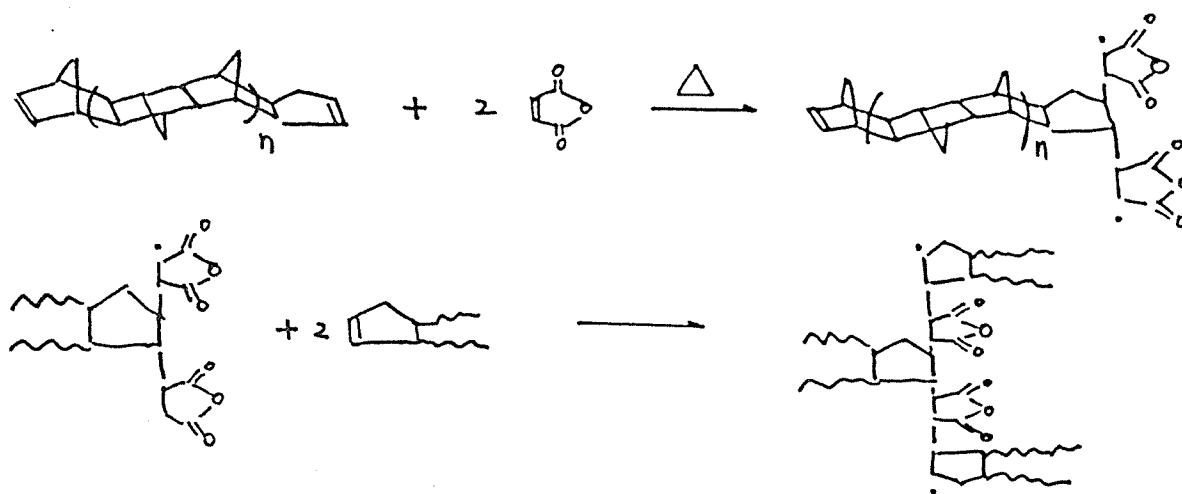


Because there are four functional groups at the ends of

each PCPD molecule and the catalytic hydrogen atoms are produced during the high temperature reaction from the hydrogen donor such as glycerol, carboxyl groups are generated in situ, and react subsequently with epoxide to propagate the reaction chain, the crosslink reaction can be carried to form the three dimensional network. It is understood that pure epoxide and anhydride have no active hydrogen atoms. Therefore, for fast reaction proper initiator is needed.[20]

2. via the unsaturation ends of the chain

Since wet analysis showed only 20 % PCPD having epoxide groups there must be other crosslinking reaction mechanism(s) in addition to the epoxide reaction mechanism. Many experimental data [21] indicating crosslinking occurs at the unsaturated sites. Maleic anhydride and maleates react with many materials by the double bonds. For example. they homopolymerize and copolymerize with vinyl monomers and they add anionic reagents, such as amines and certain organometallic compounds.



The effect of chain extension and crosslinking is similar to that of the epoxide mechanism except that MA in this case maintains its ring intact.

d. % Sol, Gel, and Swelling of Cured PCPD

The effects of crosslinking density of a prepolymer on physical and chemical properties of solid propellants have been well emphasized in the literatures [22-24]. Methods using swollen tension and compression to determine the crosslinking density for propellants have been described elsewhere [25-27]. In this investigation, a relatively easier swelling method was used to check the % swelling, sol, and gel for the cured polymer. Three solvents were tested as swelling agents, namely, toluene, acetone, and DMF. The results are listed in

Table 23.

Table 23. % Sol, Gel, and Swelling of Cured Prepolymer

Cured PCPD #	Solvent	Swelling %	Sol %	Gel %
19	toluene	1.13	-	-
46	toluene	0.26	0	100
46	acetone	2.7	0.14	99.86
26	DMF	5.7	1.6	98.86
ARCO R-54M	toluene	12-48	12-42	58-88
Telagen HT	toluene	24-28	6 -18	82-94

Note: 1, All experimental extractions were conducted at room temperature for 90 hours, % gel was deduced from the assumption of sol plus gel equals 100 %.

2, % swelling = $[(W_2 - W_1 * 100) / W_1]$

3, ARCO R-45 and Talagen HT are HTPB made by Arco and Aerojet. They were cured with 2,4-tolylene diisocyanate. [28]

For cured PCPD samples, DMF has the highest swelling effect on the polymer (5.7 % swelling vs 2.7 % and 1.1 % for other two solvents). This implies that the solvent is the best swelling agent for the polymer among the three. Data in gel % for the three samples, ranging from 98 to 100 % reflect

that these samples have achieved a high degree of curing with maleic anhydride. The lower gel % values for the commercial cured HTPB are quoted from literature for comparison. [28]

e, Physical properties of PCPD and CPD

Physical properties of cyclopentadiene and its polymer ^dmeasured in this project are listed in Table 24.

Table 24. Physical properties of PCPD and monomer

sample	density g/cm ³	Bulk viscosity cps	n ²⁰ _D
monomer	0.8024		1.4430
PCPD # 8	0.9897	7.4	1.5155

The remarkably low viscosity of the polymer, 7.4 cps, affords its high capacity of solid loading as binder (will be shown later). Bulk viscosity of polybutadiene (PB) was not obtainable because an insufficient amount of polymer was synthesized. However, referring to the intrinsic viscosity in Fig.4 and Table 15, the intrinsic viscosity of PB is 3 times higher than that of PCPD of similar molecular weight.

Some physical properties of the cured PCPD are listed in table 25.

Table 25. Some physical properties of cured PCPD

sample #	density g/cm ³	RW.hardness	T.S. psi	E. %
86	1.2795	77	7300	3

Note: The tensile strength (T.S.) and elongation (E) were measured on instron at 25 °C at a strain rate 0.74 in/in/min. Rockwell hardness (RW) on Wilson instrument calibrated with brass bar (hardness 68).

The tensile strength of the cured PCPD is 7300 psi, relatively strong, the low elongation of the polymer allows a rigid matrix for formulation of propellant.

Formulation of solid propellant with PCPD as binder

Propellant behavior is widely varied with respect to its formulation, ingredients, process and test. Obviously, the optimization of formulation of propellant needs sophisticated equipment, coordinated team work, experience in the field, and special safety precautions, which were not available to this project. The intent of this work was to give a preliminary investigation to the feasibility of a new polymer PCPD as a potential propellant binder. The most important

factors investigated were the compatibility of polymer with other ingredients , fuel values and mechanical properties.

a, Compatibility

As a binder, the polymer must be chemically and physically stable in the presence of the oxidizer at normal storage and operation temperature. Experiments showed the PCPD polymer system has very good compatibility with other inorganic fillers necessary for a solid composite propellant within the concentration range of binder between 10 and 45 % by weight.

A typical formulation of propellant is:

PCPD binder	10 - 15 %
Al powder	15 - 20 %
AP	65 - 75 %
Antioxidant 754	0.1 %
Formulation of binder (premix or prepolymer)	
PCPD polymer	75 %
MA	15 %
GL	5 %
Dietyl Apitate	5 %
lecithin	0.05 %
antifoam CO-52	0.05 %

It was observed that polymer binder readily wets the solid

particles and mixes with ingredients, and particles are distributed evenly at as low as 10 % binder concentration. It is curable in the presence of oxidizer and metal powder and there are no bubbles present in the cured propellant if the mass is properly processed. The low binder mass fraction in the propellant affords a desirable high solid loading up to 90 % .

A typical formulation of HTPB propellant is [29],

HTPB binder	12 - 16 %
AP	60 - 84 %
Al	2 - 20 %
stabilizer	0 - 1 %
curing agent	0.2 - 1 %

A comparison of the foregoing two formulation reveals that the use of PCPD as a binder is more desirable because a lower mass fraction of the binder allows a higher loading of the solids.

The compatibility of binder was evaluated by swelling the propellant in toluene and DMF at room temperature for 6 weeks, the results are given in table 26.

Table 26. Swelling of cured PCPD propellant

sample #	solvent	Time hrs	swell %	sol %	gel %
83	toluene	1000	5	1	99
81	DMF	1000	17.5	6.2	93.8

After 1000 hrs soaking in toluene the whole piece of cured propellant still remained intact. However, sample soaked in DMF did show some small pieces chipped out of the material edges of the propellant although the whole peice was still in good shape. This is a sound proof of good compatibility of binder with other ingredients of the propellant.

The formulations of propellants 81 and 83 are:

	81	83
	(%)	(%)
Prepolymer 86 (Tab. 21)	10	15
Al powder	20	20
Potassium chloride	70	65

Potassium chloride was used instead of ammonium perchlorate for safety consideration.

b, Physical properties of PCPD propellant

Table 27 is comparison of physical properties of PCPD and the commercial HTPB propellants.

Table 27. Some physical properties of propellants

sample	T.S. psi	E. %	density g/cm ³
PCPD 81,125	187 - 227	4 - 4.4	1.9879
ARCO R-45M	49 - 130	24 - 66	
Telagen HT	120 - 160	14 - 47	1.7713 [28]

Note: Tensile strengths of R-45M and Telagen HT were performed on Minithin at 70°F, at a strain rate 0.54 in/in/min. The PCPD sample was tested on Instron at a strain rate 0.74 in/in/min at 25 °C.

The formulation of propellant 125 is in Table 32.

6. Heat of combustion of PCPD propellant

Combustion of the propellant converts potential thermochemical energy into kinetic energy to propel the rocket. The rate of energy conversion in a rocket motor is a product of two factors, the energy converted per unit weight and the weight burned per unit time. There are many studies on burning rate of propellant [30], but few studies have been reported on inherent energy of the propellant. This study of the heat of combustion of PCPD polymer and its propellant is to obtain enough information about combustions of the system, so that a prediction of the fuel value of the propellant could become possible.

Heat of combustion of PCPD polymer

1.0123 gm of PCPD polymer sample P-5-13 was weighed accurately and charged to the bomb calorimeter with 30 atm oxygen. As a result of the combustion of the sample, the temperature rise in the aqueous reservoir was recorded in the following Table 28.

Table 28. Measurement of heat of combustion of PCPD polymer

time min	Temperature °C	t °C
0	21.830	
1	21.835	+0.005
2	21.840	+0.005
3	21.840	0
4	21.845	+0.005
5	21.850	+0.005
5.75	24.72	+2.87
6.0	25.27	+0.55
6.25	25.58	+0.31
6.5	25.84	+0.26
6.75	25.92	+0.08
7	26.020	+0.10
8	26.140	+0.12
9	26.165	+0.025
10	26.170	+0.005
11	26.165	-0.005
12	26.155	-0.01
13	26.145	-0.01
14	26.135	-0.01
15	26.125	-0.01
16	26.115	-0.01

From Table 28, the following data are determined:

$$a = 5$$

$$c = 11$$

$$b = 5.67$$

$$T_a = 21.850$$

$$T_c = 26.165$$

$$r_1 = 0.02 / 5 = 0.004$$

$$r_2 = - 0.01$$

$$e_1 = 19.05$$

$$e_3 = (10 - 3.9) * 2.3 = 14.03$$

$W = 2407 \text{ cal /g}$

b is calculated from 60 % total temperature rise by interplate between neighboring points as follows:

total temp. rise = 4.320

60 % t t r = 2.592

temperature at 60 % ttr = $21.850 + 2.592 = 24.442$

from a plot of temperature rise with time as shown in Fig. 28

b is obtained as 5.67

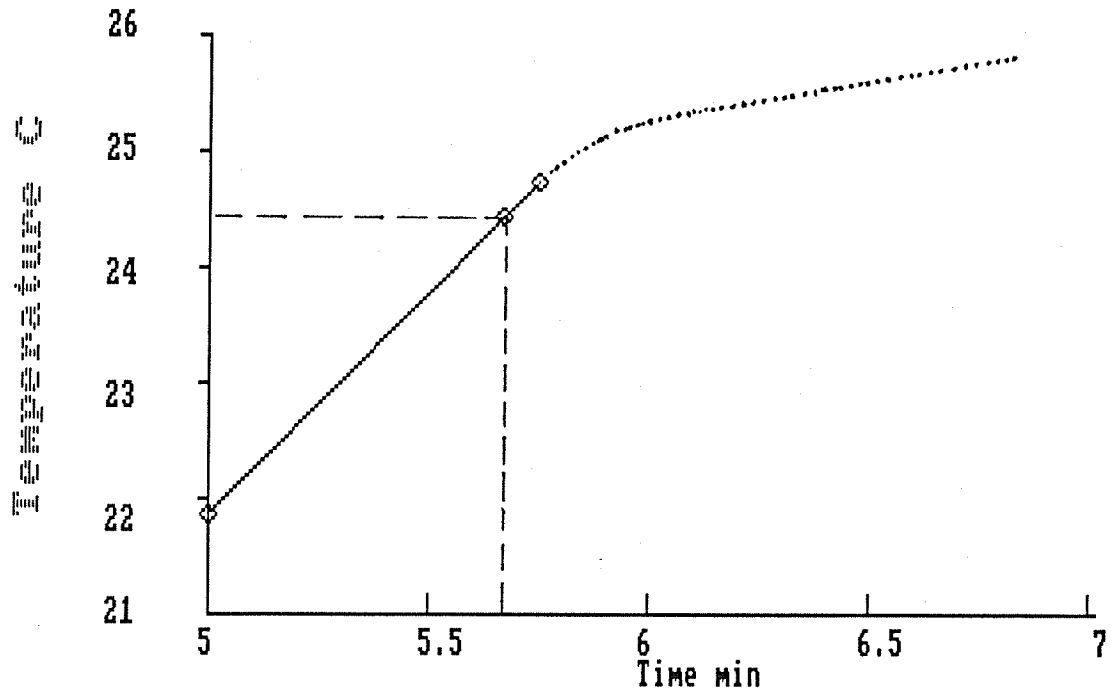


Fig 25. Temperature at 60 % total temperature rise

So that the corrected temperature rise is

$$T = T_c - T_a - r_1 (b - a) - r_2 (c - b)$$

$$\begin{aligned}
 &= 26.165 - 21.850 - 0.004(5.67 - 5.0) + 0.01(115.67) \\
 &= 4.36
 \end{aligned}$$

and the gross heat of combustion is

$$\begin{aligned}
 H_C &= (T W - e_1 - e_3) / m \\
 &= (4.366 * 2407 - 19.05 - 14.03) / 1.0123 \\
 &= 10,349 \text{ cal/g}
 \end{aligned}$$

Alternatively, the temperature rise with time could be constructed by way of Fig 26.

It has been proven mathematically that the points on two tangent lines located by the line that makes two shaded areas equal give the corrected temperature rise on y axis. Fig 29 shows $t_1 = 21.860$, $t_2 = 26.270$, so $t = t_2 - t_1 = 4.410$ and the heat of combustion therefore calculated as

$$\begin{aligned}
 H_C &= (4.410 * 2407 - 19.05 - 14.03) / 1.0123 \\
 &= 10,453 \text{ cal/gm}
 \end{aligned}$$

The relative standard deviation of the two different methods is about 0.7 %. thus the results of the alternative methods are statistically acceptable.

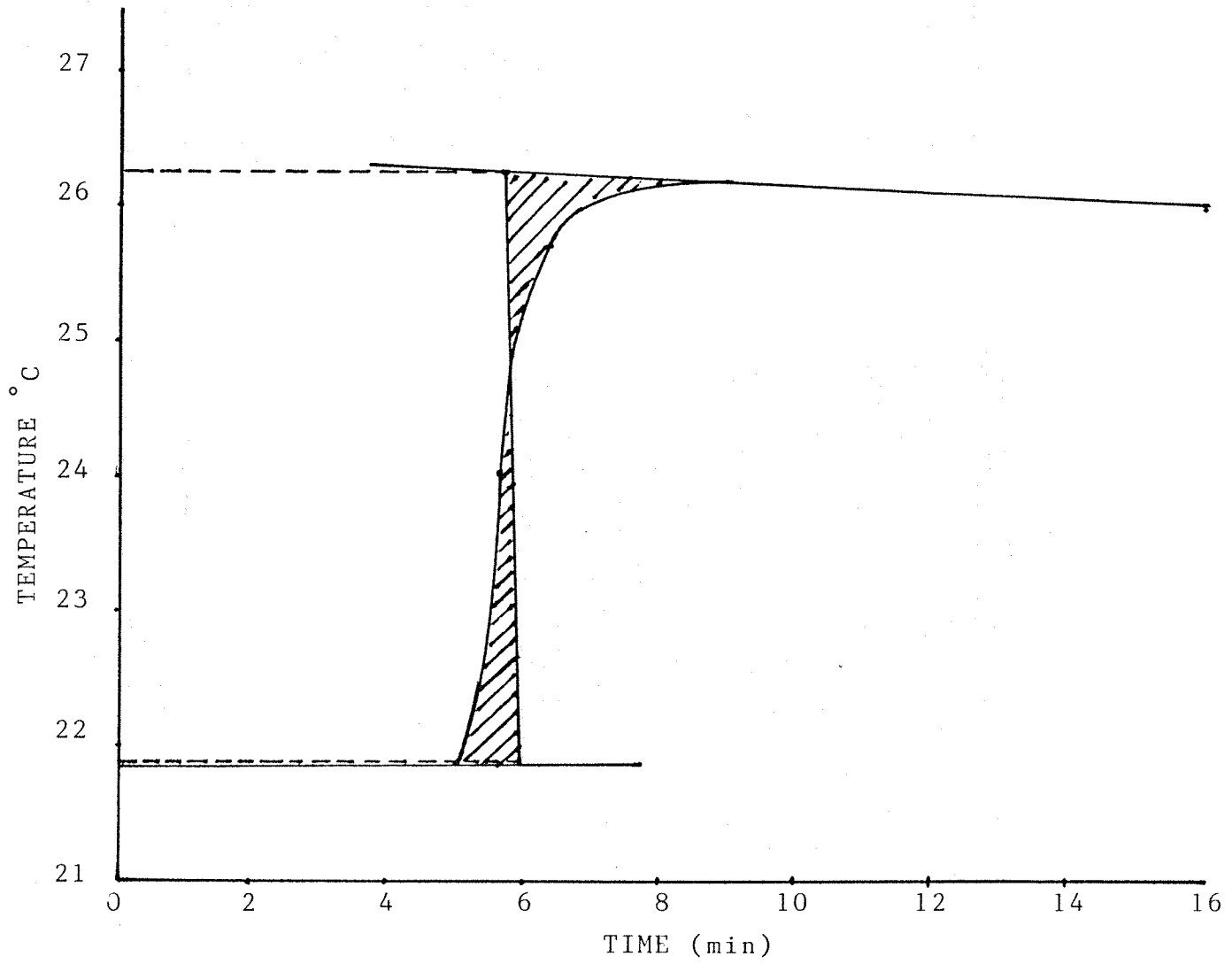


Fig 26. Graphic method of measurement of TTR

Reproducibility of the method

Table 29. Results of duplicates of heat of combustion

sample #	ΔH_c cal/g	mean	R S D %
P-5-13	10,349	10,313	0.50
	10,276		
P-2-9	9,000	9,018	0.28
	9,036		

Data show the oxygen bomb calorimetry has very good reproducibility, relative standard deviation is only 0.3 to 0.5 %.

Heat of combustion of PCPD polymer

The heats of combustion for several commercial polymers are compared in Table 30.

Table 30. Comparison of heat of combustion with commercial polymers

Polymer	ΔH_c cal/g	references
PCPD P-5-13	10,313	
PB 10 (Tab.3)	9,692	
PMMA	6,286	[31]
PVC	4,761	[31]

Among them, PCPD has the highest energy released, 10,313 cal/g. Although the heat of combustion changes with the molecular weight of the polymer (see Table 31) the change is rather mild. For instance, molecular weight increases by 44 times from monomer to polymer, the heat of combustion increases only by 16 %.

Table 31. ΔH_C of PCPD with different \bar{M}_n

sample	\bar{M}_n	ΔH_C cal/g
monomer	66	8,877
F-5-13	102	9,479
P-5-13	2920	10,313

Heat of combustion of the propellant

Experiments showed PCPD propellants did not completely combust at 30 atm oxygen pressure. To help combustion of propellant, the combustion aid benzoic acid was added, mixed with the powder of propellant and pressed into a pellet. The heat of benzoic acid was then subtracted from the total observed amount to obtain the net value for the propellant. The following example illustrates the way to calculate the

H_C of the propellant.

A mixture of 1:1 of propellant # 127 and Benzoic acid weighed 0.6951 g, the total temperature rise is 1.445 °C. H_C released in 0.6951 g mixture is 3,451 cal. Subtracting the heat contributed by benzoic acid, $3451 - 0.34755 * 6318 = 1255.2$ cal, which is contributed alone by the propellant if there is no other interference between propellant and benzoic acid. Then the heat of combustion of propellant is

$$H_C = 1255.2 / 0.34755 = 3,613 \text{ cal/g}$$

It may be surprising to see that the propellant has a lower combustion heat than that of the binder alone. This is because AP does not burn in the bomb calorimeter. (Experiments showed AP alone at 30 atm oxygen pressure simply did not burn). This phenomenon has also been reported in the literature [32].

As mentioned in the introduction, a typical propellant consists of HTPB binder, ammonium perchlorate oxidizer and aluminum metal. The energy evolution for such a propellant is about 1500 cal/g [1]. The heat of combustion for PCPD propellant, 3612 cal/g, is more than twice of this value. Unfortunately, the commercial HTPB propellant was not available for us to compare.

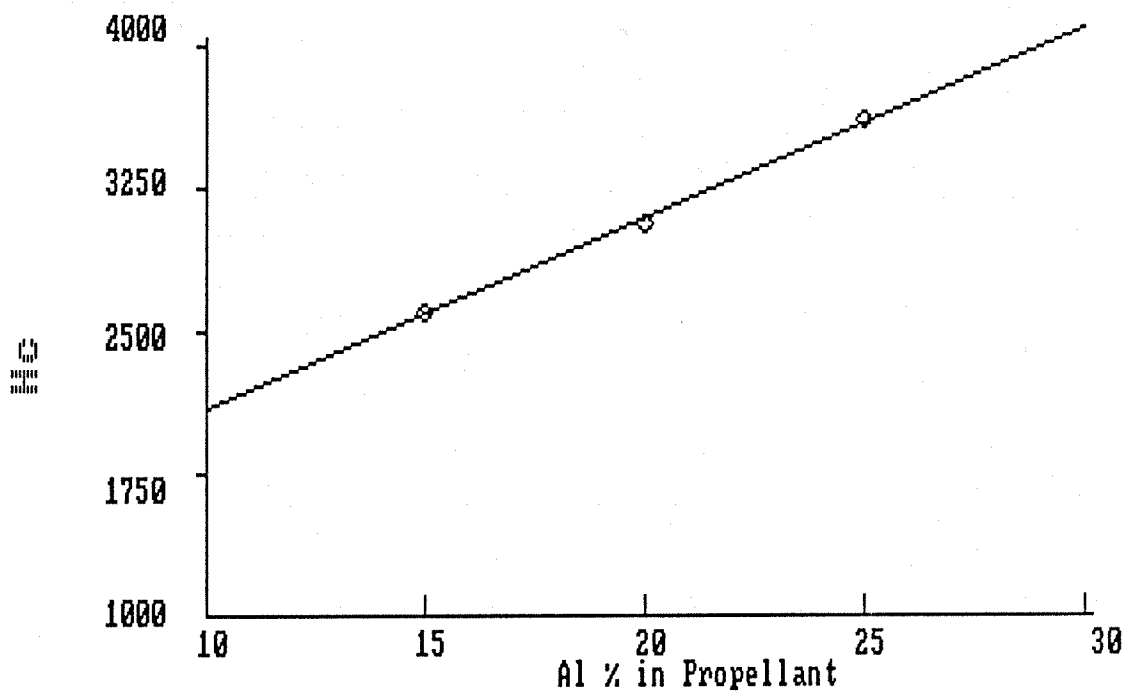
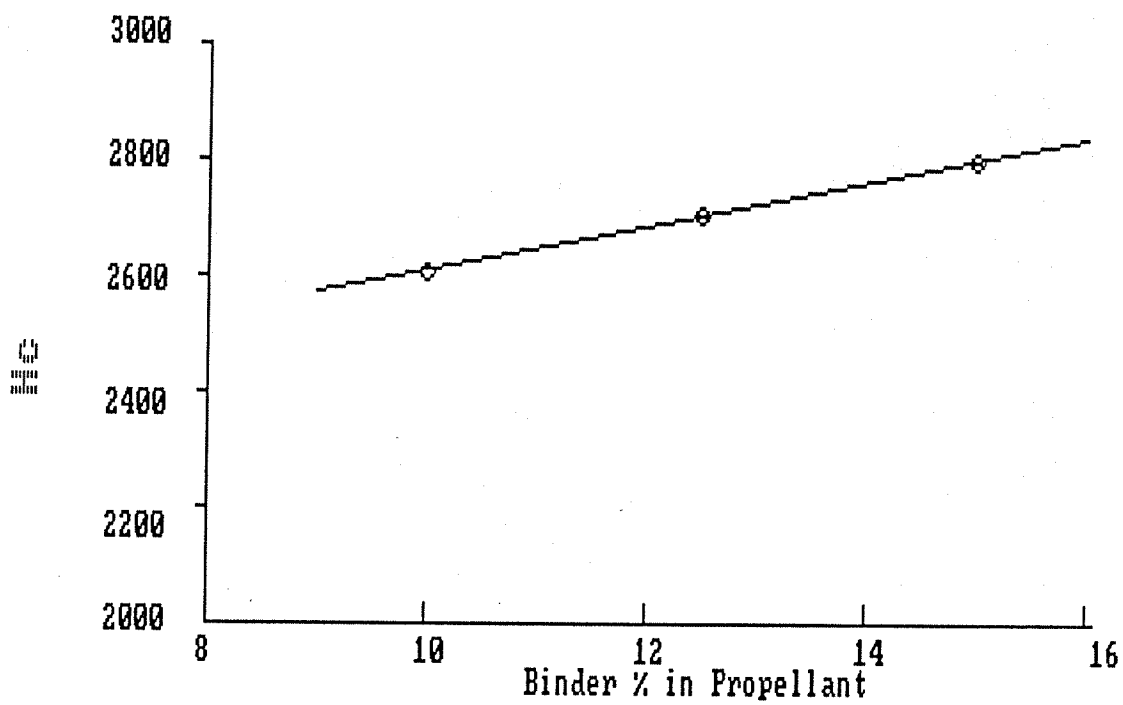
Heats of combustion of PCPD propellant with different compositions were also studied, the results are given in

table 32 and Fig 27 and 28.

Table 32. H_C of PCPD propellant with different compositions

sample #	Al %	binder %	AP %	H_C cal/g
125	15	10	75	2609
126	20	10	70	3059
127	25	10	65	3612
129	15	15	70	2802
130	15	12.5	74	2710

Note: the formulation of prepolymer is listed as # 67 in Table 21

Fig 27. Effect of Al % in propellant on ΔH_C Fig 28. Effect of binder % in propellant on ΔH_C

From the slopes of the two graphs, the effect of amount of Al is found more significant than that of the binder; each percent of Al increment gives 100 cal/g heat of combustion for each gram of propellant and each percent of binder increment gives only 38 cal/g.

CONCLUSIONS AND SUGGESTIONS

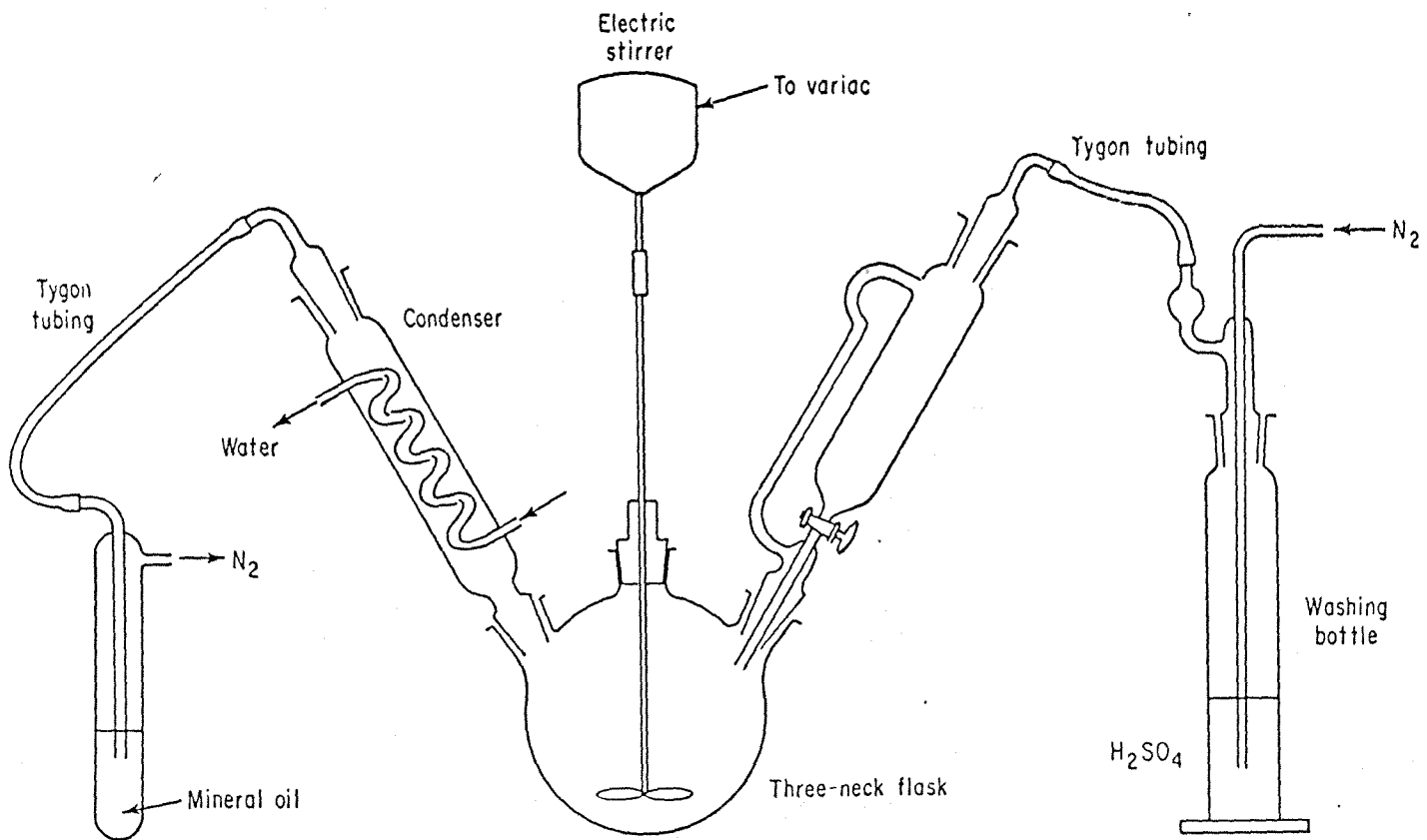
It has demonstrated that cyclopentadiene can be polymerized by Diels Alder reaction to form a low bulk viscosity liquid polymer, 7 cps. It has also demonstrated that PCPD can be cured with MA to a high degree of crosslinking network with strong and rigid mechanical properties of tensile strength 7300 psi and elongation 4 %.

The heats of combustion of uncured PCPD sample were found in the range of 8,877 - 10,313 cal/g, indicating that PCPD prepolymer is indeed a high energy binder suitable for formulating high energy propellants.

PCPD was also found compatible with propellant ingredients such as Al and ammonium perchlorate. Because of the low viscosity of PCPD, a high loading density, high energy propellant has been achieved.

For future work, I would like to suggest following areas of studies:

- 1) curing optimization and mechanism,
- 2) thermal stability, aging and degradation,
- 3) mechanical properties and microstructure,
- 4) Screening of low temperature curing agents.



Experimental set up for synthesis of PCPD

APPENDIX

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