8-30-1991

Low-temperature crosslinking of polycyclopentadiene

Lawrence Peters
New Jersey Institute of Technology

Recommended Citation

Peters, Lawrence, "Low-temperature crosslinking of polycyclopentadiene" (1991). *Theses*. 2598.
https://digitalcommons.njit.edu/theses/2598

2) # LOW-TEMPERATURE CROSSLINKING OF POLYCYCLOPENTADIENE.

by

1) **LAWRENCE PETERS**

Thesis submitted to the Department of Graduate Studies of
New Jersey Institute of Technology in partial fulfillment of
the requirements of the degree of
Master of Science in Chemistry Division of the Department
of Chemistry and Chemical Engineering.

APPROVAL SHEET

Title of Thesis : **LOW-TEMPERATURE CROSSLINKING OF POLYCYCLOPENTADIENE.**

Name of candidate : **LAWRENCE PETERS**

Master of Science in Engineering Science

Thesis and Abstract approved by:

Dr. George Lei
Associate Professor
Dept. of Chemistry, Chemical
Engineering.

Dr.Howard Kimmel
Professor, Dept. of Chemistry
and Chemical Engineering.

Dr. Reginald P.T. Tomkins
Professor, Dept of Chemistry
and Chemical Engineering.

VITA

Name: Lawrence Peters

Current address:

Degree and date to be conferred: Master of Sci., 10/91.

Date of birth:

Place of birth:

Secondary education: St. John's School, Sekondi, Ghana
September 1977 - June 1984

Collegiate institutions attended	Dates	Degree
New Jersey Inst. of Techonology	9/89-10/91	M.S
Univ. of Sci. and Tech., Ghana	10/85-11/88	B.Sc(Hons)

Undergraduate project: Analysis of particulate matter composition in selected environments in Kumasi, Ghana.

Positions held: Assistant Coordinator, Pre College Programs, NJIT. (1/91 to present)

Graduate Teacher in Newark elementary schools under Pre College Programs (9/89 to present).

Secondary School Math and Science teacher in Ghana (1984-1988).

ABSTRACT

Title of Thesis: **Low-temperature Crosslinking of Polycyclopentadiene**

LAWRENCE PETERS, Master of Engineering Science, 1991

Thesis directed by: **Professor George Lei**

Cyclopentadiene was polymerized via a Diels-Alder mechanism at 174°C under an inert atmosphere. The polymer obtained after 11hrs of reaction had a low bulk viscosity of 8 cps and a viscosity-average molecular weight, $\overline{M_V}$, of up to 3000. An unsaturated polyester was synthesized from maleic anhydride and ethylene glycol in the presence of chlorosulfonic acid at room temperature. The polyester had an intrinsic viscosity of 0.024 cps. At 60°C, polycyclopentadiene (PCPD),and the unsaturated polyester were reacted to yield a viscous liquid which was crosslinked at room temperature over 48 hours in the presence of styrene, triethyleneglycol dimethacrylate (TEGDMA), N,N'-dimethyl-p-toluidine and benzoyl peroxide. The hard, crosslinked material is thermally stable at 250°C and possesses a high degree of crosslinking in acetone, toluene and dimethylformamide (DMF).

ACKNOWLEDGMENTS

My sincere thanks and appreciation go to Prof. George Lei, my advisor, who supervised this research and gave all the necessary assistance to make it a success. Special thanks also go to Dr. Howard Kimmel and Dr Reginald Tomkins who took time out to read this piece. I am indebted to Lisa Novemsky, who helped me in getting the IR spectra copied, in addition to her great concern about this work.

Last but not the least, my appreciation goes to my best friend, Eleanor Armah, and to all loved ones, who supported and encouraged me in diverse ways to go ahead, and to myself for patience and courage to have come this far by faith.

DEDICATION

This book is dedicated to the NEWMANS and the CUMMINS, who mean more to me than words could ever describe.

TABLE OF CONTENTS

CHAPTER PAGE

I INTRODUCTION 1

II EXPERIMENTAL 6

1. Recovery of CPD monomer 6
2. Synthesis of PCPD 7
3. Characterization of PCPD samples
   - (a) Infrared Spectroscopy 7
   - (b) Viscosity-average molecular weight 9
   - (c) Vapor pressure osmometry 10
   - (d) Bulk Viscosity 11
   - (e) Density 11
   - (f) Refractive indices 12
4. Synthesis of polyester 12
   - (a) Dilute solution viscosity 13
   - (b) Vapor pressure osmometry 13
   - (c) Infrared 13
5. Copolymerization of MA and CPD 14
6. Characterization of Copolymer 15
   - (a) Infrared 15
   - (b) Solution viscosity 15
7. Curing of PCPD 16
   - % Sol, gel and swelling 22

III RESULTS AND DISCUSSION 24
1. Purified monomer 24
2. PCPD synthesis 25
(a) Infrared 27
(b) Molecular weights 33
(c) Bulk viscosity 38
(d) Density 38

3. Polyester

(a) Polymerization 39
(b) Curing 41
(c) Intrinsic viscosity 41
(d) Vapor pressure osmometry 42
(e) Infrared 43
4. CPD-MA Copolymer 46
(a) Intrinsic viscosity 47
(b) Infrared 47
5. Curing of PCPD 49
(a) % Sol, gel and swelling 55
(b) Thermal stability 56

IV CONCLUSION 57

INTRODUCTION

Crosslinked polymers are polymers in which the molecules are linked to each other at points other than their ends. Crosslinking can be made to occur during the polymerization process by the use of appropriate monomers. It can also be brought about after the polymerization by various chemical reactions. When the number of crosslinks is sufficiently high, a three-dimensional or space network is produced in which all the polymer chains in a sample have been linked together to form one giant molecule. Light crosslinking is used to impart good recovery (elastic) properties to polymers to be used as rubbers whereas high degrees of crosslinking are used to impart high rigidity and dimensional stability to polymers [1].

The presence of compounds with more than two functional groups leads to the formation of branched and crosslinked macromolecules. A branched macromolecule should not, however, be considered equivalent to a partly crosslinked one. As long as the compound is still soluble, it is considered branched, and one speaks of side chains or branches. If, however, the compound is insoluble (limited solubility) in all solvents, one speaks of crosslinked polymer systems. Crosslinked polymers are insoluble in all solvents. However, according to the degree of crosslinking they can be swollen to a smaller or larger extent. The uncrosslinked polymers show a gradual transition from swelling to the formation of a viscous solution. However, with crosslinked polymers, swelling is limited. Crosslinking can also come about through secondary valence forces. Examples of macromolecular compounds crosslinked through secondary valence forces are the different polysaccharides and protein gels which play an important role in nature and living organisms [2].

Crosslinking is distinguished by the occurence of gelation at some point. At this point, termed the gel point, one first observes the visible formation of a gel or insoluble polymer fraction. The gel is insoluble in all solvents at elevated temperatures under conditions where polymer degradation does not occur. There is a dramatic physical change that occurs during the process of gelation. The reaction mixture is transformed into a polymer of infinite viscosity.

The crosslinking reaction is an extremely important one from the commercial standpoint. Crosslinked plastics are increasingly used as engineering materials because of their excellent stability toward elevated temperatures and physical stress. They are dimensionally stable under a wide variety of conditions due to their rigid network structure. Such polymers will not flow when heated and are termed thermosetting polymers or simply thermosets. The commercial importance of the thermosets is seen from the fact that of the over 30 billion pounds of plastics produced annually in the United States, almost 5 billion pounds were crosslinked [1].

Much work has been published on cyclopentadiene polymers and copolymers. A succesful attempt to crosslink polycyclopentadiene has been described by Ning [3]. He concluded that cyclopentadiene can be polymerized by a Diels-Alder reaction to form a low viscosity liquid prepolymer, 7 cps. This polymer can be further crosslinked with maleic anhydride to a high degree of three-dimensional network, with tensile strength of 7300 psi and elongation 4% [3]. However, the curing process must take place at temperatures over 150^{o}C and a reaction time more than 50 hours. Although the product possesses good mechanical properties, the reaction temperature is far too high and the reaction time is far too long. Therefore, the objective of this research is geared toward producing crosslinked cyclopentadiene polymer or copolymer at a lower temperature and a shorter reaction time.

At room temperature, cyclopentadiene spontaneously forms the dimers. The approximate dimerization rate is 3.5 mol %/hr [4]. Heating the dimers at about 200°C yields up to the pentamers. Oligomerization is believed to involve partial dissociation of dimers 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 [5].

Polymerization of cyclopentadiene initiated by $SnCl_4$, $TiCl_4$, BF_3.etherate, $AlCl(C_2H_5)_2$, and $AlCl_2C_2H_5$ at -60 to -90°C in various solvents gives polymers insoluble or partially soluble in hydrocarbons [6]. A search for a less active cationic catalyst that would give soluble, high molecular weight polycyclopentadienes led to the choice of n-$C_4H_9OTiCl_3$. With this initiator, soluble polymers with intrinsic viscosity as high as 1.4 dL/g can be obtained in short polymerization periods [7].

Cyclopentadiene can be copolymerized with maleic anhydride between 80 and 205°C in the presence of peroxides [8]. When the peroxide has a short half-life at the polymerization temperature, a product is obtained with a 1:2 molar ratio of cyclopentadiene to maleic anhydride.

Terpolymers of ethylene, propylene and a small amount of a diene are termed EPDM elastomers. Dicyclopentadiene was one of the first dienes examined for this application and is still used in commercial products [9]. These materials are easily crosslinked by peroxides.

Although much work has been published about cyclopentadiene polymers, Ning's report on the high energy potential of cyclopentadiene prepolymer as a binder for solid rocket propellants is also a driving force for this research.

EXPERIMENTAL

1 Recovery of Cyclopentadiene monomer

Chemical: Dicyclopentadiene (fw 132.21) 95%, Aldrich.

Procedure:

Dicyclopentadiene was placed in a two-necked round-bottomed flask equipped with a thermometer and an upright Friedrichs-type condenser (through which warm water at about 50°C was circulated). The ground glass outlet of the Friedrichs condenser was connected to the side arm of a simple distillation head fitted with a thermometer and attached to an efficient water-cooled condenser held in a vertical position. The lower end of this condenser was connected to a two-necked round-bottomed flask immersed in ice.

The flask containing dicyclopentadiene was heated by means of an electrical mantle connected to a Thermo-watch constant temperature regulator. With a couple of boiling stones added, heating was maintained at approximately 160°C until cyclopentadiene was smoothly distilled at 38-46°C

[10]. The distillate, cyclopentadiene, obtained was either used immediately or stored in a refrigerator for later use. Figure 1 shows the diagram of the monomer recovery set-up.

2 SYNTHESIS OF POLYCYCLOPENTADIENE (PCPD)

A three-necked round-bottomed flask was equipped with a refluxing condenser, a stirrer, a thermometer and an inlet and outlet of nitrogen gas. The freshly-distilled monomer was charged into the flask under nitrogen. The monomer was gently heated up to refluxing by a temperature-controlled mantle. The reflux was carried out between 41.5 and 175^{o}C for over a period of 13 hours. Samples of prepolymer were drawn out from the polymerization flask from time to time during the polymerization period.

3 CHARACTERIZATION OF SAMPLES

(a) Infrared Spectra

For liquid samples, several drops of each sample were carefully smeared onto the flat surfaces of the salt plates and evenly spread between them. The plates were mounted on a holder and the infrared spectra were taken with a Perkin-Elmer 1310 IR Spectrophotometer.

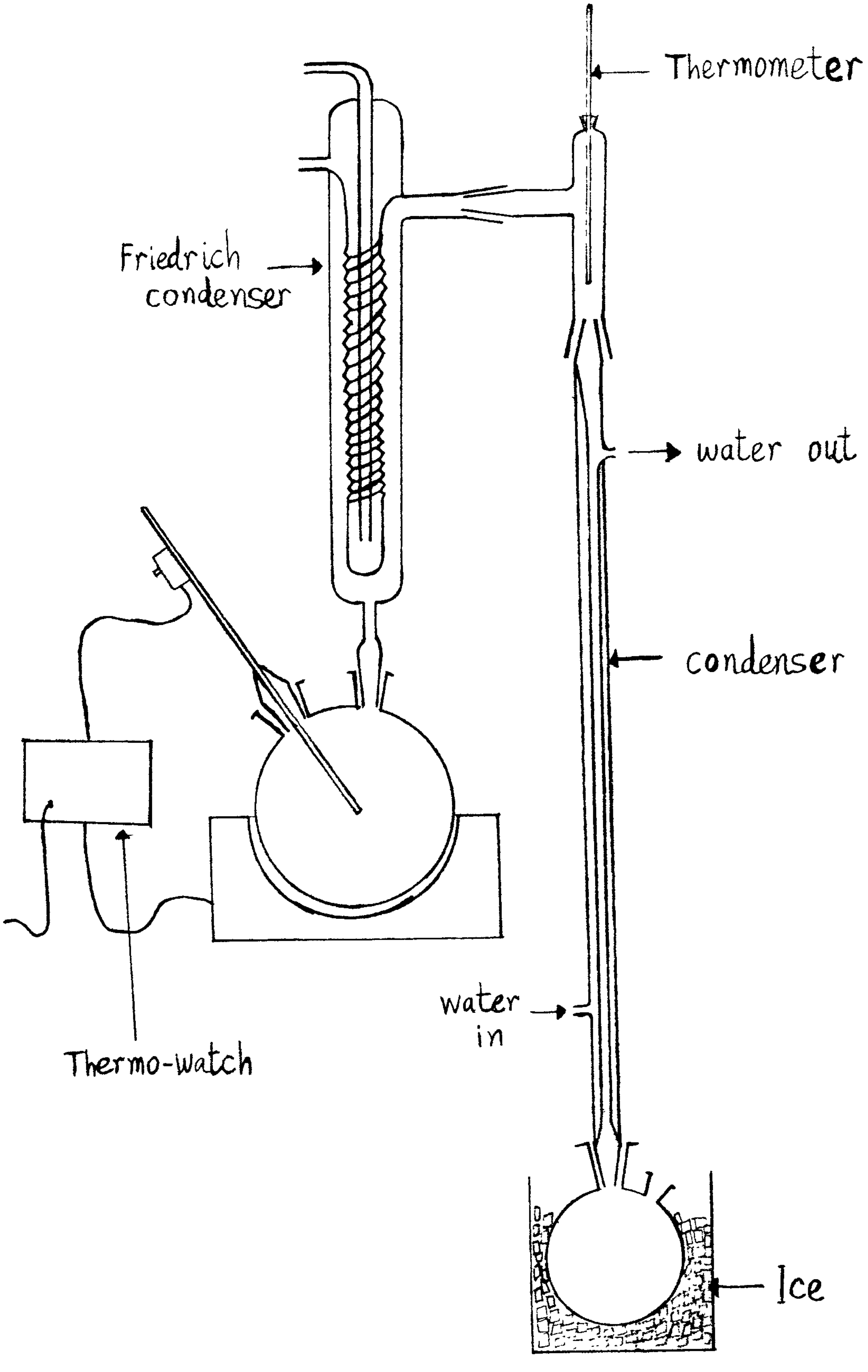


Figure 1 Experimental set-up for monomer recovery.

For solid samples, 1 mg of the sample and 0.060 g of KBr were carefully weighed and finely ground using a mortar and pestle. A small amount of the finely ground powder was taken and pressed into a transparent disc. The disc was then placed on the IR spectrophotometer to run the spectra.

Conditions for running the spectra were as follows:

Chart expansion : 1
Scan time : 3 minutes.

(b) Viscosity Average Molecular Weight $\overline{M_V}$

An Ubbelohde viscometer was employed to determine the viscosity average molecular weight $\overline{M_V}$ of PCPD prepolymer.

The Ubbelohde viscometer was cleaned with toluene and dried. The viscometer was securely fastened in a constant-temperature water bath maintained at 25 ± 0.02 °C. With a pipet, 12ml of the prepolymer stock solution, 1g/dL, (toluene was the solvent) was transferred into the viscometer. After temperature equilibrium had been attained, the solution was brought to the level above the upper graduation mark of the bulb by applying pressure through a second limb of the viscometer, meanwhile the third limb of the viscometer was closed by a finger. The solution was then allowed to run down the capillary tube, freely to the bulb, by releasing the pressure and finger off the other two tubes. The flow time for the solution to travel between the upper and lower marks on the viscometer was recorded. The process was repeated at least once in order to obtain an average precise flow time.

The concentration of the polymer solution was changed by adding 2 ml of the solvent to the solution. For each new concentration, the flow time of the solution was determined by the same procedure as described above. Five different concentrations were made and their flow times were determined. Finally, the efflux time of the solvent was also determined.

The constants, *a* and *k* for the Mark-Houwink equation, $[\eta] = k\overline{M_V}^a$ were taken from the literature to be 0.86 and 5.39×10^{-5} dL/g respectively [3]. They were used in calculating the viscosity average molecular weight, $\overline{M_V}$, of PCPD.

(c) Vapor Presure Osmometry (VPO)

A Wescan vapor pressure osmometer was used to measure the vapor pressure lowering of dilute polymer solutions of PCPD. The concentrations of the solutions ranged from 2-10 g/L. The instrument was calibrated using standard benzil solutions in acetone. The vapor pressure lowering of the standards, which the instrument indicated in terms of voltage difference between the solvent and sample solution was used to determine the calibration factor, K. Using the calibration factor, K, the number average molecular weight, $\overline{M_n}$, of PCPD was determined from the measured voltage differences between the solvent and dilute polymer solutions.

(d) Bulk Viscosity of liquid PCPD

The bulk viscosity of liquid PCPD was determined by a Brookfield viscometer at 60 rpm with spindle model LV #2 at room temperature (~ 21 ^{o}C).

(e) Density of Polymer

A 10-ml pycnometer was used to determine the density of the polymer. The pycnometer was first calibrated with distilled water at room temperature (~ 21 ^{o}C) , which had a density of 0.9989 g/ml. Thus the density of the polymer was compared to that of distilled water under similar room temperature conditions.

(f) Refractive Indices of Monomer and Polymer Samples

The refractive indices of monomer and polymer samples were obtained through measurements on a refractometer at room temperature (~ 21 °C). The instrument was first calibrated with distilled water, which gave a reading of 1.333.

4 SYNTHESIS OF POLYESTER

(a) Chemicals

Maleic anhydride (fw 98.06) certified, Fisher
Ethylene glycol(fw 62.04) Reagent, Brothers
Chlorosulfonic acid (fw 116.52) >98% Fluka.

(b) Synthesis

The polyester was synthesized as a precursor to some of the formulations for the crosslinking of PCPD. In the presence of chlorosulfonic acid, a 1:1 molar ratio of maleic anhydride and ethylene glycol was readily polymerized to polyester. To a weighed amount of finely ground maleic anhydride, approximately 60 g, about 5% (by weight of total composition) chlorosulfonic acid was added and stirred for about a minute. Approximately 40 g ethylene glycol was then added to the mixture and stirring continued for another 3-5 minutes while the reaction continued. With time, the solution got thicker and thicker with the formation of a white viscous liquid while stirring continued.

(c) Dilute Solution viscosity of polyester

A 10g/dl solution of polyester in acetone was prepared and dilute-solution viscosity measurements were taken using the procedure outlined in section 3(b).

(d) Vapor Pressure Osmometry (VPO)

Procedure used was similar to that described in section 3(c).

(e) Infrared Spectrum of polyester

A solution of the polyester in acetone was made. About 4 -5 drops of the solution were smeared onto the surfaces of the IR salt discs. The solvent was allowed to evaporate and the discs were carefully mounted on the window of the spectrophotometer. The IR spectrum of the sample was obtained under the same conditions given in section 3(a).

5 COPOLYMERIZATION OF MALEIC ANHYDRIDE AND CYCLOPENTADIENE

(a) Chemicals

Maleic anhydride (MA) (fw 98.06) certified, Fisher
Cyclopentadiene (CPD),(purified)
Tert-butyl peroxide (fw 146.23) Reagent, Merck.

(b) Procedure

A solution of 0.2 % (by weight of total composition) *tert*-butyl peroxide catalyst in 36.10 g freshly distilled cyclopentadiene was charged into a three-necked round bottomed flask containing 24.18 g molten maleic anhydride, and equipped with a thermometer, stirrer and an inlet and outlet of nitrogen gas. CPD was added in 4 portions over a period of 10 minutes. After the addition, the reaction was carried out at 80 ^{o}C for an additional hour and then cooled to room temperature. The copolymer was then placed in acetone until all of it dissolved. The acetone-soluble sample was reprecipitated by addition of hexane. The solution was then filtered, and the copolymer was dried [11]. It was further characterized and used at another point in the research.

6 CHARACTERIZATION OF COPOLYMER

(a) Infrared spectrum

Procedure similar to that described in section 4(c).

(b) Solution Viscosity.

A stock solution of the copolymer in acetone was made by dissolving 10 g copolymer in 50 ml solvent contained in a 100 ml volumetric flask. The solution was further diluted to 100 ml. Using the method described in section 3(b), the efflux times of five concentrations of the sample were taken and the intrinsic viscosity of the copolymer was determined. Due to the lack of the two constants, *a* and *k*, in the Mark-Houwink equation the viscosity average molecular weight of the copolymer could not be calculated.

7 CURING OF POLYCYCLOPENTADIENE PREPOLYMER (PCPD)

(a) Chemicals

PCPD (obtained from procedure described in section 2)
Cyclopentadiene (CPD) (distilled)
Maleic anhydride (fw 98.06) certified, Fisher
Ethylene glycol (62.04) Reagent, Brothers
N,N′ dimethyl aniline (promoter) Technical, Du Pont
N,N′ dimethyl-p-toluidine (promoter) Pfaltz and Bauer
Chlorosulphonic acid (fw 116.52) >98%, Fluka
Glycerol (fw 92.15) Reagent, Brothers
Benzoyl peroxide (initiator)
Di-tert butyl peroxide (fw 146.23) reagent, Merck
Styrene
Triethylene glycol dimethacrylate (crosslinker)
(fw 286.33) technical, 90-95% Fluka
Divinyl benzene (crosslinker) Pfaltz and Bauer

(b) Procedure

In the process of formulating a crosslinked polycyclopentadiene from the chemicals listed above a lot of formulations were tried. Several of them led to partly crosslinked or uncrosslinked materials. At different stages of the research the chemical compositions of the formulations had to be changed in order to enhance the quality of the product.

(i) Free radical curing of PCPD.

The first thing that was done in curing polycyclopentadiene was to duplicate Ning's work [3]. As expected the polymer could be cured without catalyst at high temperatures and long reaction time as described in his thesis. In order to find out the effect of free radicals on curing , three samples of 1:1 molar ratio of distilled CPD to MA were heated separately with 5% glycerol and 0.1% free radical-producing initiator to 170°C. The initiators used varied from benzoyl peroxide (BPO), azobisisobutyronitrile (AIBN), to *tert*-butyl peroxide (t-BPO).

(ii) Curing of CPD with molten MA

It has been described in literature [11] that MA , when it is in liquid form or in the molten state reacts well with CPD and PCPD. This led to two choices, either to dissolve MA in a solvent which may also be a crosslinking agent, or to melt it by heating. Both methods were tried and interesting results were observed.

Maleic anhydride melts between 53-55^{o}C so that reactions of MA in its molten state were carried out above 55^{o}C. Normally, the initiator decomposes at 80^{o}C. Therefore it was necesarry to introduce a promoter capable of promoting the decomposition of initiator to free radicals at room temperature and a crosslinking agent that could be initiated to react by radicals. At this point divinyl benzene (DVB) and N,N'-dimethyl aniline were chosen as curing agent and promoter respectively. The formulations in this section were made using 2 mixtures. Mixture A contained CPD (mononer) and t-BPO (initiator), and mixture B contained glycerol, DVB and N,N'-DMA. Mixture A was added to the molten MA, immediately followed by mixture B.

(iii) Chlorosulfonic initiated Curing of CPD

In another set of formulations, chlorosulfonic acid (CSA), a cationic initiator for diene monomers [12] was used to dissolve MA. (Chlorosufonic acid is a good solvent for MA). However, the amount of CSA used to completely dissolve MA also caused CPD to decompose instantaneously.

The immense heat generated from the decomposition resulted in the reaction mass being burnt to yield a carbonaceous residue.

By trial it was found that MA dissolves in ethylene glycol and glycerol to some extent. To overcome the problem of burnt products, a mixture of ethylene glycol, EG (larger amount), and CSA was used to dissolve MA. It must be pointed out here that it was at this point that it was realized that the mixture of MA, EG and CSA is actually an unsaturated polyester (CSA acts as cationic catalyst).

(iv) Curing of CPD/PCPD mixture

When the above formulations failed to yeild cured polymers a new promoter and curing agent were applied. In commercial polyesters, styrene is often used as crosslinker. In order to have an enhanced effect, besides styrene, triethyleneglycol dimethacrylate was also added as an additional curing agent to replace divinylbenzene. Meanwhile, N,N′-dimethyl- aniline was replaced by N,N′-dimethyl-p-toluidine.

With these chemicals, two mixtures, A and B, were formulated. Addition of mixture A, which consisted of monomer (cyclopentadiene), crosslinking agent (TEGDMA/ styrene), promoter (N,N′-DMPT) and initiator (BPO), to mixture B, which consisted of freshly made polyester prepolymer, resulted in a sharp rise in temperature of the reaction mixture (up to about 80^{o}C). However, the heat could not be sustained to cure the mixture.

In a similar set of formulations, CPD was replaced by the more viscous PCPD. For this set of curing reactions, no appreciable amount of heat was generated. However, a mixture of PCPD and CPD in a ratio of about 10:1 (by volume) resulted in an exothermic reaction. The heat given off by the reaction was sufficient to make the product more viscous. The observation made here was that with more viscous PCPD in the formulation, it resulted in a more viscous end product. Thus, the choice of PCPD sample A-11 for later fomulations was based on this observation. Although the formulations with a combination of monomer and polymer, CPD/PCPD, failed to cure at room temperature, but they were indeed cured at 60^{o}C. It became clear that CPD had no significant impact on curing at room temperature and therefore it was abandoned in later formulations.

(v) Curing of PCPD and polyester mixture

In an attempt to understand the crosslinking process, a number of selected reactions were carried out step by step.

The initial step involved the formation of an unsaturated polyester prepolymer, by reacting MA and EG in the presence of CSA (as previosly described). The next step involved the addition of PCPD followed by other additives. The following observations were made:

1. Adding PCPD only to the polyester prepolymer formed two distinct layers with PCPD as the top layer. The two layers remained immiscible even after vigorous stirring. However, heating at 60^{o}C for about 10 minutes caused mixing between the two layers to form a homogeneous liquid which was more viscous than both initial liquids.

2. When heat was removed from the system after homogenization had taken place, the liquid sample began to increase in viscosity but could dissolve in acetone.

3. Addition of styrene, with BPO dissolved in it, and triethyleneglycol dimethacrylate, with N,N-dimethyl-p-toluidine dissolved in it, to PCPD-polyester mixture that had been homogenized and cooled to room the temperature resulted in a crosslinked product after 48 hours.

4. The curing time of the formulation mentioned in 3 could be reduced to 2 hours when the curing reaction was carried out at 60^{o}C.

(c) % Sol, gel, and swelling

% sol, gel, and swelling were determined for the cured PCPD by swelling a weighed amount of sample in acetone, N,N'-dimethylformamide or toluene. The solvent to sample ratio was about 100:1 and the total extraction time was 72 hours. At the end of the extraction period, the samples were taken out of the solvents and the excess solvent on the surface of the sample was removed. The swollen polymers were weighed in stoppered weighing bottles and the % swelling was calculated as follows :

$$\% \text{ Swelling} = [(W_2 - W_1) \text{ X } 100] / W_1 \text{ .... eq 1}$$

where

W_1 = weight of dry sample before swelling and

W_2 = weight of swollen sample

% of sol content was determined by the ratio of the extractable sample weight to the initial weight of the sample. To determine the weight of the extracted solid, the extraction solution was filtered through a filter paper and the filtrate was allowed to evaporate to dryness The weight of the solid residue was determined. The % sol and gel were calculated according to the following equations:

$$\% \text{ Gel} = [100 \times W_3\,]/\,W_1 \quad \ldots\ldots\ldots \text{ eq } 2$$

$$\% \text{Sol} = 1 - \% \text{ Gel} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{ eq } 3$$

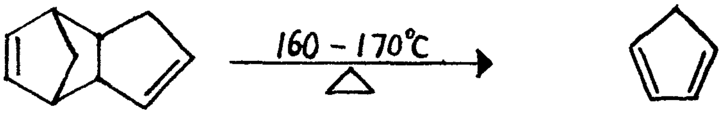
where

W_3 = weight of solid residue after filtration.

RESULTS AND DISCUSSION

1 PURIFIED MONOMER

Thermal cracking of the dimer, dicyclopentadiene, to the monomer, cyclopentadiene at temperatures between 160 - 170°C can be represented by the following equation :



dicyclopentadiene cyclopentadiene

Some of the properties of the monomer measured are listed in Table 1.

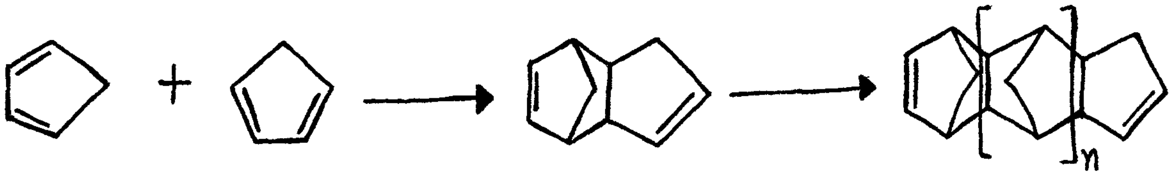
Table 1 Properties of 1,3 cyclopentadiene

Property	Value
Density, 25 °C, g/mL	0.8024
Boiling point, °C	41.5
Refractive index, *n*	1.5085

2 POLYCYCLOPENTADIENE SYNTHESIS

(a) Mechanism

The synthesis of PCPD from its monomer, CPD, has been found to occur via a Diels-Alder mechanism where one CPD molecule acts as a diene while another as a dienophile. The dimer which is formed also has two double bonds but they are not conjugated as is the case for the monomer. The dimer, thus reacts with a monomer in another Diels-Alder fashion, acting as the dienophile and the monomer, the diene. This mechanism is followed in the formation of oligomers and high polymers.



[13].

The reaction is followed by observing time and temperature change of the reactant as the reaction proceeds. Samples are drawn out from the reaction mass on hourly intervals for later check of their degrees of polymerization through IR spectra and refractive indices. Table 2 lists the reaction time / temperature and the refractive index for each sample taken.

Table 2 Polymerization of CPD

Sample	Time hrs	Temp °C	Ref. Index
CPD	0	25	1.5085
A-1	1	53	1.5090
A-2	2	63	1 5095
A-3	3	130	1.5135
A-4	4	155	1.5150
A-5	5	161	1.5170
A-6	6	164	1.5175
A-7	7	168	1.5180
A-8	8	170	1.5190
A-9	9	172	1.5195
A-10	10	174	1.5200
A-11	11	174	1.5202

The sample taken at the 12th hour became cloudy as it was cooled to room temperature, and was partially insoluble in acetone.

Figure 2 is a plot of temperature and refractive index against the reaction time. It is of interest to note that within the first two hours the rise in temperature and refractive index are relatively low. That indicates a small fraction of the monomer is converted to the oligomer. The sharp rise in temperature and the refractive index between the second and fourth hours of reaction indicates a high conversion of monomer to oligomers. Between 5 to 11 hours of reaction, the change in temperatures and refractive index become gradual and tend to level off. After 11 hours of reaction, the samples that are drawn out become cloudy when allowed to cool to room temperature. The solid precipitate obtained does not dissolve in acetone which suggests the presence of high molecular weight or partially crosslinked polymers.

(b) Infrared analysis of CPD and PCPD

Figures 3-9 show the IR spectra of CPD and other samples of PCPD at different polymerization times. Some of the vibrational bands that are worth considering are:

2900 cm^{-1}	CH_2 stretch
1590 cm^{-1}	C=C stretch
1360 cm^{-1}	=CH in-plane bend

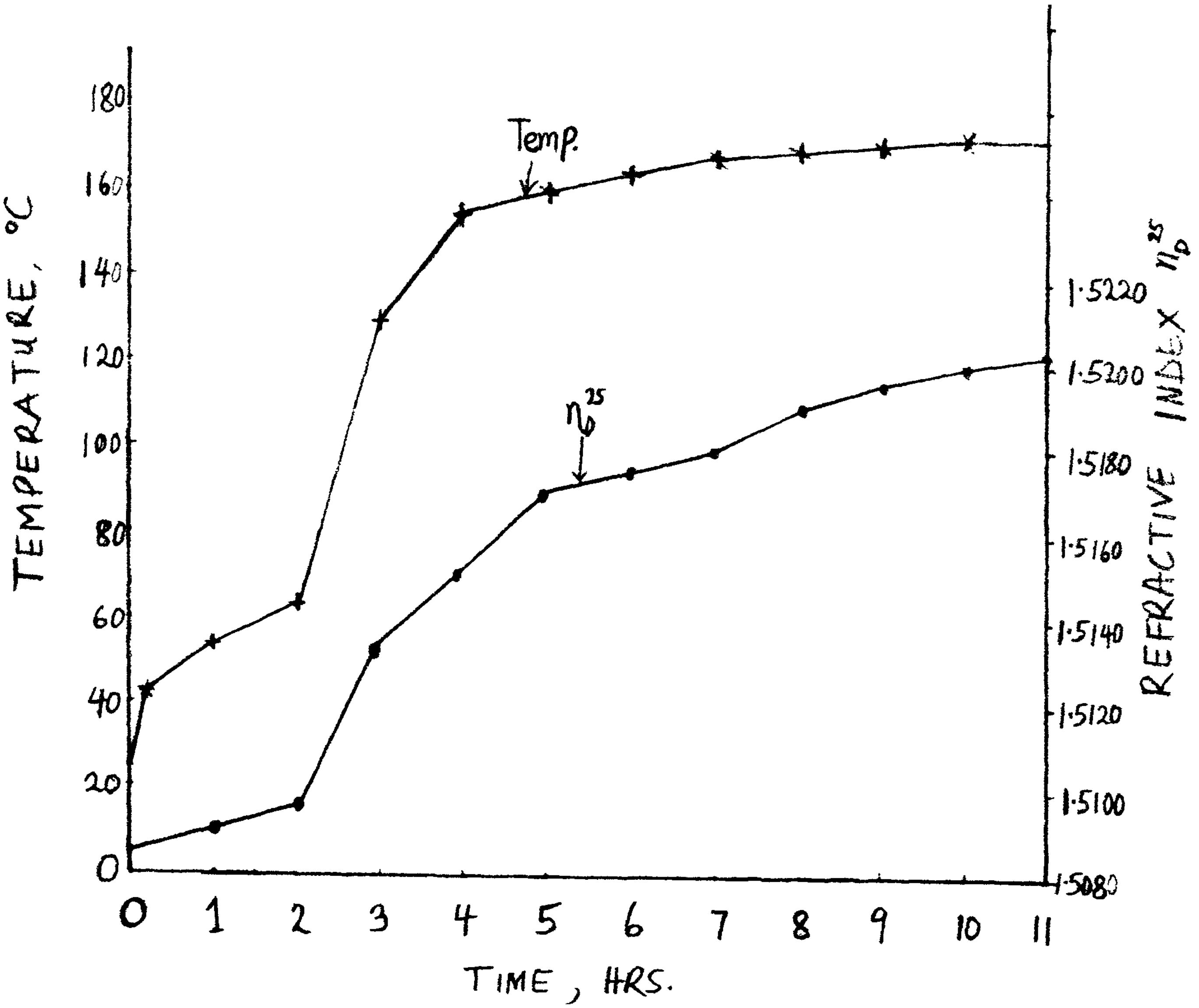


Figure 2 Plot of Temperature and Refractive Index against Time of polymerization of PCPD

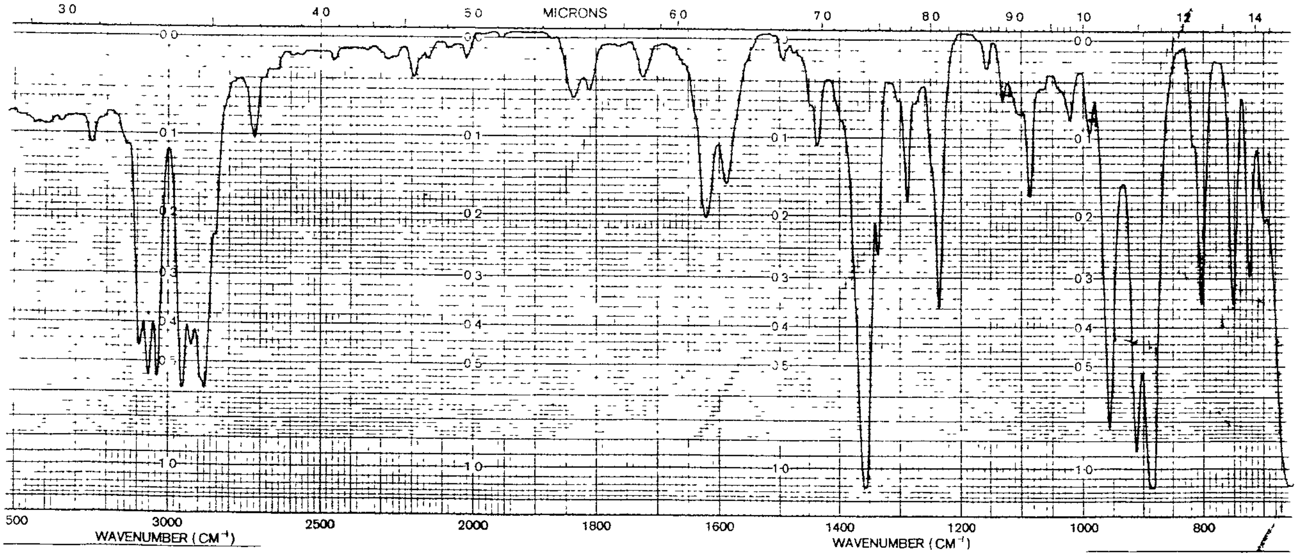


Figure 3 IR of CPD monomer.

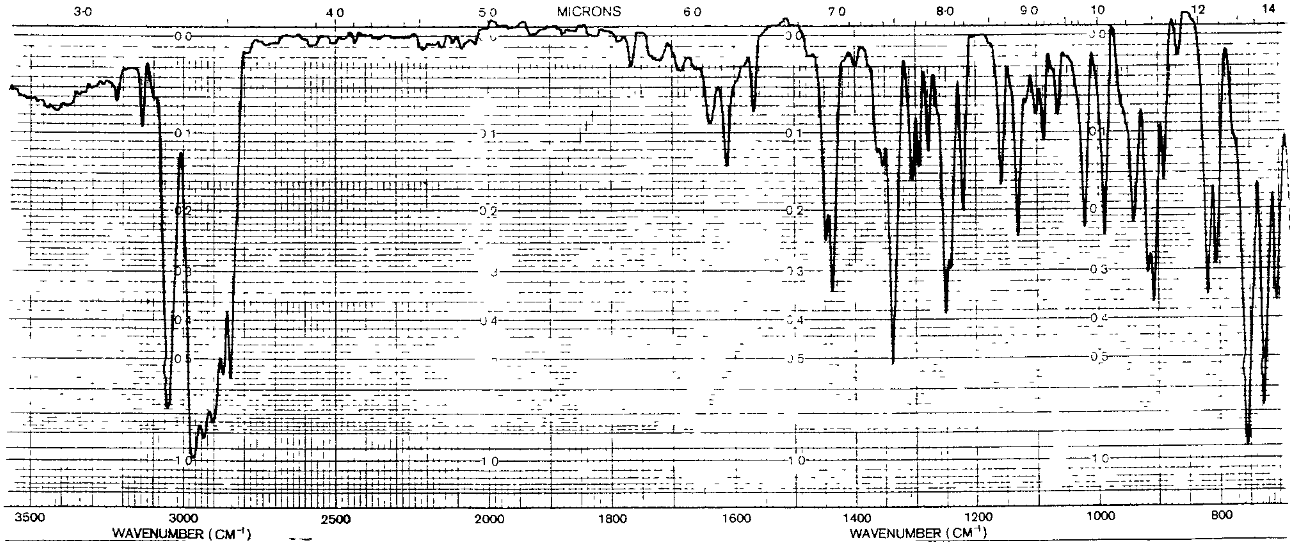


Figure 4 IR of PCPD, A-1

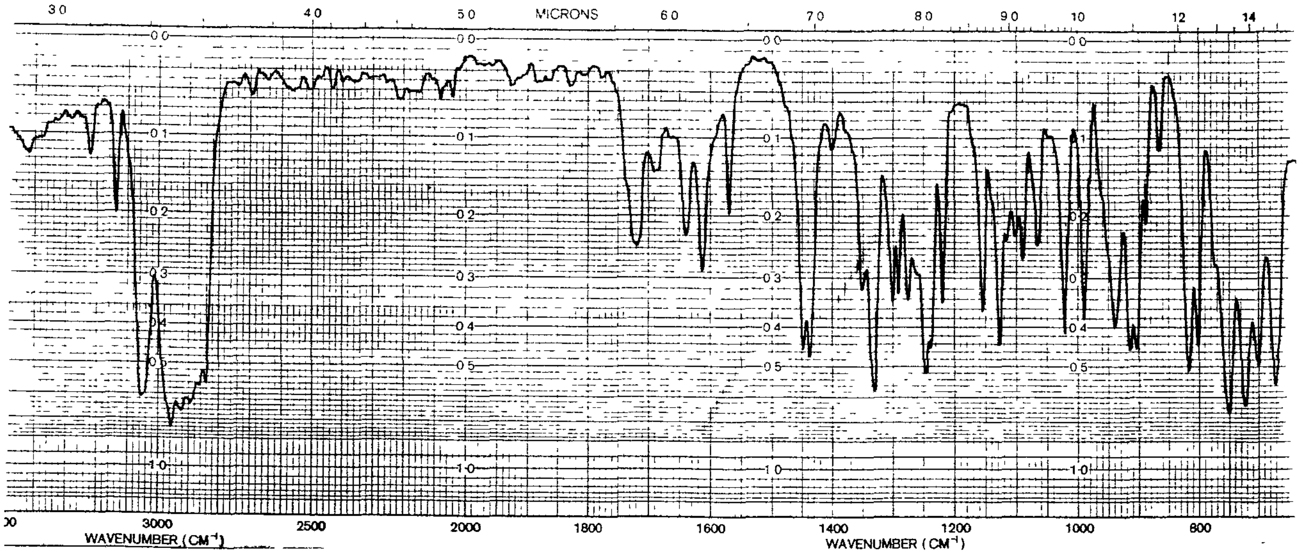


Figure 5 IR of PCPD, A-3

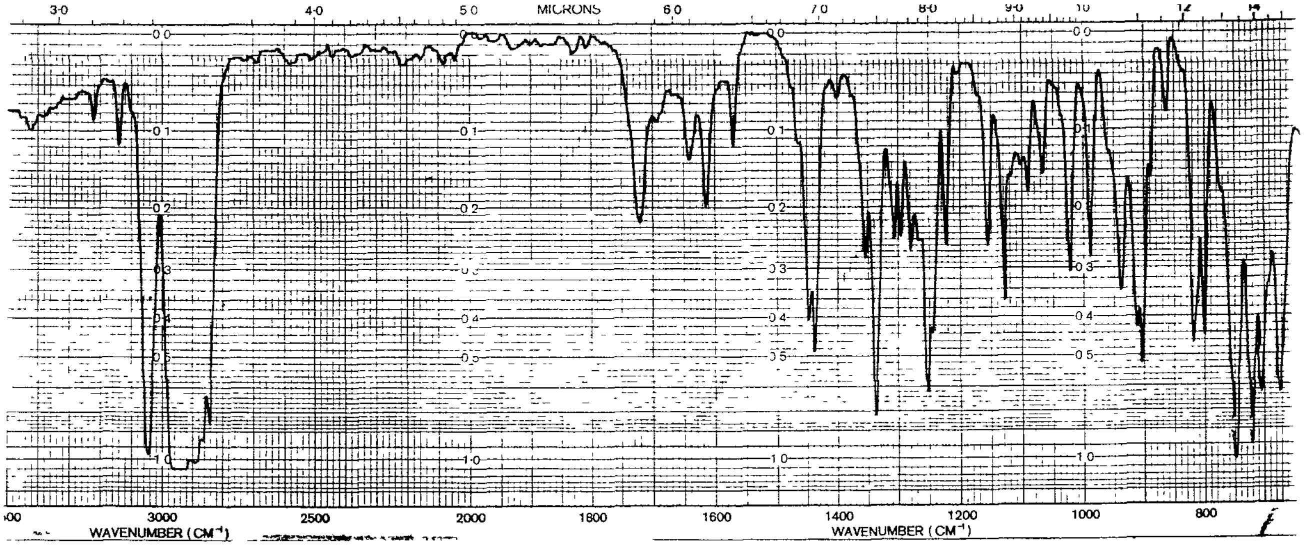


Figure 6 IR of PCPD, A-5.

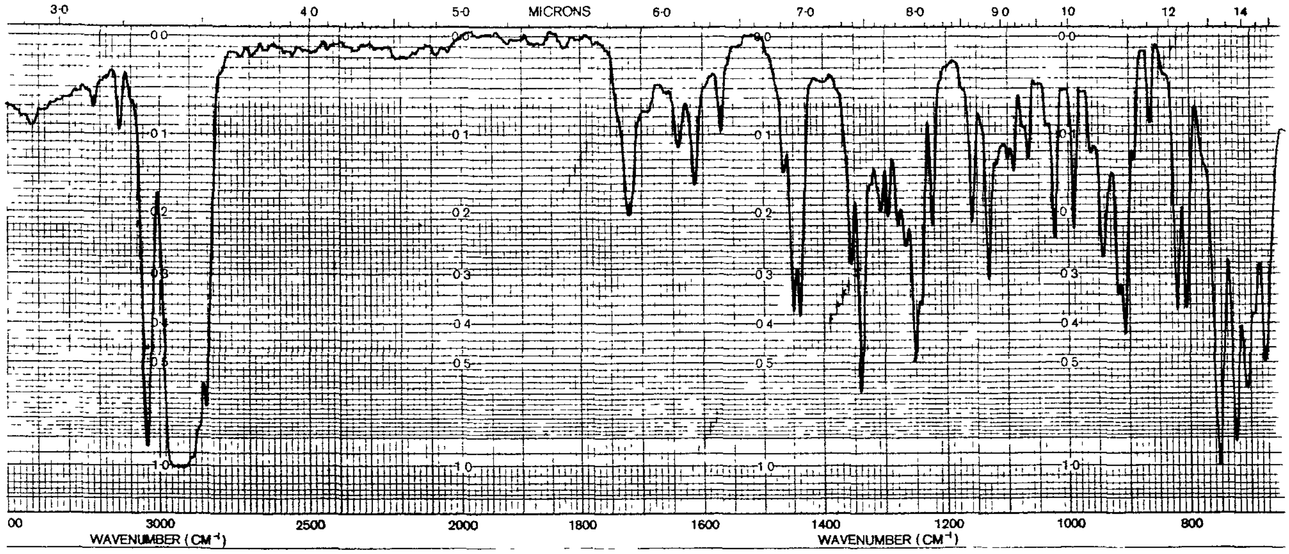


Figure 7 IR of PCPD, A-7.

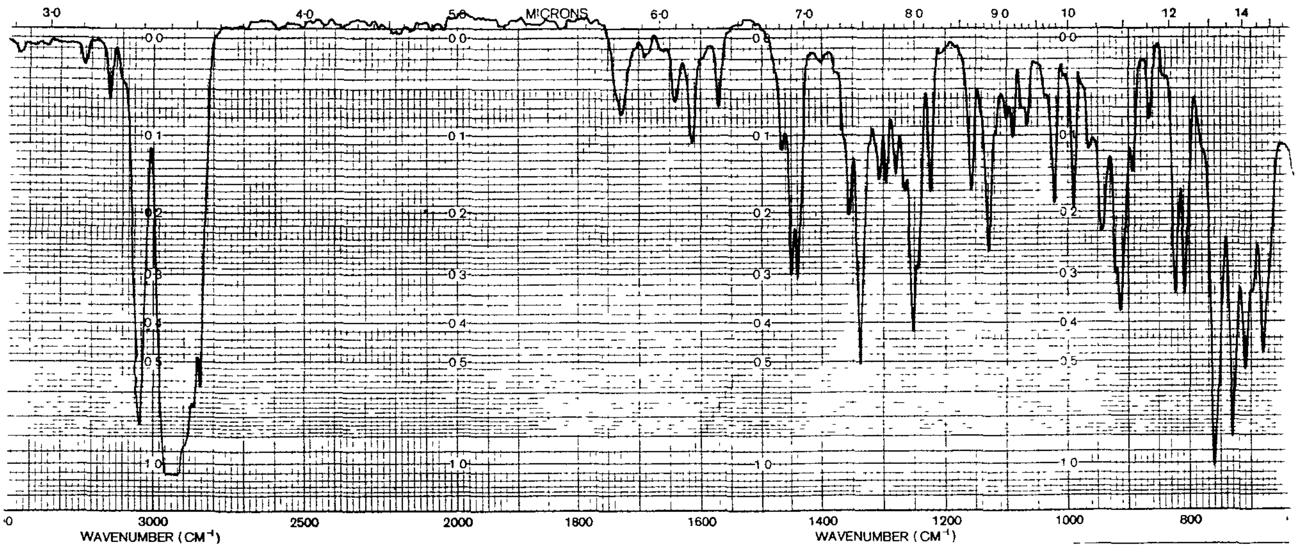


Figure 8 IR of PCPD, A-10.

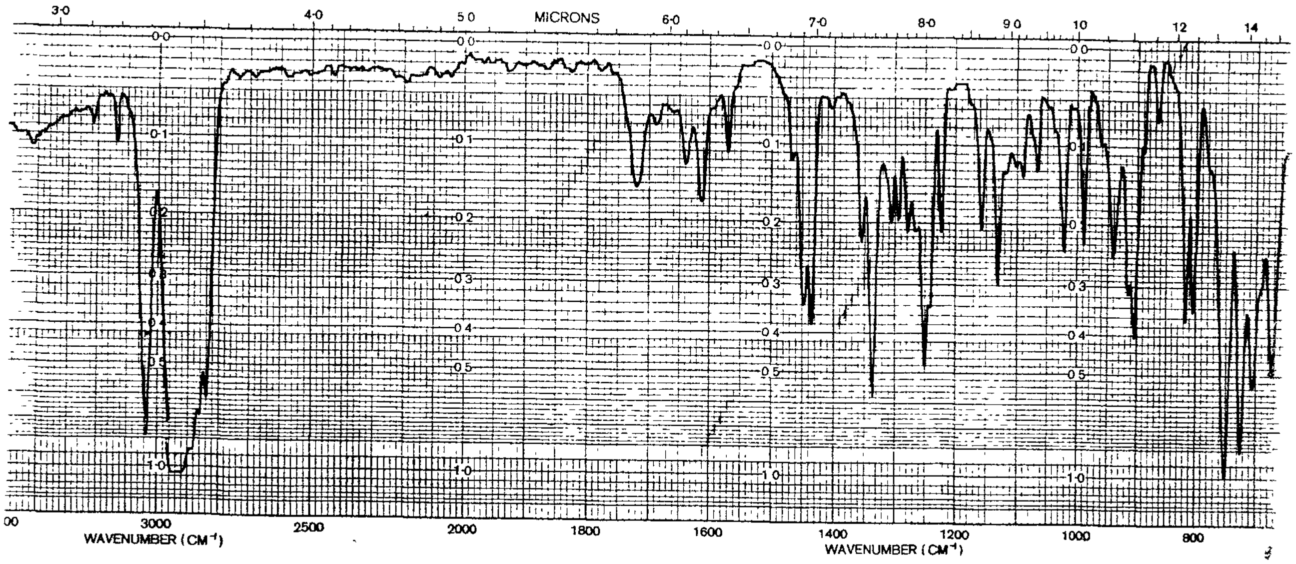


Figure 9 IR of PCPD, A-11.

There are several IR spectra of CPD that have been published. However, some of the published spectra show bands that are due to DCPD, which is known to form readily from the monomer at room temperature. As a consequence, the proposed assignments are partly contradictory and more or less incomplete. A combination of spectra obtained from solid, liquid and gas phases has been reported as a way of solving the problem [14].

The monomer shows a CH_2 stretching band (2900 cm^{-1}) which is quite strong. However, a look at the other spectra shows that the band gets much stronger with time. It is consistent with the fact that the monomer, CPD, has one single CH_2 group, the dimer has two, the trimer three and so on. In the case of the C=C stretch (1590 cm^{-1}) and =CH bending (1360 cm^{-1}), CPD shows moderate and strong absorptions respectively but in the process of polymerization, these two band intensities decrease. This can be accounted for by the fact that chain addition involves breaking of double bonds, hence depleting the system of C=C groups.

(c) Molecular Weight of PCPD (Sample A-11)

(i) By dilute solution viscometry

The previous work by Ning included measurements of the viscosity-average, $\overline{M_v}$, and the number-average, $\overline{M_n}$, molecular weights of PCPD polymerized over different periods of time. From the results of $\overline{M_n}$ obtained by vapor pressure osmometry, VPO, the values of the constants *a* and *k* in the Mark-Houwink equation, $[\eta] = k\overline{M_v}^a$ have been determined [3]. In calculating the molecular weight of sample A-11, which proved to be successful for the curing process in this research, Ning's *a* and *k* values have been used.

At a constant temperature of 25 ±0.02 °C, and using toluene as the solvent for the measurements, Table 3 shows the results of dilute-solution viscosity measurements using an Ubbelohde viscometer.

Table 3 Data for PCPD viscosity measurements

t_o(sec)	t(sec)	$t/t_o(\eta_r)$	η_{sp}	C g/dl	η_{sp}/C	$\ln\eta_r/C$
64.33	71.275	1.108	0.108	1	0.108	0.1026
	69 85	1.086	0.086	0.857	0.100	0.2370
	68.775	1.069	0.069	0.75	0.092	0.3544
	68.215	1.060	0.060	0.667	0.089	0.4632
	67.77	1.053	0.053	0.600	0.088	0.5627

Note: $\eta_{sp}=(t-t_o)/t_o$

A plot of η_{sp}/C against C is shown in figure 10. The vertical intercept of 0.0527, gives the intrinsic viscosity $[\eta]$, of PCPD labelled A-11. Using the Mark-Houwink equation,

$$[\eta] = k\overline{M_v}^a$$

with k = 5.39 X10^{-5} dl/g and a = 0.86 the viscosity average molecular weight of the polymer, $\overline{M_v}$ is 3000. This value indicates that the polymerization reaction produces oligomers even after 11 hours of reaction.

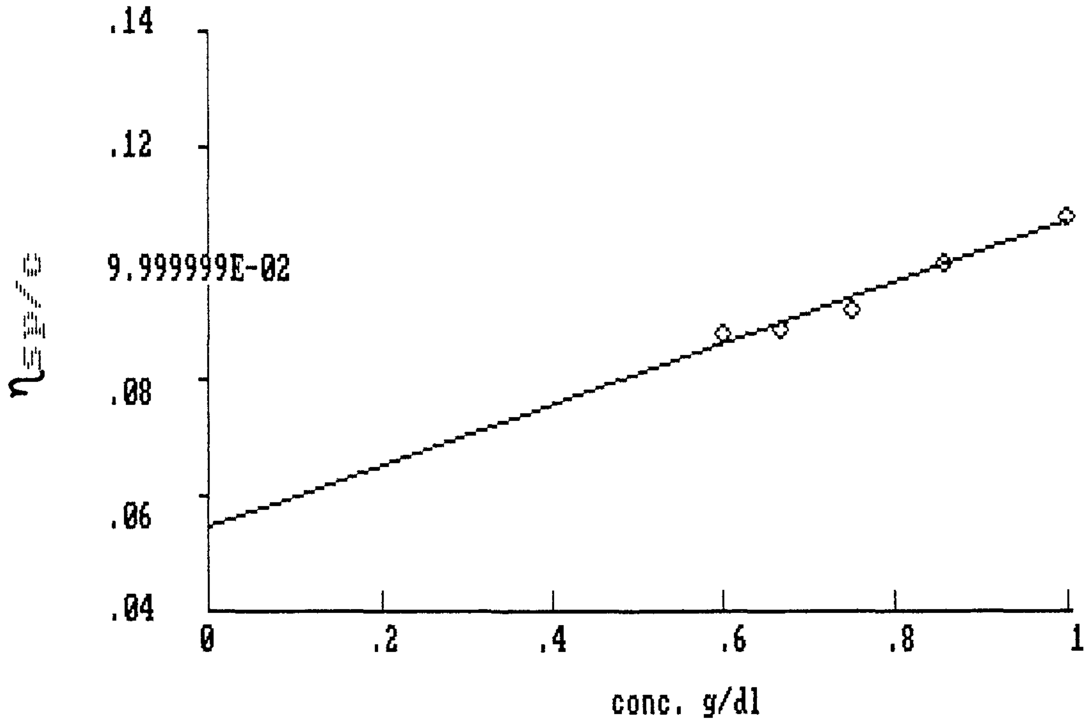


Figure 10 Plot of ηsp/C vs. C for PCPD-Toluene system.

(ii) By Vapor Pressure Osmometry (VPO)

The standard benzil solutions used for VPO measurements and their corresponding voltage reading are tabulated in Table 4.

Table 4 Vapor Pressure Osmometry data for Benzil

Concentration (g/L)	Reading, V (microvolts)	ΔV $(V-V_o)$	$\Delta V/C$
2.5	43.55	37.75	15.10
5.32	84.85	79.05	14.86
7.5	115.0	109.2	14.56
8.5	129.3	123.5	14.5
10.0	147.8	142.0	14.2

Solvent, $V_o = 5.8$

A plot of $\Delta V/C$ against C shown in Figure 11 gives a straight line with a vertical intercept of 15.45. This data plot is based on the following equation:

$$\Delta V/C = K/\overline{M_n} + A_2CK$$

where V = signal response in microvolts

C = concentration in g/L

K = calibration factor

A_2= second viral coefficient and

$\overline{M_n}$= number average molecular weight.

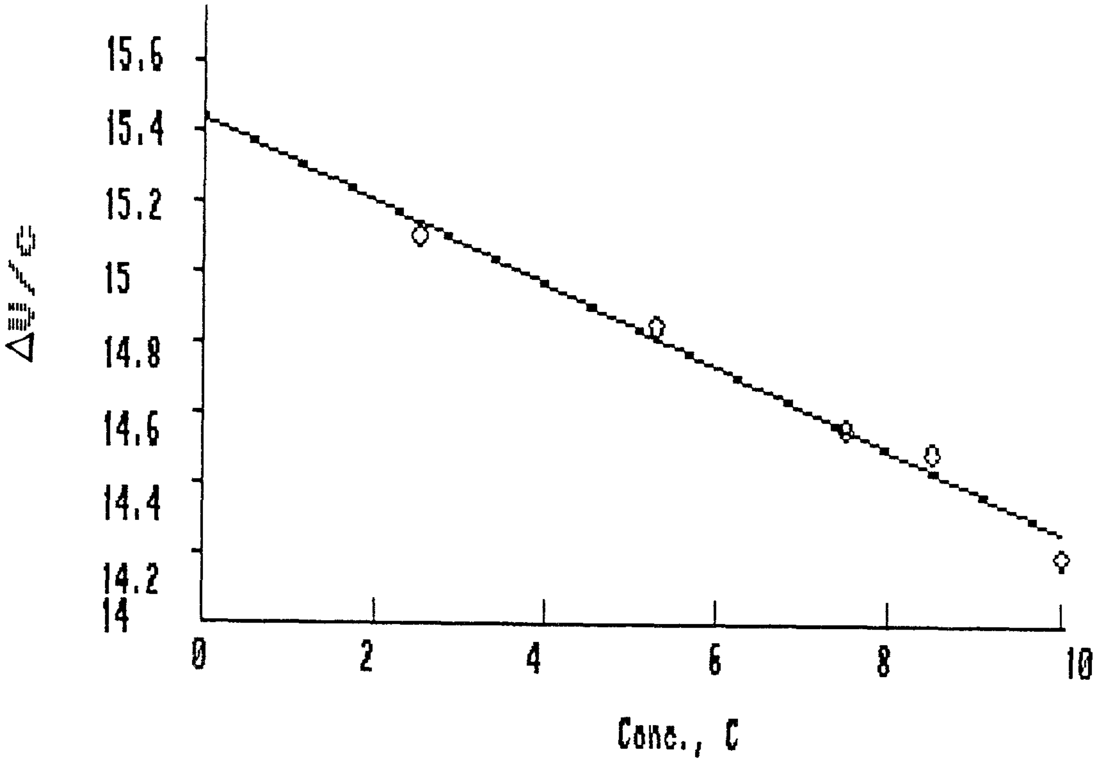


Figure 11 Calibration plot of $\Delta\nu$/C vs. C of Benzil

From the vertical intercept, the calibration factor is calculated to be 3240 (the molecular weight of benzil is 210.23).

Figure 12 shows the plot of $\Delta\nu$/C against C for the polymer sample after the 11th hour. From the vertical intercept, the molecular weight of the sample is calculated to be 3100, which is consistent with the 3000 that resulted from intrinsic viscosity measurements (page 34).

(d) Bulk Viscosity of PCPD

The average value of the readings obtained from the Brookfield viscometer is 1.6. With a multiplication factor of 5, and LV #2 spindle at 60 rpm, the bulk viscosity of the polymer sample A-11 is 8.0 cps.

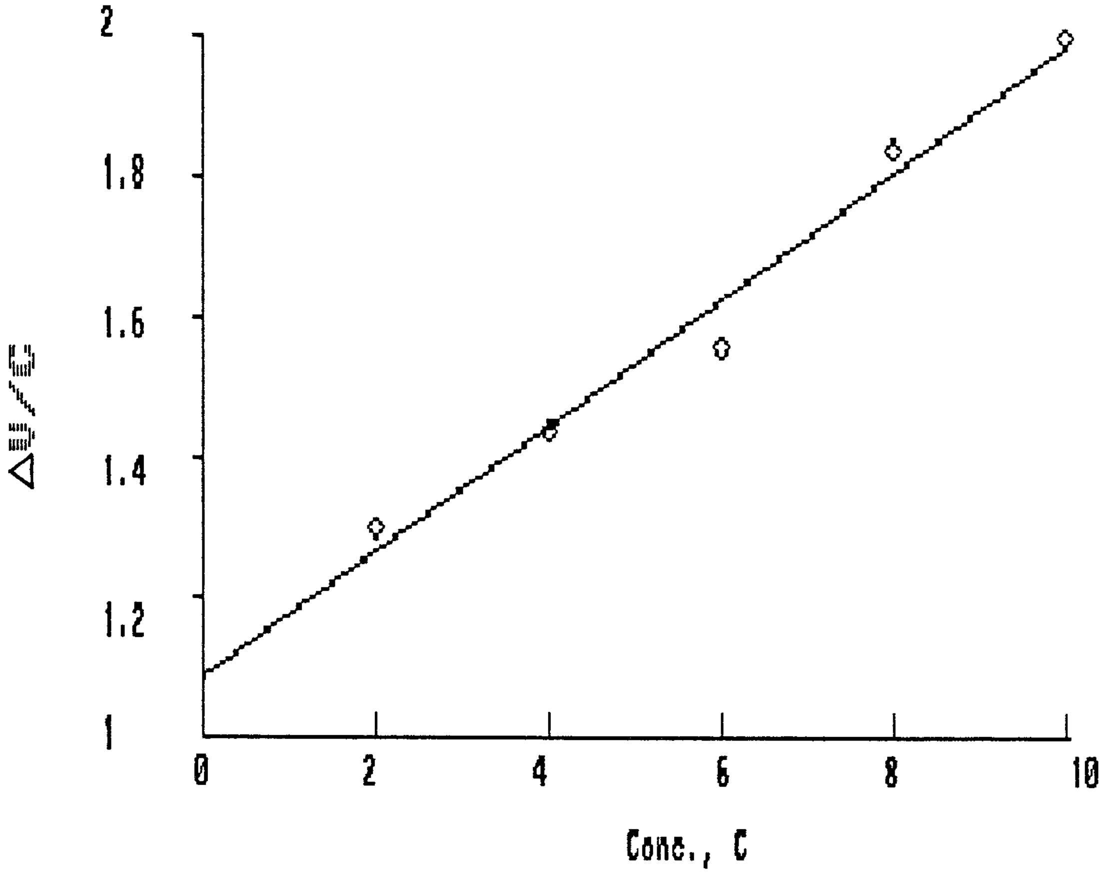


Figure 12 Plot of ΔV/C vs. C for PCPD (A-11).

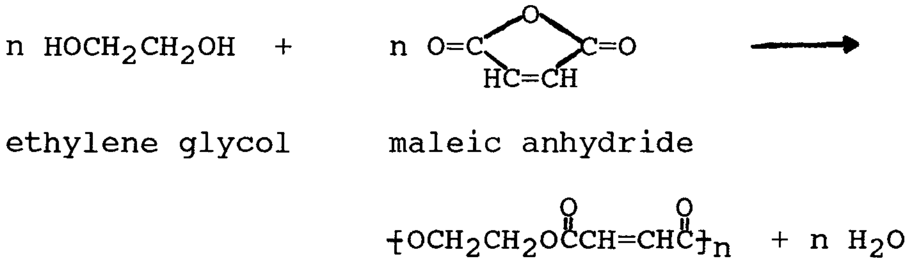
(e) Density of PCPD

The density of the polymer is found to be 1.0133 g/ml, slightly larger than that of water, 0.9989 and the monomer, 0.8024 g/ml.

3 POLYESTER

(a) Polymerization Mechanism

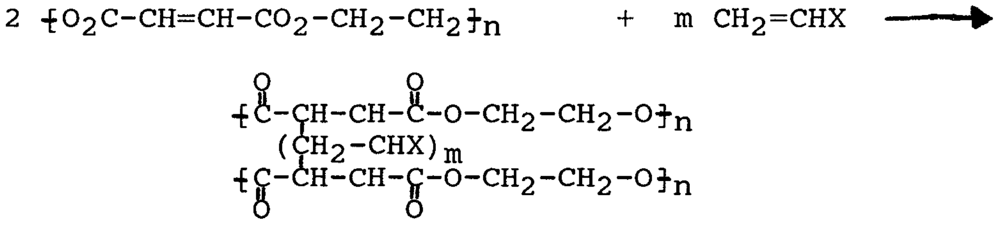
Generally, the formation of a polyester can be classified under one of several categories based on the mechanism of its synthesis. The major reaction types include: (a) direct reaction of a dibasic acid and a glycol (b) interchange reaction between a glycol and an ester and (c) reaction between an acid anhydride and a glycol [15]. The polyester made in this project is based on the third mechanism. With the cationic catalyst, chlorosulfonic acid, the polymerization of maleic anhydride and ethylene glycol proceeds with the formation of unsaturated polyester and water:



unsaturated polyester

The first step of the reaction, which involves the addition of the initiator, chlorosulfonic acid, to maleic anhydride is endothermic. As maleic anhydride begins to dissolve in the chlorosulfonic acid the temperature of the mixture drops rapidly to 10°C from room temperature, about 21°C. However, in the second step of addition of ethylene glycol to the mixture, the temperature of the reaction mass rises to about 82°C. The overall reaction can therefore, be described as exothermic. The polymer is formed within 15 - 20 minutes after the addition of ethylene glycol. The unsaturated polyester is a viscous liquid and is soluble in acetone.

It has been shown that crosslinking of unsaturated polyesters can be carried out by copolymerization with a difunctional compound [16,17,18,19]. Low molecular weight unsaturated polyesters can be transformed to a thermoset plastic by heating them with a vinyl monomer and a free radical initiator. The crosslinking process which involves the copolymerization of the added monomer with the double bonds of the polyester can be represented by the following equation:



$$2\ \left[O_2C-CH=CH-CO_2-CH_2-CH_2 \right]_n \quad + \quad m\ CH_2=CHX \longrightarrow$$

$$\begin{array}{c} \left[\overset{O}{\overset{\|}{C}}-CH-CH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O\right]_n \\ (CH_2-CHX)_m \\ \left[\underset{O}{\underset{\|}{C}}-CH-CH-\underset{O}{\underset{\|}{C}}-O-CH_2-CH_2-O\right]_n \end{array}$$

The mechanical properties of the crosslinked product depend on the number of crosslinks between polyester chains and the length of the crosslinks. The number of crosslinks per polyester chain depends on the relative amount of the unsaturated diacid used in synthesizing the prepolymer, and the length of the crosslinks depends not only on the relative amounts of the prepolymer and the monomer but also on the copolymerization behaviour of the two double bonds [20].

(b) Curing of Polyester

The curing process is effected at room temperature by adding styrene (monomer), benzoyl peroxide (initiator) and N,N'- dimethyl-p-toluidine (promoter) to the polyester with vigorous stirring for about half hour. The mixture becomes cured (solid) in about 2 hours, on standing. The cured polymer is no longer soluble in acetone. In another case, the combination of triethylene glycol dimethacrylate and styrene has been proved to be more effective in curing of the polymer.

(c) Intrinsic Viscosity

The polymer dissolves in acetone and therefore acetone was used to determine the intrinsic viscosity of the polymer. However, since values of the two constants a and k in the Mark-Houwink equation can not be found in the literature for this particular polymer, its viscosity-average molecular weight, $\overline{M_v}$, can not be calculated. Table 5 shows the results of solution viscosities measured in a Ubbelohde Viscometer at 25°C.

Table 5 Viscosity data for the polyester.

t_o(sec)	t(sec)	$t/t_o(\eta_r)$	η_{sp}	C(g/dl)	η_{sp}/C
42.315	56.35	1.3317	0.3317	10	0.0332
	53.68	1.2686	0.2686	8.57	0.0313
	52.04	1.2297	0.2297	7.5	0.0306
	50.74	1.1989	0.1989	6.67	0.0289
	49.79	1.1767	0.1767	6.0	0.0294

where t_o and t denote the flow time of the solvent and the solution respectively, and C, the concentration of the solution.

Figure 13 shows a plot of $(t-t_o)/t_oC$ or η_{sp}/C against C The intercept on the vertical gives the intrinsic viscosity, $[\eta]$ 0.0237 dl/g, of the polymer. This suggests that the polymer has a low molecular weight.

(d) Vapor Pressure Osmometry (VPO)

Figure 14 shows the plot of $\Delta V/C$ against C from data obtained from VPO measurements. With a vertical intercept of 1.35, the number average molecular weight, $\overline{M_n}$, of the polyester is calculated to be 2400.

(e) Infrared spectrum of polyester.

The IR spectrum of the polyester is shown in Figure 15. No literature spectrum is found for this polymer.

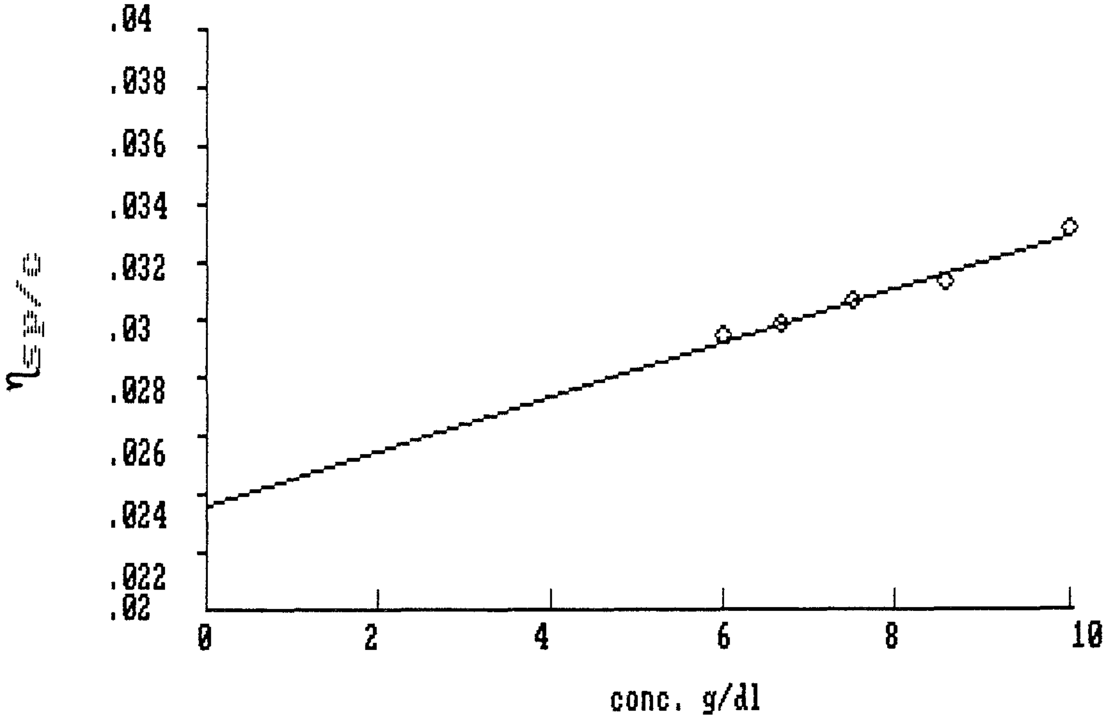


Figure 13 Plot of ηsp/C vs. C for polyester-acetone system

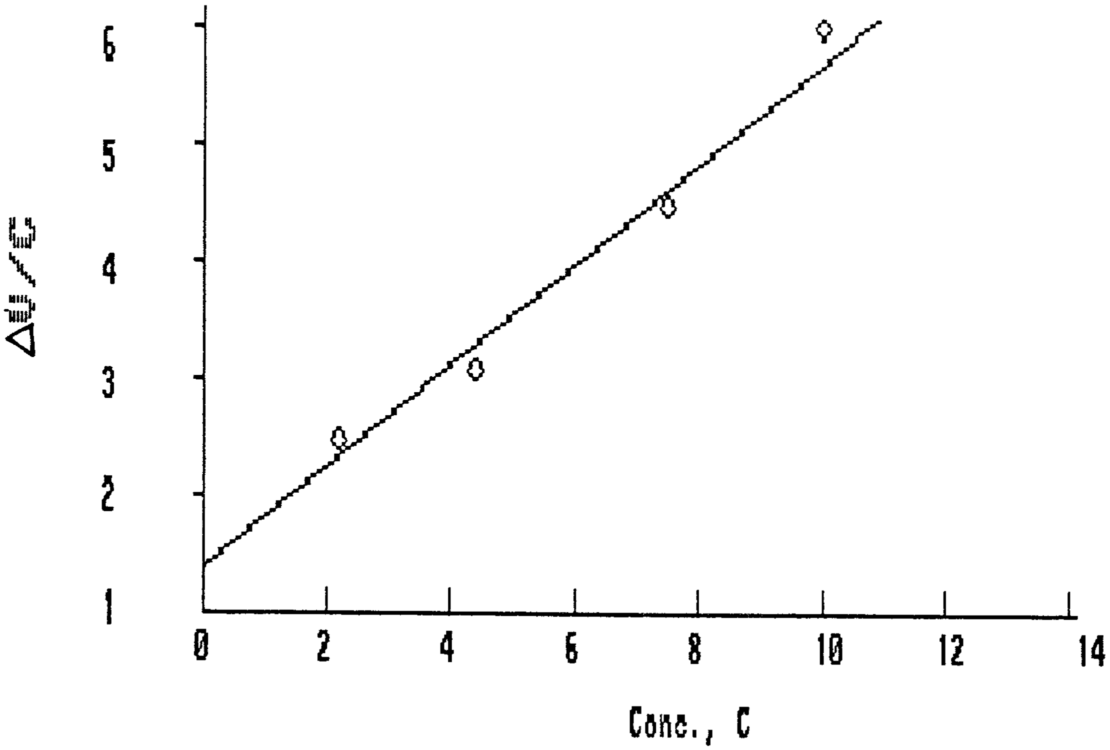


Figure 14 Plot of ΔV/C against C for polyester.

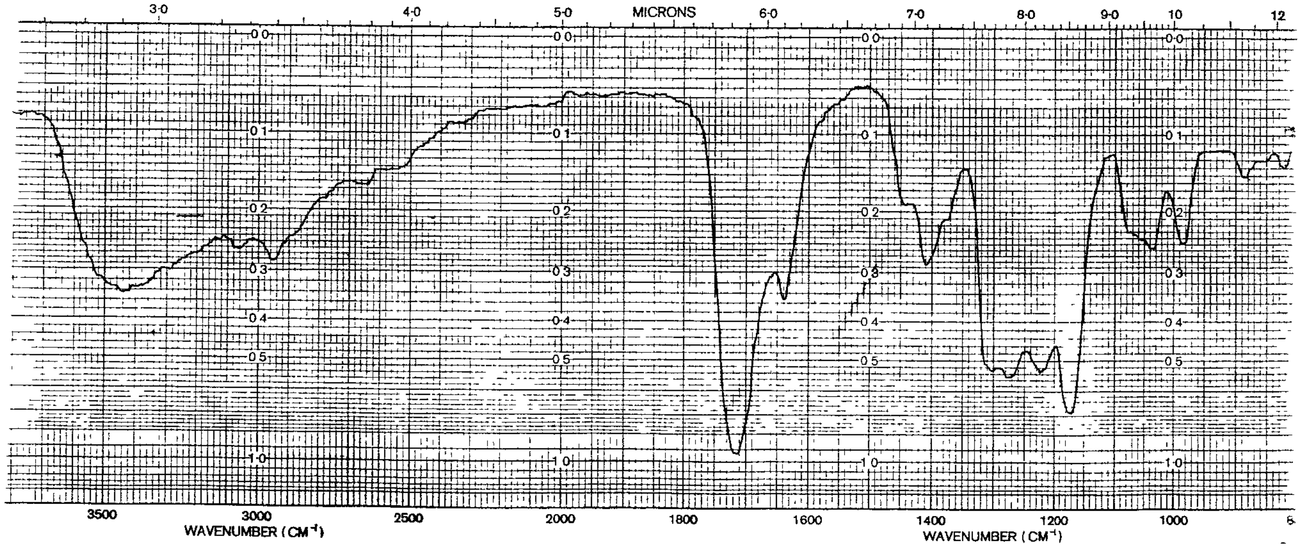
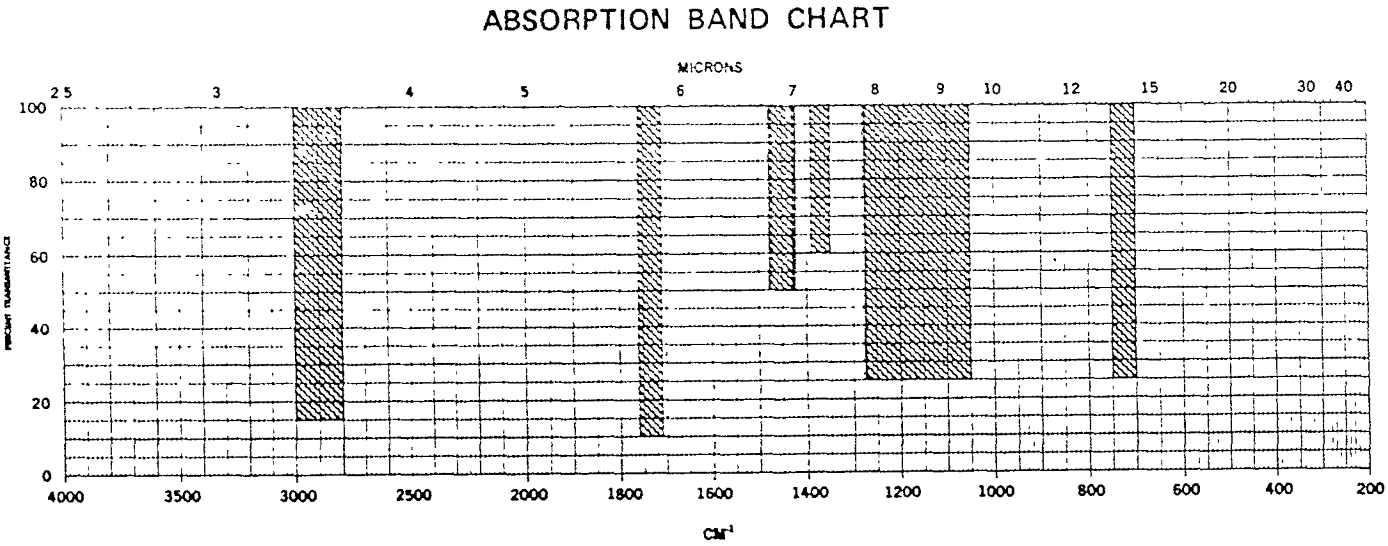
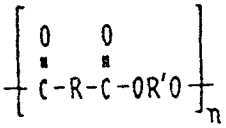


Figure 15 IR of Polyester.

POLYESTERS





$$-\left[\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OR'O\right]_n-$$

The principal absorbance bands of the polyesters include the C—H stretch near 3000 - 2800 cm^{-1}, the C=O stretch near 1740 cm^{-1}, the aliphatic ether C—O—C stretch in the 1275 - 1050 cm^{-1} region and the long chain CH_2 rocking motion near 730 cm^{-1}. Also present in the spectra are peaks near 1450 and 1380 cm^{-1} representing CH_2 and CH deformation vibrations respectively.

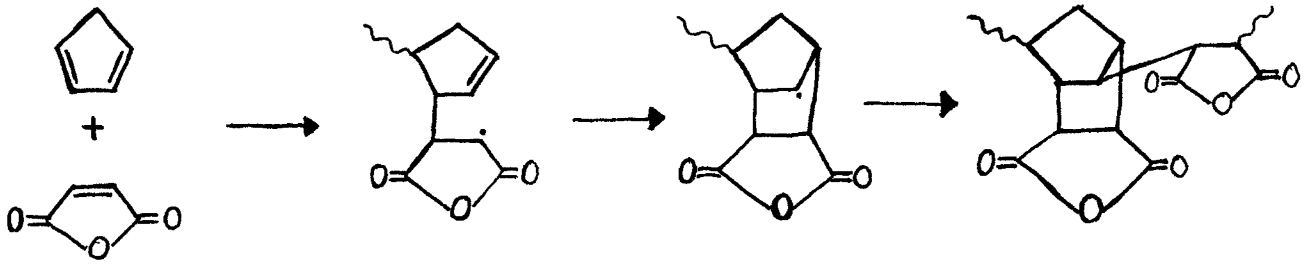
Figure 16 Principal absorption bands of Polyesters [21].

However, there are spectra on maleic anhydride copolymerized with other monomers, and ethylene glycol with other monomers. Figure 16 shows the principal absorption bands that are generally observed for polyesters. The spectrum of the sample made in this project shows a C-H stretch near 3000 cm^{-1}, a strong C=O absorption at 1740 cm^{-1} and an aliphatic C-O-C stretch in the 1275 -1050 cm^{-1} region.

4 COPOLYMERIZATION

(a) Chemical Structure of the Copolymer

It has been found that the copolymerization of CPD and MA may be carried out at temperatures as low as 80°C and the copolymers obtained over the range of 80-205°C are 1:2 CPD-MA copolymers. The 1:2 CPD-MA copolymer composition is independent of the initial charge and it is formed when a free radical catalyst is used at a temperature where it has a short half-life. The reaction is believed to yield a cyclic Diels-Alder adduct, endo-cis-5-norbornene-2,3-dicarboxylic anhydride [22]:



(b) Intrinsic Viscosity of the Copolymer

The solution viscosities of CPD-MA copolymer taken at 25°C using acetone as the solvent are summarized in Table 6 below:

Table 6 Data for MA-CPD copolymer viscosity.

t_o(sec)	t(sec)	t/t_o (η_r)	η_{sp}	C g/dl	η_{sp}/C
64.33	80.54	1.2520	0.2520	10	0.0252
	77.40	1.2032	0.2032	8.57	0.0137
	75.28	1.1702	0.1702	7.5	0.0227
	73.73	1.1461	0.1461	6.67	0.0219
	72.55	1.1277	0.1277	6.0	0.0213

A plot of η_{sp}/C vs. C is shown in figure 17. From the plot, the intrinsic viscosity, $[\eta]$ is determined as 0.0154 dl/g. This reveals that the molecular weight of the copolymer is quite low. In fact, it has also been stated in the literature that the copolymer has a molecular weight of 530-1000 [22]. The molecular weight of the copolymer can not be calculated via the Mark-Houwink equation because the constants *a* and *k* are not available in the literature.

(c) Infrared spectrum of MA-CPD coploymer

As the chemical structure of the copolymer suggests, one would expect strong absorptions at 1740 cm^{-1}

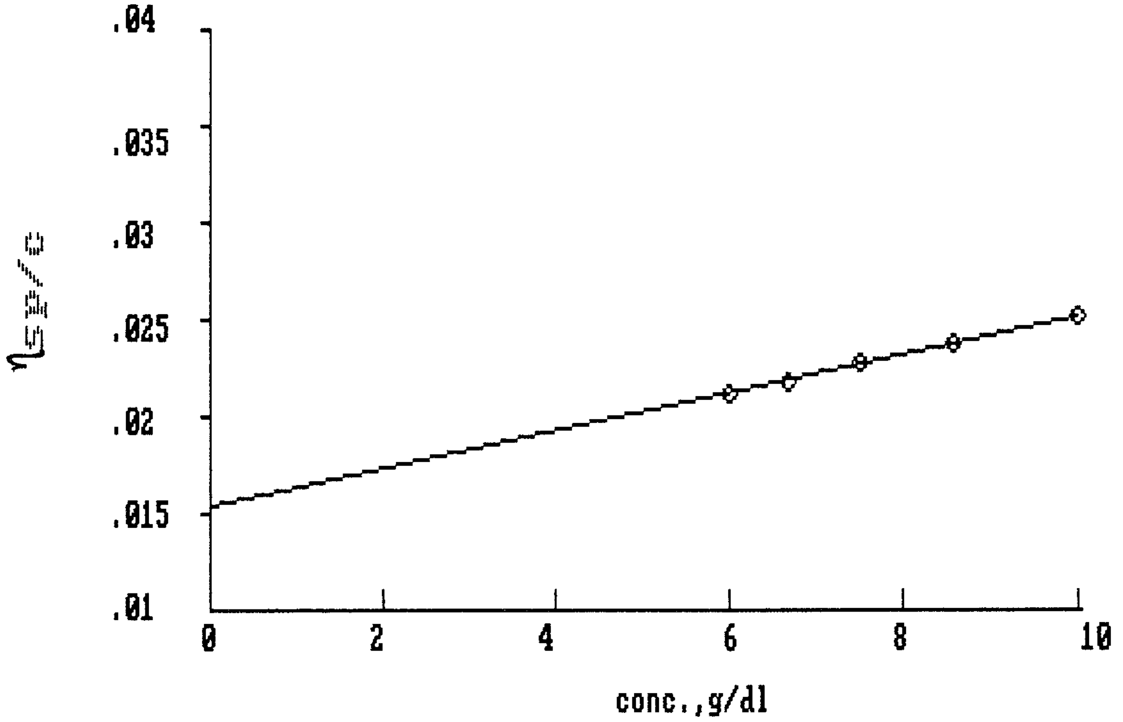


Figure 17 Plot of η_{sp}/C vs. C for MA-CPD copolymer system.

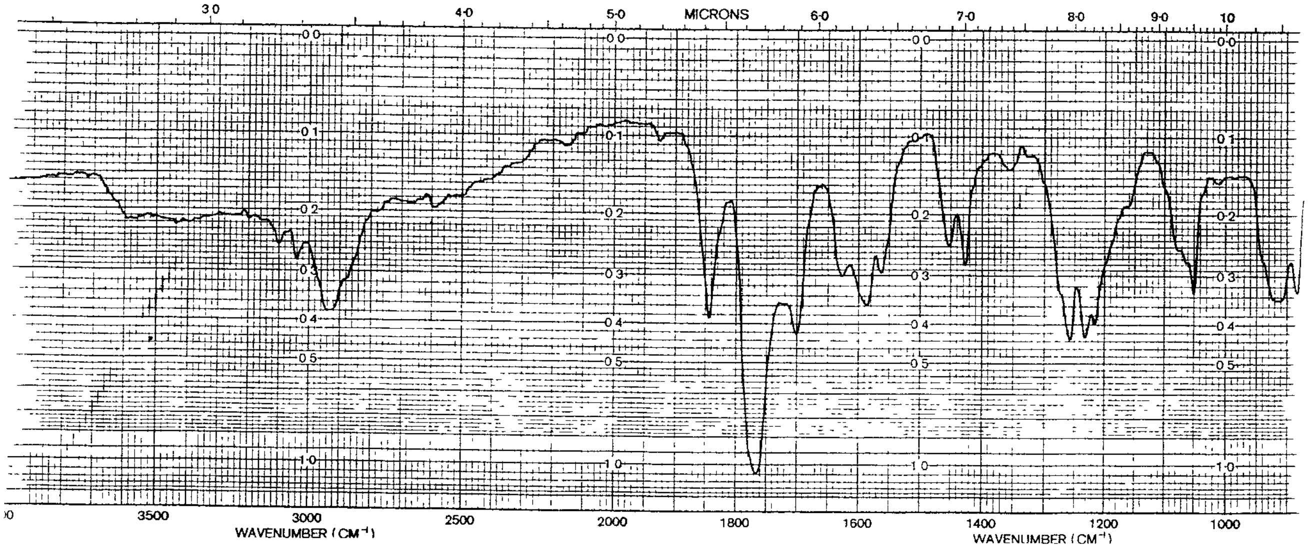


Figure 18 IR of MA-CPD copolymer.

for C=O stretch, and at 1275 and 1050 cm^{-1} for the C-O-C aliphatic ether stretch. The IR spectrum of the sample in Figure 18 shows indeed, a strong, and a moderate absorption at the respective frequencies.

5 CURING OF POLYCYCLOPENTADIENE

(a) Reactions and mechanism

Since the main objective of this project is to obtain a cured PCPD product, much work has been expanded to formulations that would give the desired product.

Table 7 shows a summary of the results from free radical curing of CPD. All three samples are cured within 2 to 3 hours at 170°C, with different initiators.

Table 7 Effect of free radicals on curing time

Formulation					Curing time (hrs)
E-1:	CPD ~47%	MA ~47%	Gly ~5%	t-BPO ~0.1%	~2
E-2:	CPD ~47%	MA ~47%	Gly ~5%	AIBN ~0.1%	~2.5
E-3:	CPD ~47%	MA ~47%	Gly ~5%	BPO ~0.1%	~3

Table 8 tabulates formulations and results that have been made using molten maleic anhydride (60-75^{o}C),and CPD. As indicated, all samples are not cured.

Table 8 Formulations and Results of curing CPD-MA

Sample	E-5	E-6	E-7	E-8
chemicals				
CPD	5 ml	5 ml	5 ml	5 ml
Gly	0.2 ml	-	0.2 ml	0.2 ml
t-BPO	0.2 ml	0.2 ml	0.2 ml	0.2 ml
DVB	1 ml	1 ml	1 ml	1 ml
N,N'-DMA	0.4 ml	0.4 ml	0.4 ml	0.4 ml
MA	4.311g	4.311g (s)	4.311 g (s)	4.311g
Temp.(^{o}C)	75	21	21	60
Results	brittle, uncured	soft, uncured	soft, uncured	brittle, uncured

(Note: All the above formulations were achieved by adding a mixture of the the first five components to MA. E-6 and E-7, were obtained by using finely ground MA powder. They all resulted in uncrosslinked products).

In the next set of formulations, chlorosufonic acid and ethylene glycol have been used to dissolve maleic anhydride. Table 9 summarizes the formulations and results for CSA initiated reactions.

Table 9 Summary of CSA initiated reactions

Sample	E-9	E-10	E-11	E-12	E-13	E-14
Chemicals						
CPD	5 ml	5 ml	5 ml	5 ml	5 ml	5 ml
DVB	1 ml	0.8 ml	0.8 ml	0.8 ml	1 ml	1 ml
N,N'-DMA	0.2 ml	0.2 ml	0.2 ml	0.2 ml	0.2 ml	0.2 ml
MA	4.3 g	4.3 g	4.3 g	4.3 g	4.3 g	4.3 g
EG	0.3 ml	0.4 ml	1.4 ml	0.6 ml	0.6 ml	-
CSA	1.8 ml	1.2 ml	0.4 ml	0.9 ml	0.9 ml	0.9 ml
t-BPO	-	-	-	-	0.2 ml	0.2 ml
Results	burnt, uncured	hard, uncured	soft, uncured	soft, uncured	soft, uncured	soft, uncured

(Note: All of the above reactions are exothermic, with some reaching approximately 100°C).

Table 10 is a list of formulations with a combination of PCPD/CPD or PCPD/polyester and other necessary ingredients. The results from this section are of particular interest because samples P-5-J, P-5-K and P-5-L are highly cured.

Table 10 Formulation and curing of PCPD/CPD

Sample	P-5-F	P-5-G	P-5-H	P-5-J	P-5-K	P-5-L
chemicals						
PCPD	1 ml	1 ml	1 ml	1 ml	1 ml	1 ml
CPD	0.2 ml	0.2 ml	0.2ml	0.2 ml	0.2ml	-
Styrene	-	-	0.5 ml	-	-	0.5ml
Glycerol	-	0.05 ml	0.1 ml	0.1 ml	-	-
EG	-	-	-	-	0.1ml	0.1ml
N,N-DMPT	-	0.1 ml	0.1 ml	0.1 ml	0.1ml	0.1ml
TEGDMA	0.5 ml	0.5 ml	-	0.5 ml	0.5ml	0.5ml
CSA	0.2 ml	0.2 ml	0.2 ml	0.2 ml	0.2ml	0.2ml
MA	1 g	1 g	1 g	1 g	1 g	1 g
BPO	0 05g	0.05g	0.05g	0.05g	0.05g	0.05g
^{o}C/hrs	60/12	60/20	60/12	60/12	60/2	21/48
Results	-	-	-	+	+	+

Note: + denotes cured, - for uncured.

As indicated in the table, sample P-5-K has the shortest curing time, 2 hours at 60^{o}C. (The surface of the cured sample appears a bit tacky, but this problem disappears when the curing is carried out under N_2). Up to formulation P-5-H, all attempts to make crosslinked PCPD at room-temperature have failed. But it is clear, though, that the heat released by the reaction of CPD and CSA is not sufficient to sustain the curing. It is especially of interest to note that formulation P-5-L, which contains no CPD monomer at all is highly crosslinked at room temperature except, it takes a longer time, 48 hrs. Table 11 shows a summary of selected reactions at 60°C or room temperature (21°C), curing of PCPD and their results.

Table 11 Formulations and results of curing at 60°C or room temperature.

Sample	P-5-M	P-5-N	P-5-P	P-5-Q
chemicals				
PCPD	1 ml	1 ml	1 ml	1 ml
MA	1 g	1 g	1 g	1 g
EG	0.6 ml	0.6 ml	0.6 ml	0.6 ml
CSA	0.2 ml	0.2 ml	0.2 ml	0.2 ml
TEGDMA	-	-	0.5 ml	0.5 ml
N,N'-DMPT	-	-	-	0.1 ml
Styrene	-	-	0.3 ml	0.3 ml
BPO	-	-	-	0.05 g
oC / hrs	21/2	60/48	60/0.25 21/48	60/0.25 21/48
Results	-/-	-	-	+

(Note 1: In each of the above formulations, a polyester prepolymer was obtained by reacting MA and EG in the presence of CSA.

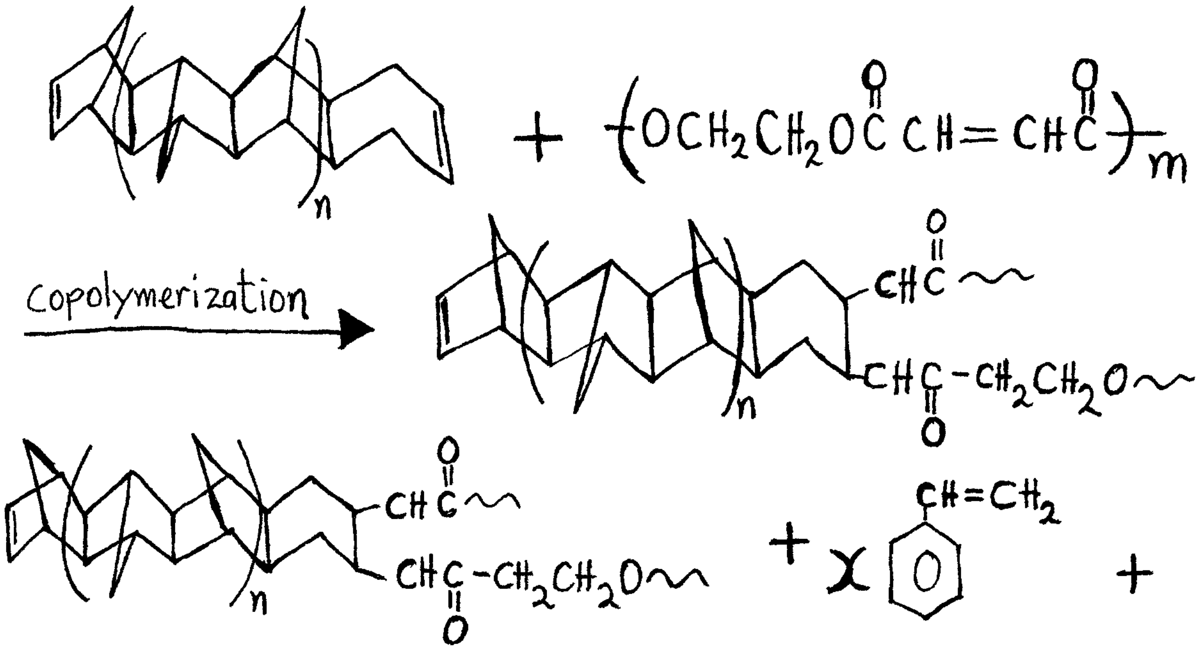
Note 2. Denotations:

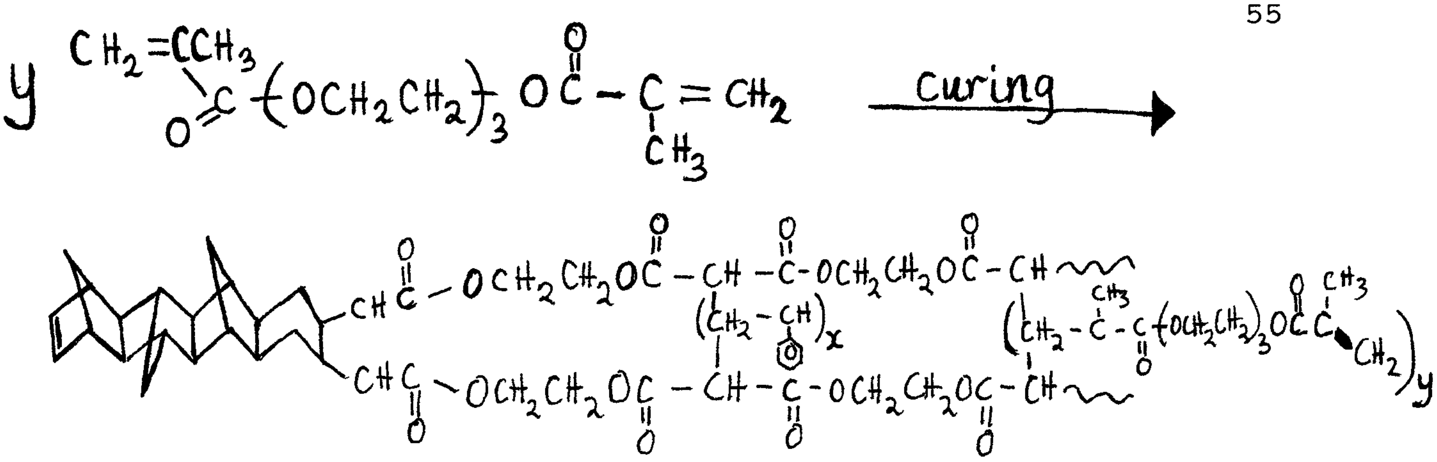
-/- denotes formation of two immiscible layers.

\- denotes uncured homogeneous product

\+ denotes cured solid sample)

From the experimental results above, one may conceive that the copolymerization reaction occurs at the unsaturated ends of PCPD and the double bonds of the unsaturated polyester chain. As a result, the molecular weight of the copolymer increases. VPO and intrinsic viscosity measurements gave M_n and [ ] values of 4600 and 0.0715 respectively, which are higher than that of PCPD and polyester individually.





The presence of N,N‵-dimethyl-p-toluidine causes BPO to generate free radicals in the system at room temperature which catalyzes the crosslinking process by styrene and TEGDMA. Styrene and TEGDMA are both curing agents for the copolymer.

(b) % Swelling, Sol and Gel of cured PCPD

Methods using swollen tension and compression to determine the crosslinking density for rocket propellants have been described [23,24]. This research, however uses a relatively simpler swelling method to check the % swelling, sol, and gel of the cured polymer. Three different solvents, acetone, toluene and N,N‵-dimethylformamide (DMF) are used separately as swelling agents and the results are listed in Table 12.

Table 12 % swelling sol and gel of cured samples

Sample	Solvent	% Swelling	% Gel	% Sol
P-5-K	acetone	2.6	92.89	7.11
	toluene	9.8	97 88	2.12
	DMF	16.6	99.80	0.20
PCPD-26*	DMF	5.7	98.86	1.6

* Sample PCPD 26 is quoted from previous work only for comparison reasons [3].

The % gel values obtained from the three samples show that the degreee of crosslinking achieved is high. DMF shows the highest swelling % - 16.6, which means it is the best swelling agent for the cured polymer.

(d) Thermal Stability of cured PCPD

The cured PCPD has been tested for thermal stability by subjecting it to high temperatures. The crosslinked polymer, when placed on a hot plate and heated to temperatures of over 250 °C, does not melt. A metal thermometer has been used for temperature reading, and it is found that the polymer may emit some gas at high temperatures but does not melt.

CONCLUSION

Results have shown that low molecular weight polymers can be formed from the polymerization of CPD by a Diels-Alder mechanism at 170 ^{o}C .

An unsaturated polyester can be readily formed from maleic anhydride and ethylene glycol at room temperature with chlorosulfonic acid (a cationic initiator), as catalyst, and that the polyester can be cured at room temperature in the presence of a peroxide, promoter and styrene.

The unsaturated polyester, together with PCPD can form a crosslinked polymer in the presence of peroxide, promoter,and crosslinking agents like styrene and triethyleneglycol dimethacrylate at room temperature within 48 hours.

Future work should emphasize the following aspects:

1 The applicability of the formulation for composites and
2 Other practical uses of the polyester formed at room temperature.

SELECTED REFERENCES

1. Odian G., *Principles of Polymerization*, Chap.1, Wiley-Interscience, New York, 2nd Ed., 1981.
2. Vollmert B., *Polymer Chemistry*, Chap. 1, p 27, Springer-Verlag, New York Inc., 1973.
3. Ning Jiang-guo, *High-Energy Curable Polycyclopentadiene Binder for Solid Rocket Propellants*, Master's thesis (NJIT),1988.
4. Fefer M. and Small A.B. in M. Grayson ed., *Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. 7*, Wiley-Interscience, New York, p.418 1979.
5. Staudinger H., *Helv. Chim. Acta.*, **7**, 23 (1924).
6. Sigwalt D. and Vairon J.P., *Bull. Soc. Chim. Fr.* 482 (1964).
7. Kuntz I., "Cyclopentadiene Polymers" in *Encyclopedia of Polymer Science and Technology*, 1st ed., Vol. 4, pp 563-568, Wiley-Interscience, New York 1966.
8. Gaylord N.G., Deshpande A.B. and Martan D., *J. Polym. Sci., Part B*, **14**, 679 (1976).
9. Baldwin F.P. and Ver Strate G., *Rubber Chem. Technol.*, **45**, 709 (1972).
10. Rabjohn N., *Organic Syntheses, Collective Volumes, Vol. 4*, John Wiley and Sons Inc., New York 1963, p. 238.
11. Gaylord N.G. and Deshpande A.B., *J. Macromol. Sci., Chem.*, **A 11** (10) PP. 1795-1807 (1977).

12.Plesch P.H., *The Chemistry of Cationic Polymerization,* Chap. 8, Macmillan, New York 1963.

13. Stevens M., *Polymer Chemistry*, Chap. 14, p.368, Addison-Wesley Inc., Mass., 1975.

14. Callinella E., *J. Molecular Spect.*, **24**, 345 (1963)

15. Billmeyer F.W. Jr. *Textbook of Polymer Sci.*, Chap. 8, 2nd ed., Wiley-Interscience, New York (1971).

16. Sanders K.J., *Organic Polymer Chem.*, Chapman and Hall, London (1973).

17. Brydon J.A., *Plastic Materials*, Van Nostrand Reinhold, New York (1970).

18. Cook W.D. and Delatycki O., *J. Macromol. Sci., Chem.*,**A 12**, 769 (1978).

19. Sakaguchi K., *J. Macromol. Sci., Chem.*, **A 8** , 477 (1974)

20. Odian G., *Principles of Polymerization*, Chap.6, Wiley-Interscience, 2nd ed. (1981).

21. Sadtler *The Spectra Atlas of Monomers and Polymers,* p 413, Sadtler Research Labs. Inc., Philadelphia 1980.

22. Gaylord N.G. Deshpande A.B. and Martan M., *J. Polym. Sci., Polym. Letters ed.*, **14**, 679 (1976).

23. Groetzinger N.H. III, *American Rocket Society Journal*, **30**, 498 (1960).

24. Landel R.F., *American Rocket Society Journal*, **31**, 599 (1961).