STUDIES ON THE POLYMERIZATION CHARACTERISTICS OF NATURALLY OCCURRING (RENEWABLE) MONOMERS

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This is to certify that the thesis bound herewith is an authentic record of the research work carried out by Mrs. S. Manjula, M.Sc., under my supervision in partial fulfilment of the requirements for the Degree of Doctor of Philosophy of the University of Kerala and further that no part thereof has been presented before for any other degree.

(DR. C.K.S. PILLAI)
Supervising Teacher

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SCOPE AND OBJECTIVES

Renewable resources for energy and chemicals has been the subject of intense research all over the world during the last few years. Considering the fact that production of more than 90% of the polymers today are based on petroleum, attempts to substitute the monomers or polymerized products from biological and renewable resources became very important. Though there are a number of biomonomers which are potentially polymerizable, it has to go a long way before the economical viability of production and availability in large quantities of these monomers are realized. However, there exist monomers like cashewnut shell liquid and furfural which are cheap and at the same time available in sufficient quantities for industrial exploitation.

The main objective of the present work is to provide a brief insight into the naturally occuring monomers available for polymerization and to study the polymerization characteristics, related structure - property relationship and thermal stability studies of cardanol, the major constituent of cashewnut shell liquid. Studies on polymerization of coconut shell tar are also included in this work.

Cardanol, the major constituent of cashewnut shell liquid, is abundantly available in India and some African countries. Cashewnut shell liquid, although is used currently for the production of some industrial products like brakelining material, scope exists for wider industrial exploitation of this material due to its interesting phenolic unsaturated structural features and availability at low costs.

Cardanol is a meta substituted phenol. The substitution is a long chain unsaturated hydrocarbon and thus provides opportunities for oligomerization/polymerization through side chains as well as through aromatic rings by formaldehyde condensation. The mechanical properties of cardanol-formaldehyde polymer could be improved by interpenetrating the network with other polymer networks of poly(methyl methacrylate), polystyrene, etc. The poor mechanical properties of cardanol-formaldehyde could be thought as due to the long side chains and the properties could perhaps be improved by oligomerization through double bonds and further formaldehyde condensation through aromatic rings.

The objectives of the present work could be summarised as follows:

1. Literature survey on biomonomers.
2. Study of the oligomerization characteristics of cardanol.
3. Synthesis of cardanol-formaldehyde (novolac and resol).
4. Synthesis and structure-property correlation of cardanol-formaldehyde - poly(methyl methacrylate) simultaneous interpenetrating networks.
5. Comparative study of the thermal stabilities of cardanol-formaldehyde polymer and the different cardanol formaldehyde - PMMA IPNs.

6. In addition, another monomeric system studied for the work is coconut shell tar (CST). CST is a byproduct of the destructive distillation of coconut shell and is abundantly available in southern parts of India. It contains 22% acetic acid and 30% phenolics. The present study is intended to enrich the phenolic components for polymerization purpose.

CHAPTER 1

GENERAL INTRODUCTION

CHAPTER I

GENERAL INTRODUCTION

1.1 Over view

Petroleum provides the source and raw material for the production of majority of chemicals and fluctuations in the production and price of petroleum has a direct impact on the chemical industry[1]. The predicted scarcity of petroleum in the time to come, and continuous and increasing consumption both in energy and chemical industrial fronts could lead to serious problems in the industrial world. This and the sudden rise in oil prices during early seventies has prompted intense research activities all over the world to find alternative sources for energy and chemicals.

The dependence of chemical industry on petroleum resources could be reduced by the full utilization of the renewable natural biomass resources whenever it is possible. Ranging from algae to wood its availability is limited only by the photosynthetic efficiency of the plant[2]. It is renewable, availability is flexible through crop switching and is also adaptable through genetic manipulations[3]. Cellulose, starch, sugar, lignin, oils, fatty acids, etc. provide a variety of naturally occurring starting materials from which a host of chemicals like alcohol, ethylene, glycerol, hydrocarbons, etc. could be synthesized[3]. The biomass system present opportunities to continue the production of chemicals that are needed at reasonable prices while conserving fossil resources and it could be grown to satisfy changing end use chemicals on both quantitative and qualitative basis.

Cellulose, starch and natural rubber are among the most important and useful naturally occurring polymers and more than 90% of the synthetic polymers are derived from petroleum. There are a variety of monomeric components that exist in free or in combined form that could be obtained by extraction, cleavage or depolymerization from biomass. When plant tissues are extracted with solvents, the polymeric constituents such as lignin, carbohydrate polymers, proteins and nucleic acids are separated[1]. Bifunctional fatty acids, furan, furfuraldehyde, phenolic compounds and a variety of other monomers could thus be obtained from naturally occurring sources and polymerization of many of these monomers have been reported[4].

The relevance of an integrated effort to utilize the biomass resource for the synthesis of new polymers or substitution of existing polymeric materials is, no doubt, important. In this thesis an effort is made to collect and codify the available data on various monomeric constituents of biomass. The following studies are also included in this thesis (1) to oligomerize/polymerize cardanol (obtained from cashewnut shell liquid) by acid catalysts, (2) to synthesize and study the mechanical properties of simultaneous interpenetrating networks of cardanol-formaldehyde polymer and poly(methylmethacrylate), (3) thermogravimetric studies of cardanol-formaldehyde polymer and cardanolformaldehyde-poly(methylmethacrylate) interpenetrating networks, and (4) studies on coconut shell tar.

1.2 Literature survey on naturally occuring monomers

1.2.1 Classification

In general, naturally occuring organic polymers are classified into the following groups: Hydrocarbon polymers (natural rubber, gutta percha etc.), carbohydrates(starch, cellulose etc.), polyphenolic compounds (lignin and other polyphenols), proteins and nucleic acids[5]. Monomers associated with the above polymers can be found free in nature, though it cannot be taken as a general rule (for eg., though natural rubber is polyisoprene, the plant does not produce isoprene, the monomer as such). However, a preliminary survey indicated the availability of innumerable number of monomers from various sources such as alkaloids, terpenes, lipids, fatty acids, amino acids etc. For the sake of clarity, the naturally occuring monomers have been classified as shown in Fig.1·1. The following discussion is organised into subgroups and only those that are considered more potential in terms of polymerization are discussed. Compounds whose functionality is more than one is considered as a potential monomer but actual polymerization may depend on many factors. For eg. steric hindrance may inhibit a potential monomer from polymerization.

1.2.1.1 Terpene monomers: Terpenes constitute one of the largest groups of natural products. They embrace a vast family of chemical compounds which are isolated from essential oils and resins of plants[6]. This class also includes naturally occuring and synthetic alcohols, aldehydes, ketones and other derivatives having same carbon skeleton as parent terpene hydrocarbon called terpenoids. Some of the terpenes are excellent monomers whose structure, source and properties are given in Table 1.1·

1.2.1.2 Fatty acid monomers: The fatty acids most frequently occuring as components of natural fats and oils can be classified into several series. One is saturated fatty acid and other group is characterised by the presence of one or more double bonds. Table1·2 gives structure, source and properties of some fatty acid monomers.

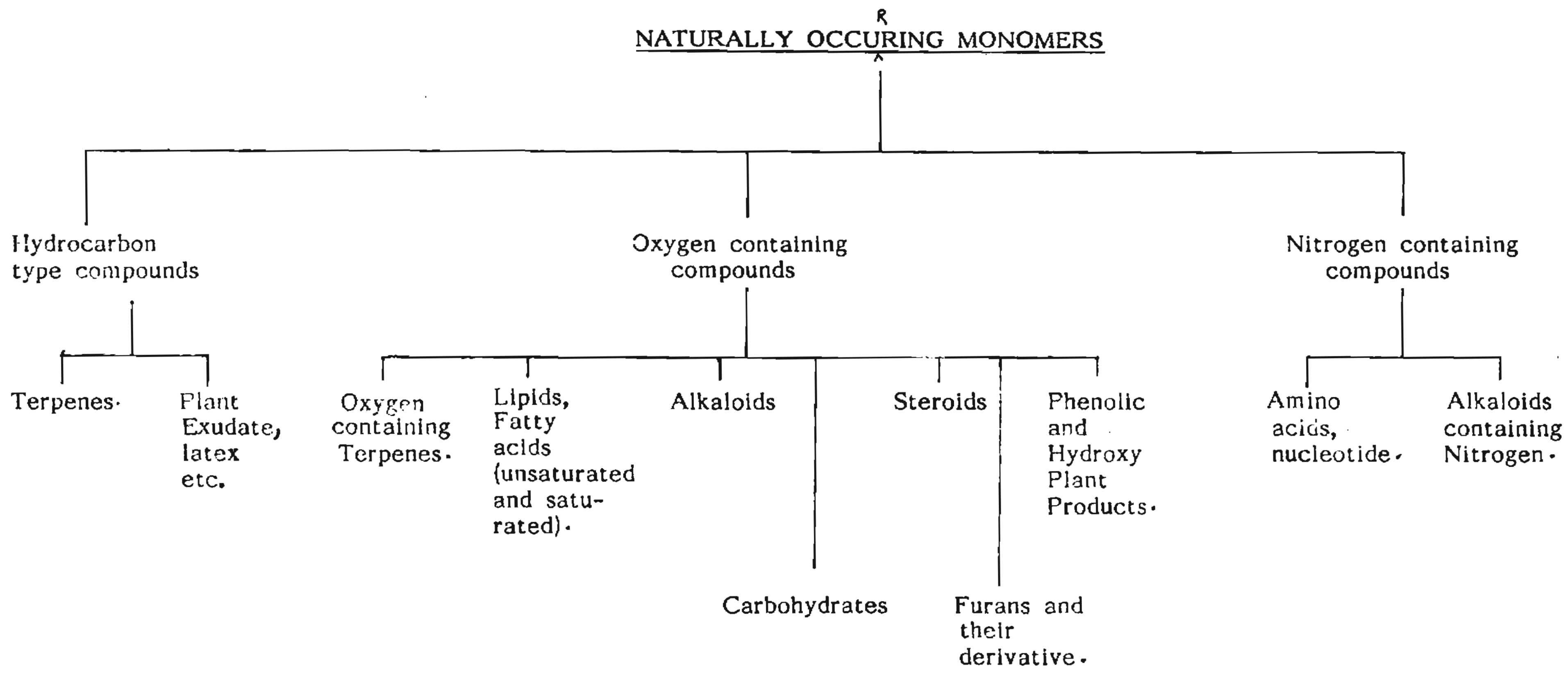


Fig. 1.1 Classification of Naturally Occuring Monomers

1.2.1.3 Alkaloid monomers: They constitute one of the largest group of natural products. They occur throughout the animal and plant kingdom and display a diversity of structure unmatched by any other group of naturally occuring compounds and exhibit an extraordinary array of pharmacologic activities. A few alkaloids which can be considered as monomers are listed in Table 1.3.

1.2.1.4 Monomers based on phenolic and hydroxy compounds: They form another major category of the natural products. Phenolic compounds and their quinones are o wide spread occurance in nature[21]. They are abundant in plants and fruits as chromones, glucosides, coumarin derivatives, essential oils, lignin etc. They occur also in animals. Table 1.4 provides a list of monomers of phenolic origin.

1.2.1.5 Amino acid monomers: They are a broad class of organic compounds that contains both amino and acid functional groups. Here only polymerizable amino acids containing primary or secondary amino groups and carboxylic groups will be considered. Some of the amino acids are excellent monomers whose structure, source and properties are given in Table 1.5.

1.2.1.6 Monomers based on furans and derivatives: Furfural and its derivatives comprise an industrially significant class of heterocyclic compounds. These compounds are found in agricultural wastes such as corn cobs, bagasse, rice husks, coconut shell etc.[41] Table1.6 gives structure, source and properties of some monomers of furfural origin.

1.2.1.7 Steroid monomers: Steroids are ubiquitous members of a large class of marine and terrestrial organic compounds. Included under the designation of steroids are the naturally occuring and synthetic substances[54]. Table1·7 gives structure, source and properties of some steroid monomers.

1.2.1.8 Monomers based on carbohydrates or sugars: There are a large number of sugar monomers that exist in nature. As it takes a lot of space to cover all the monomers, the relevant literature may be referred for a comprehensive understanding[57].

1.2.2 Methods of polymerization and applications

It should be noted that some of the naturally occuring monomers have already found applications in the polymer field. The monomer can either be modified to other suitable monomers or can be polymerized directly into an useful polymer. An example for the latter is furfural which acts as a precursor to hexamethylenediamine and adipic acid, the latter two utilized to form nylon - 6,6[1]. Furfural or its derivatives are known to be utilized for the production of phenolic resins[41].

Another example of modification is the dry distillation of castor oil to get sebacic acid, a monomer for the production of nylon[14]. Another example is that of terpene resins polymerized from terpenes such as β -pinene. Terpene resins have found use as pressure sensitive adhesive, coating etc[6]. Natural oils such as linseed oil, tung oil etc., have formed the basis for paints (drying involves an oxidative polymerization at the double bonds leading to a cross-linked network[58]). The alkyd resins can also be considered in this case, although they are partly synthetic[14].

Since the methods of polymerization and characterization of polymers are now well established[59], a detailed discussion on it is out of place here. The application of a particular polymerization technique generally depend upon the structure of the monomer. For example, a monomer having two or more functional groups such as hydroxyl-, carboxyl-, etc. can undergo what is generally known as condensation polymerization[60]. When unsaturated bonds are available, chain reactions can be initiated by appropriate catalysts called initiators[60]. Table I·8 provides the list of naturally occurring monomers which have already been polymerized and used commercially. Table I·9 provides probable methods of polymerization of naturally occuring monomers which have not been attempted for polymerization. Possible applications from the point of view of the structure of the monomers are also envisaged.

1.3 Selection of naturally existing monomers for the present study

The preceeding section dealt with monomers of natural origin that had been polymerized or that have potential for polymerization. Among these monomers, unsaturated long chain hydrocarbon phenols occupy a very important position.

Cashewnut shell liquid (CNSL), obtained as a byproduct of cashew industry, is a rich source of unsaturated long chain hydrocarbon phenols[33]. CNSL is one of the monomeric systems selected for the present work because of its ready availability in large quantities, its regional importance, and its ability to polymerize through double bonds as well as through the phenol-formaldehyde type condensation. CNSL occurs as a reddish brown viscous liquid in the soft honey comb structure of the shell of the cashewnut which is a plantation product obtained from cashew tree, Anacardium occidentale.L which is cultivated in a large number of tropical and subtropical countries[85]. The tree is native to Brazil and the coastal areas of Asia and Africa. Cashewnut production has increased world wide and it holds a share (20%) almost the same as the almond and the hazel[33]. Cashewnut attached to a cashew apple is a grey coloured kidney shaped structure and is 2.5 - 4 cm long. The cashewnut consists of an ivory coloured kernel covered by a thin brown membrane (testa) and enclosed by an outer brown porous shell that is the mesocarp which is around 3 mm thick and contains CNSL[33]. The nut thus consists of the kernel (20-25%), the shell liquid (CNSL) (20-25%) and the testa (2%), the rest being the shell. The kernels freed from testa contains 1.6% water, 10% protein[86], 57.4% fat, 5.3% carbohydrate, 2.4% ash and 0.9% fibre. The CNSL is present to 18-27% of the total raw nut weight, kernel is approximately 20-25% and the balance is the shell weight and the testa[87] (2%).

Another monomeric source selected for the present work is coconut shell tar (CST). This is a byproduct obtained during the destructive distillation of coconut shell, and as a material that is abundantly available in India some studies on the polymerization characteristics of CST components were also carried out. Materials based on the coconut tree form a major renewable resource of the tropical regions of the world. Among other materials, the tree gives coconut shells to the tune of about 4.2 million tons/year[88]. The coconut shells on destructive distillation give coconut shell char which is used as a filler in plastics and for the development of activated carbon. Coconut shell tar is a byproduct obtained during the distillation process and was considered as a waste so far. But it can also be considered as a phenolic source.

1.4 Literature survey on CNSL

The literature on CNSL is now enriched with hundreds of patents and reports. The Cashew Export Promotion Council (CEPC), India, had compiled lists of patents that originated from USA, UK, Japan and India upto 1962[89,90]. It also brought out two other publications[91]. A few reviews have appeared emphasising the significance of CNSL and its products as versatile industrial raw materials[92,93,94].

1.4.1 Extraction

1.4.1.1 Hot oil bath process: Indian processors of cashewnuts roast them in an open perforated drum, when CNSL leaks out or is burnt in the air. The most common method of commercial extraction is the hot oil bath which extracts around 50% of the liquid contained in the nuts. In this method, the raw nuts are heated at 180-190°C while held on a slowly travelling conveyor belt submerged below the liquid level. When the outer part of the shell bursts open, CNSL is released. Another 20% could be extracted by passing the spent shells through an expeller and the rest by solvent extraction technique[95]. This expeller oil can be upgraded by acid washing followed by centrifugation and heating. This method is largely used in some parts of India[96].

1.4.1.2 Expeller method[97]: Another method of extraction employs manually operated cutting machines to cut shells of lightly roasted nuts, keeping the kernel intact. The shells are then fed to the expeller to recover 90% of the oil.

1.4.1.3 Kiln method[97]: In this method nuts are shelled after sun drying or after drum roasting. The liquid obtained is crude and contaminated.

1.4.2 Production and export in India

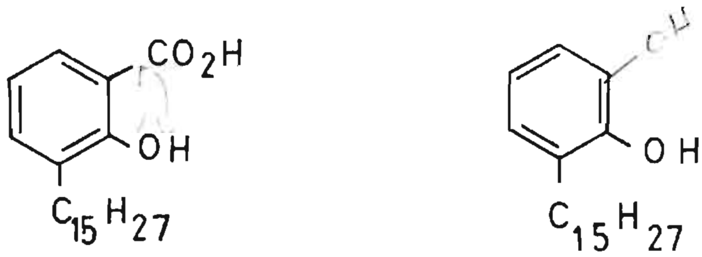
The average annual production of CNSL in India is of the order of 10,000 to 14,000 tons, though the potential availability of the liquid is about 37,000 tons. Due to the adoption of the expeller method another 30% could be added. The export of CNSL from India which was 14,000 tons in 1963-64 is only 7011 tons in 1975-76 and 10699 tons in 1980[97]. The price of CNSL registered a rise in 1978-79 and it began dropping in 1980. The potential availability of CNSL in the world is around 125,000 tons/year of which only a fraction is, in fact, used[97]. India used to be the major exporter of CNSL with a peak export of 14,400 tons in 1964 and lost her first position to Mozambique in 1971 which exported 11,500 tons followed by Brazil with 6500 tons, India coming thrid with 5500 tons[98,99].

1.4.3 Chemistry of CNSL

CNSL is said to be the most widely distributed and abundant natural phenolic lipids source. The phenolic lipids present in CNSL are (1) phenolic acid - anacardic acid[100,101], (2) dihydric phenol - cardol[100,102], (3) monohydric phenol-cardanol[103], and (4) 2-methyl cardol[104]. Table 1.10 shows the % of each component in natural and technical CNSL[33]. Anacardic acid is the major component of natural CNSL but during the hot oil bath process it gets decarboxylated to cardanol. Cardol and 2-methyl cardol are the most widely distributed dihydric phenols through their presence in natural and technical CNSL. Cardanol is the minor component of natural CNSL and the major one in technical CNSL[105].

1.4.3.1 Structure of phenolic lipids of CNSL:

Städeler in 1847 first investigated CNSL systematically and separated cardol from anacardic acid and decarboxylated anacardic acid[100]. But the correct formula for the acid, $C_{22}H_{32}O_3$ (this is the molecular formula for the diene which is the average unsaturation) was not established till 40 years later[106]. A.J.H. Smit, in 1931 recognised the presence of salicylic acid system and a pentadecadienyl sidechain[107] and P. Von Romburg put forward the structure of anacardic acid and anacardol (the name anacardol was used for cardanol in the early years but changed into cardanol by M.T. Harvey) by analogy with work on pelandjauic acid and pelandjauol[108] (Fig. 1.2).

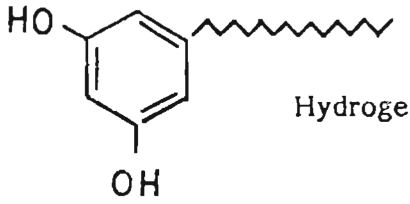


anacardic acid anacardol

Fig. 1.2

Backer and Haack isolated 3-methoxyphthalic acid and 3-methoxybenzoic acid together with palmitic acid by the oxidative degradation of hydrogenated and methylated anacardic acid and anacardol respectively and synthesised anacardol[109]. A.A. Durrani and J.H.P. Tyman synthesized anacardic acid by two different methods[110].

Städeler first isolated cardol from natural CNSL and examined its structure. Then Backer and Haack reinvestigated the structure and the molecular formula, $C_{15}H_{27}C_6H_3(OH)_2$ was put forward for what they considered to be pentadecadienyl resorcinol[109]. The hydrogenated material was assigned the following structure since the oxidation of methyl ether gave 3,5-dimethoxybenzoic acid and palmitic acid (Fig. 1.3).

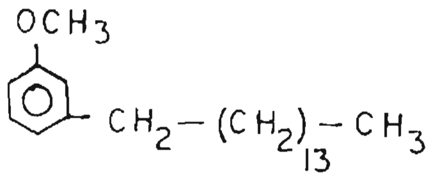


Hydrogenated cardol - Fig.1.3.

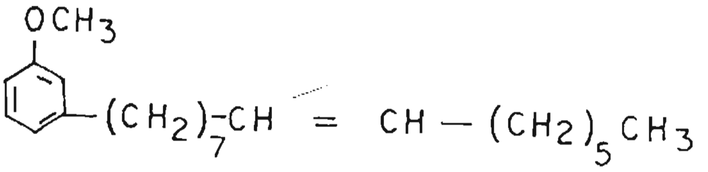
Later D. Wasserman and C.R. Dawson confirmed the structure in 1948 by synthesis[111].

2-methyl homologues of cardol were separated by argentation TLC and are structurally investigated by mass spectrometry and $^{1}H'$ nmr[104].

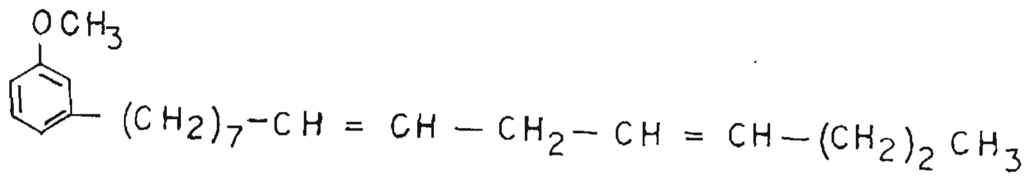
Dawson and Wasserman examined the structure of cardanol and showed that it is identical except for the degree of unsaturation with the product of solvent extraction of natural CNSL followed by thermal decarboxylation[112]. In the early structural work, it was universally believed that a pentadecadienyl side chain was present in the phenols[33]. Later cardanol was shown to consist of a mono- and a di-olefin which formed crystalline glycols separable by fractional crystallization[33]. B.G.K. Murthy et al in 1968 had reported the separation of cardanol and cardol from technical cardanol using silica gel thin layer chromatography and silica gel column chromatography. They also separated cardanol into 4 components viz. saturated, mono-, di- and tri-olefins using silver nitrate impregnated silica gel TLC and column chromatographic techniques. The 4 components were characterized by consideration of their properties and hydrogenation[113] values. In 1953, William F. Symes and C.R. Dawson found that methyl ether derivative of cardanol can be separated by chromatography on alumina into 4 components which vary only in their degree of unsaturation in the side chain. They established the structue of 4 components by oxidative degradation. The saturated component was proven to be identical with the catalytically reduced methyl cardanol. The olefins were subjected to ozonization and the products were analysed. The aromatic fragment resulting from ozonolysis was oxidized. Again the pure olefin was oxidized with potassium permanganate and all the products were analyzed. The formation of the degradation products indicated the monoolefine to be 3- (pentadecenyl - 8') anisole, diolefin to be 1-methoxy-3- (pentadecadienyl -8', 11') benzene and triolefin to be 1-methoxy-3- (pentadecatrienyl - 8', 11', 14') benzene[114] (Fig. 1.4).



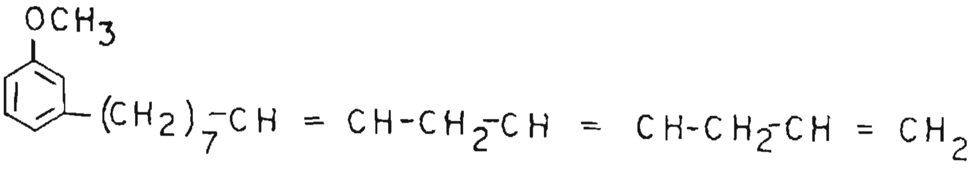
(Saturated, 5.4 %)



(Mono olefin, 48.5 %)



(Diolefin, 16.8 %)



(Triolefin 29.3 %)

Fig. 1.4.

J.H.P. Tyman and J. Caplin synthesized monoene, diene and triene constituents of cardanol[115]. Paul and Yeddanappalli isolated the mono-, di- and triene constituents of anacardic acid by low temperature crystallization (from acetone at -80°C) followed by potassium permanganate oxidation and showed the unsaturation to be present at 8', 11' and 14'[114].

In the early years trans configuration was assigned to the 8', 11' unsaturation in the constituents of cardanol, anacardic acid and cardol. The synthetic 3- (8'-pentadecenyl) anisole[116] which was considered to be the cis isomer because of the final hydrogenation step, was converted into a glycol different in melting point from that derived from cardanol monoene methyl ether. From this it was concluded that natural monoene had the trans configuration. IR of the natural product revealed a band at 960 cm^{-1}, characteristic of the C-H band in a cis olefin which is also present in the diene and triene. Dihydroxylation of natural (cis) cardanol monoene methyl ether with osmic acid gave the same glycol as the dihydroxylation with performic acid of trans cardanol monoene methyl ether, itself obtained by the isomerization of cis isomer with selenium[117]. This is represented in the following figure 1.5[118]. The existence of unsaturated constituents in the cis configuration had been shown in the H' nmr by the coupling constant value of the olefinic hydrogen[119].

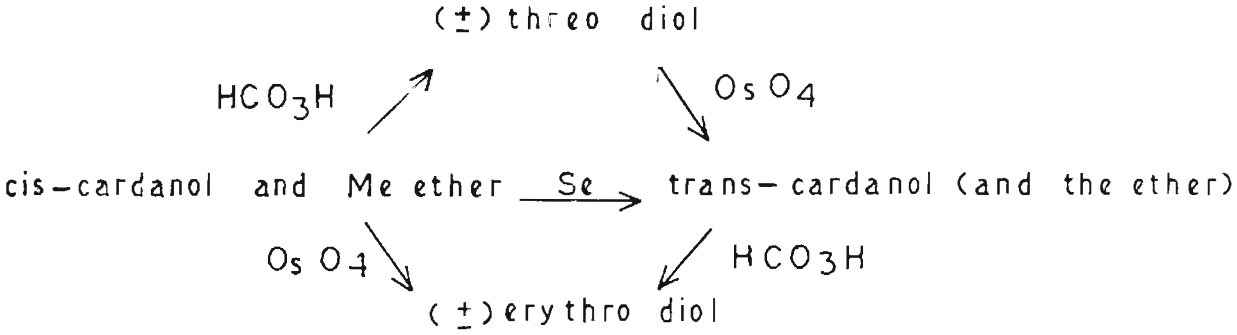


Fig 1.5

1.4.3.2 Quantitative compositional examination of phenolic lipids by various physical methods:

Column chromatography was used in the separation of cardanol and IR spectrum was used in the configurational studies[117]. G.K. Murthy et al reported that TLC separation of natural and technical CNSL with a multiple development technique followed by

UV spectrophotometry either in an indirect elution method or by direct densitometry enable quantitative analysis of phenols[120]. R.F.K. Meredith had shown that HPLC with a reverse phase technique effected a direct separation of the components of phenols[121]. Adsorption chromatography of natural CNSL after the preliminary removal of anacardic acid on alumina followed by separation of remaining components on silica gel was used as an analytical as well as preparative technique[104].

Gas liquid chromatography (GLC) of natural and technical CNSL were reported[122]. J.H.P. Tyman et al reported the composition of natural and technical CNSL from various regional sources using hydrogenated and methylated component phenols[87].

S. Kopp et al had reported that reverse phase HPLC can be used for the separation of cardanol from CNSL and later identified by mass spectrometry. This method was also used to isolate and identify for the first time, cardanol triene from the extracts of green fruits of Schinus Molle[123].

Mass spectrometry had proved to be of great value for the rapid and reliable method for the quantitative analysis of different components of CNSL, all of which have a comparable volatility and differ by two mass units[124]. H' nmr spectroscopy and UV spectrophotometry had been useful for structural and quantitative work[164].

Sood et al in 1986, reported the separation of cardanol from technical cashewnut shell liquid by liquid chromatography on silica gel H 60 with solute/absorbent in the range 1 : 5 - 1 : 6. Concentrates of the monoene, diene and triene constitutents of cardanol had been prepared by argentation liquid chromatography on silica gel H 60 with dry incorporation of 15% silver nitrate[125].

1.4.4 Polymerization characteristics:

CNSL can be polymerized in a number of ways[126]

1.4.4.1 Addition polymerization at the side chain unsaturation: Polymerization can be effected through the double bonds of the side chain employing either free radical or ionic initiators. CNSL responds easily to acidic catalysts like sulfuric acid, hydrochloric acid and diethyl sulfate[97]. When CNSL was heated with 5 ml of 25% sulfuric acid in diethyl sulfate, a gel was obtained[127]. For the production of friction dust used in brake linings, a preliminary acidic polymerization of the side chain is carried out with dimethyl or diethyl sulfate. This semi-polymerized material is then polymerized with formaldehyde to get friction dust.

1.4.4.2 Oxidation polymerization[128]: CNSL on oxidation, iodine value is quickly reduced to zero and reaction product dries very quickly at ordinary and elevated temperature. Oxidation can be carried out using nitric acid. The product when dissolved in solvents such as turpentine, naphtha or kerosene gives an excellent coating material useful for making paints, varnishes, etc. and for impregnating paper and woven fabrics.

1.4.4.3 Condensation polymerization: CNSL can be condensed with active hydrogen containing compounds such as formaldehyde, furfural, etc. at the ortho and para position of the phenolic ring under acidic or alkaline conditions to yield a series of polymers of novolac/resol type. Condensation polymers of CNSL are finding use as coating materials, adhesives, plastic and rubber compositions and automobile brake linings[97]. Reaction of cardanol and formaldehyde along with tetramethylenepentamine gives derivatives which have been used as weak anionic exchangers[129]. Cation exchange resins have been produced by the sulfonation of CNSL/formaldehyde resins prepared in the presence of hydrochloric acid[130].

1.4.4.4 Metal activated polymerization: CNSL when activated with metal or metallic compounds acquired drying characteristics[131]. When CNSL is heated with copper, aluminium, lead, etc. it is found to have superior drying properties than when it is heated alone and which can be used as a medja for paints on further cooking with drying oils[132].

1.4.4.5 Heat polymerization: When CNSL is heated at 160 - 300°C in presence of certain accelerators, excellent storing enamels are obtained[132].

1.4.5 CNSL based products

Compared to polymers from[133] petrochemical based phenols, CNSL based polymers have many advantages. They have improved flexibility (due to the internal plasticization effect of the long side chain) and hence have better processability[33]. As a result of the presence of the long chain, CNSL polymers are hydrophobic in nature. Its coatings are water repellent and resistant to weathering[126]. CNSL based rubbery products are tough and leathery. CNSL resins possess outstanding resistance to the softening action of mineral oils and high resistance to acids and alkalies[134]. In addition to this they possess resistance to cold, wear, good electrical and heat resistance, antimicrobial property, termite and insect resistance etc.[91] CNSL polymers are compatible with a wide range of polymers such as plastics and rubbers[135]. CNSL polymer is also used as an essential additive for most of the organic brakelining formulation because of their low fade characteristics on friction.

Several reviews on CNSL in coatings[136], chemicals and other useful products[137] have been reported. In 1978, Lalit Anand presented an excellent review on CNSL based polymer and their applications[93].

CNSL based products can be broadly classified under two broad heads: polymeric products and industrial chemicals. CNSL based products have a wide range of applications which cover almost all fields. CNSL and its derivatives have been used for the manufacture of insulating varnishes, oil and acid proof cold setting cements, brakelinings, mosquito larvicides[93], detergents[94], etc. Many patents have been taken for using CNSL for lacquers, resins, paints, adhesives, varnishes, canning agents, dyestuffs etc.

1.4.5.1 Brakelinings: The major consumption of CNSL is for the production of friction lining materials for automobile brakes and clutches. Though very little information is available on brakelining materials[98,133] major portion of information is available in patents[89,90]. Friction materials serve in a variety of ways to control the acceleration and deceleration of vehicles and machinaries. Brakelinings and clutch facings based on CNSL resins have the property of absorbing the heat created by friction in the braking action while retaining their braking efficiency longer[98]. Besides, cashew based friction materials give much quieter braking action and are more efficient for cold wear. Over 90% of CNSL now imported into developed countries is processed into friction linings and clutch facings mainly because of its low fade characteristics. These materials are ideal for use in low speed automobiles where the temperature generated does not exceed 250°C. During 1971-1978 , estimated consumption of CNSL by the brakelining industry in India was in the range 1200-1400 tonnes[97]. A number of CNSL based friction materials with specific functional properties had been reported[138]. Friction dust consists of fatty thermo-hardened, polymerized CNSL/aldehyde reaction product, ground into a coarse dust[134]. Friction materials with enhanced thermal stability were obtained from formulation having CNSL-based particles along with other ingredients[139].

1.4.5.2 Surface coatings[97]: Surface coating materials are another outlet for CNSL based polymers. Surface coatings are employed for decoration/ protection of a surface from the environment. Paints and varnishes developed from CNSL offer properties superior to conventional oil or synthetic resin and it could be used for insulation, protection and decoration.

1.4.5.3 Paints and primers: CNSL is used only in the manufacture of dark coloured paints and black enamels. Inhibitive and flame resistant primers based on CNSL have improved flexibility and alkali resistance[140]. Fire resisting and heat insulating paints are based on sodium silicate to which CNSL/chlorinated CNSL were added[132]. CNSL - formaldehyde condensation product in alkaline medium on styrenation gives a resin which can be applied as a varnish to yield an enamel[140]. It can be polymerized on heating in presence of metals like copper, aluminium, lead or their oxides and which form a good media for paints[140].

1.4.5.4 Cashew lacquers: The lacquer made from CNSL could be used for insulation, protective or decorative coatings for furniture, buildings, automobiles, etc.[141]. They have optimum toughness and elasticity, excellent gloss and superfine adhesive qualities. Cashew lacquers can be easily applied to the substrate by brushing, spraying or dipping.

1.4.5.5 Cashew cements: CNSL polymers react with formaldehyde to give a rubbery gel which can be used as a cement hardener over a period[142]. It can be used for cementing of floor subject to chemical attack[135].

1.4.5.6 Speciality coatings: They are required for protecting surface exposed to extreme service conditions. CNSL based polymers offer excellent resistance to such environments. To improve the adhesion and flexibility of CNSL aldehyde condensation products, drying oils, bisphenols and epoxy resins were incorporated into condensation products which could be used in paints, varnishes, etc.[140]. Molten mixture of CNSL, asphalt, rubber and petroleum resin could be used as a "rust proof" tacky composition[140]. Central Building Research Institute, Roorkee, India[143] developed a surface coating based on CNSL suitable for application for wood based products. Regional Research Laboratory, Trivandrum, India[144] had developed a coating of CNSL in presence of copper sulphate which could extend the life of coconut leaf thatch from 1-4 years.

Gopalakrishna Pillai et al had reported that a modified CNSL resin could be used as an antifouling paint for marine use. The modified CNSL resin is the condensation product of CNSL after decarboxylation, with phenol-formaldehyde at controlled conditions[145]. Speciality coatings based on CNSL modified with polybutadiene and epoxy modified CNSL had been reported[146].

1.4.5.7 Industrial chemicals: CNSL form the basic raw material for a vast number of industrially important chemicals and chemical intermediates. The various components of cardanol can be suitably modified to obtain bactericides, surface active agents, antioxidants, etc.

Chlorinated products of cardanol and hydrogenated cardanol were found to have pesticidal action[140].

Cardanol and its ether were sulphonated under different conditions and neutralized with various bases to give surface active agents, for a wide variety of applications[140]. Anionic surfactive agents based on CNSL are suitable for high temperature processes[140]. Nonionic surfactive agents are good emulsifiers for oil-in-water and water-in-oil systems[140].

Azo dyestuffs were prepared by coupling a hydrogenated phenolic component of CNSL with an aromatic diazonium salt in presence of alcoholic solution. Dyes were also prepared by coupling p-anisidine with tetrahydrofuran[140].

Styrene-CNSL reaction products serves as a plasticizer for polymers improving filler uptake and other physical properties[140]. Methyl, ethyl, etc. ethers of anacardic acid and the thickened CNSL product obtained on heating them act as plasticizers for chloroprene rubber. They act by lowering the shore hardness and improving the elongation and aging characteristics of cured rubber[31]. Sulphurated CNSL and other CNSL derivatives find use as plasticizers in PVC and synthetic rubbers[147].

Sulphonation of CNSL - formaldehyde porous polymer with conc. sulphuric acid in presence of hydrochloric acid gives a cation exchange resin[146]. Anion exchange resin had been prepared by reacting CNSL with tetrachloroethylene and formalin[140].

N.D. Ghatge in 1979 had reported that 2-pentadecylbenzoquinone dioxime synthesized from CNSL gave good heat resistant vulcanizates for SBR and butyl rubber[31]. The presence of long chain hydrocarbon imparts softness to vulcanizates and they are more extensible and less scorchy than others.

1.4.5.8 Plastic materials: Cardanol/its derivatives could be converted to phenoplasts with better processability, hydrocarbon solubility, and resistance to acids and alkalies than the conventional phenol formaldehyde systems. Stable, rigid or flexible sheets, tiles, etc. were prepared from compositions containing CNSL, formalin, natural/synthetic rubber and other conventional ingredients[140]. Foam plaster based on CNSL have been reported[148].

R.K. Jain et al had reported use of a composition based on CNSL resin and coconut pith for the development of expansion joint filler[149].

A sealant material suitable for sealing joints and cracks in buildings was developed from CNSL. It possesses very low shrinkage and does not sag or flow at temperature upto 70°C[150].

1.4.5.9 Rubber compositions: Incorporation of CNSL had been found to improve the performance of rubber products. It aids processing and enhances the vulcanizate properties. CNSL enhances the insolubility of natural rubber vulcanizates in petroleum solvents[31].

In 1930 Harvey reported that when sulphur is heated with CNSL a gummy material is obtained which can be used for coating, impregnation and as a rubber substitute. He also reported that a rubber like substance can be obtained by heating CNSL with glycerine at about 245°C[151]. (Harvey M.T. (to the Harvey Corporation) U.S. Pat. 1, 771, 785 (1930), U.S. Pat. 1, 771, 786 (1930). He had also shown that when CNSL is intermixed with natural rubber, it enhances the insolubility of vulcanizates in petroleum solvent. Presence of CNSL in rubber helps the incorporation of sulphur and other ingredients and increase the resistance to moisture[152].

Newman et al had shown that latex of SBR or nitrile rubber can be mixed with CNSL modified phenolic resin and hexamine and then mixed with fillers to get composites suitable for moulding[153].

Ghatge and Mahajan used isomeric amino-3-pentadecylphenol in styrene-butadiene rubber to evaluate as antiradation agents[154]. Cardanol based resols and modified resols were synthesised and utilized for the vulcanization of butyl rubber by Ghatge and Shinde[155]. Due to presence of the long hydrocarbon chain in the dioxime, vulcanizates containing this compound were found softer, more extensible and less scorchy than others. Thus CNSL could be used as an indigenously available raw material in lieu of high priced petroleum based chemicals required for rubber industry. Scarcity of petroleum products have created a serious problem to the rubber industrialists, so that present interest to use CNSL will solve that problem to some extent.

1.4.5.10 Miscellaneous applications: Chen et al reported the synthesis of 6 titanate coupling agents using cardanol which had high reactivity and good hydrolytic stability[156]. Some CNSL based coatings suitable for use in wood and metal were prepared by Muturi Patrick. The gloss flexibility, impact resistance and corrosion of those coatings were compared favourably to those of commercial coating[157].

Jayabalan et al prepared slow and fast curing CNSL resins alone and based on novolac/resol by internal condensation methods. The resin had flexibility and form an insoluble rubbery mass on curing. The mechanical properties of glass fiber laminates prepared from modified resins were comparable with those of phenol-formaldehyde resin[158].

Panda et al reported the preparation of a liquid rocket fuel consisting of 70% cyclopentadine blended with 30% cardanol which undergoes synergistic hypergolic ignition with red fuming nitric acid[159].

Ghatge et al reported the preparation of a self catalytic resin from cardanol. Formaldehyde and diethanolamine which was blended with polyethylene glycol and resultant blend on treatment with polymeric MDI to obtain urethane foams of different densities[160].

1.5 Literature survey on coconut shell tar

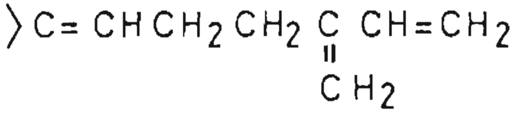
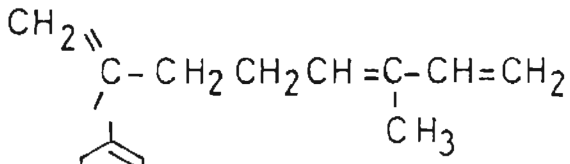
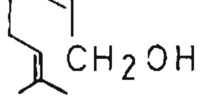
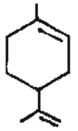
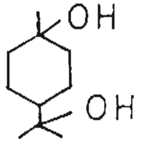
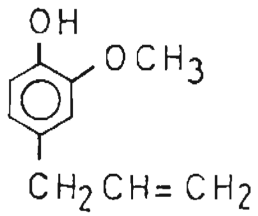
Coconut shells are commonly used as fuel and also for making ladles, scoopes, etc. But the shells used for these purposes account for only a small portion of the total quantity available. 400-500 thousand tons are available annually in India out of which only about half the quantity is collected. 2/3 of the collected material is burnt as fuel[161].

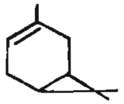
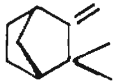
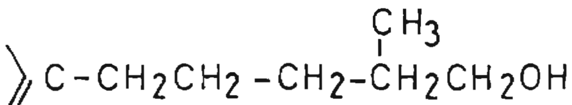
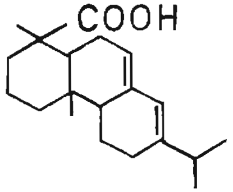
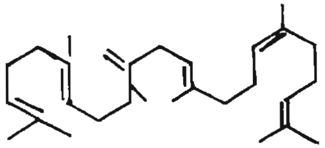
Destructive distillation of shells was undertaken on a commercial scale in Ceylon in 1939. The products obtained were: charcoal (35%), pyroligneous acid (38.2%), settled tar (5.6%) and gas. The pyroligneous acid gave crude acetic acid (13.9%) and wood spirit including acetone. The tar obtained by distillation upto 280°C contains 25% pitch[162]. Phenols constitute over 30% of the total settled tar and of this a large proportion is ordinary phenol. The higher boiling phenols have not been fully investigated[163]. Gaind and Singla had reported that an oily liquid obtained by destructive distillation at 100-240°C from shell fibres of

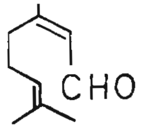
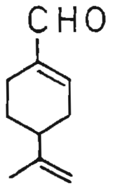
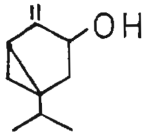
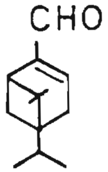
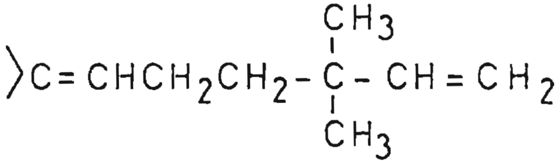
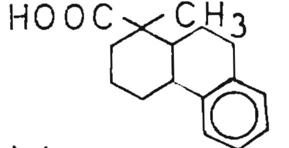
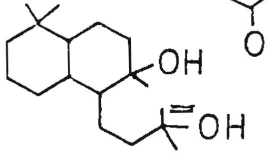
Cocos nucifera, Linn is very active against a number of pathogenic penicillin resistant gram positive and gram negative bacteria, but no chemical investigations had been carried out to find out the nature of the components of the distillate products of the shell fibres[164]. Coconut shell tar (CST) could also be obtained as a byproduct from charcoal industry[165].

CST is dark brown in colour with characteristic and unpleasant empyreumatic odour and is partially soluble in water and freely soluble in alcohol and acetone. About 4.5% of CST is steam volatile and ether soluble. The isolation of crotonaldehyde, furfural, acetic acid (22%), caproic acid, p-hydroxybenzoic acid, phenol, p-cresol and an unidentified compound of m.p. 39-40° from CST were reported[166].

TABLE - 1.1 HYDROCARBON TYPE COMPOUNDS – MONOMERS OF TERPENE ORIGIN

Name 1	Source 2	Structure 3	Properties 4
Myrcene[7] ($C_{10}H_{16}$)	Turpentine oil	 $\rangle C{=}CHCH_2CH_2\underset{\underset{CH_2}{\|}}{C}CH{=}CH_2$	Oil, pleasant odor, practically insoluble in water, soluble in alcohol, ether etc., bp. 166-168°C.
Ocinene[7] ($C_{10}H_{16}$)	Essential oil of Ocimum basilicum	 $CH_2{=}\underset{/}{C}-CH_2CH_2CH{=}\underset{\underset{CH_3}{\vert}}{C}-CH{=}CH_2$	Oil, pleasant odor, practically insoluble in water, soluble in alcohol, chloroform, bp.$_{70}$ 100°C.
Nerol[8] ($C_{10}H_{18}O$)	Neroli and bergamot oil		Liquid, odor of sweet rose, soluble in abs. alcohol.
Limonene[7] ($C_{10}H_{16}$)	Lemon, orange and bergamot oil		bp. 176-176.4°C.
Terpin[9] ($C_{10}H_{22}O_2$)	Essential oil of Myrocarpus sylvestris		Bitter taste, slight characteristic odor, sublimes 100°C, mp. 116-117°C.
Eugenol[9] ($C_{10}H_{12}O_2$)	Constituent of volatile oil of Myrtaceae and Lauraceae		Odor of cloves, spicy, pungent, mp. -9.2 to -9.1, insoluble in water, miscible with alcohol and ether.

1	2	3	4
Car-3-ene[7] ($C_{10}H_{16}$)	Turpentine oil, Swidish pine need oil		Sweet pungent odor, insoluble in water, miscible with oils bp.$_{765}$ 168-169°C.
α -pinene[7] ($C_{10}H_{16}$)	Coniferae, oil of turpentine		Practically insoluble in water, soluble in alcohol, ether, odor of turpentine bp.$_{760}$ 155-156°C.
β -pinene[9] ($C_{10}H_{16}$)	Coniferae, oil of turpentine		bp.$_{760}$ 164-166°
Camphene[8] ($C_{10}H_{16}$)	Oil of orange and Lemon oil		Insoluble in water, soluble in ether mp. 51-52°, bp.$_{760}$ 158.5-159.5°
Cintronellol[8] ($C_{10}H_{20}O$)	Rose and Lemon oil	 $\rangle C-CH_2CH_2-CH_2-\overset{\overset{CH_3}{\vert}}{C}H_2CH_2OH$	Oily liquid, slightly soluble in water, miscible with alcohol, bp.224.5°C.
Abietic acid[7] ($C_{20}H_{30}O_2$)	Oleoresin of P-Paulstris		Insoluble in water, soluble in alcohol, chloroform, mp. 172-175°.
Squalene[7] ($C_{30}H_{50}$)	Vegetable oil, Olive oil and fungi, ricebran oil		Oil, faint & agreeable odor, bp. 285° mp. -75°, Insol. in water.

1	2	3	4
Citral[8] $(C_{10}H_{16}O)$	Lemongrass oil, Mandarim oil		Insoluble in water, miscible with alcohol, strong lemon odor, bp.$_{1.6}$ 92-93°.
Perillaldehyde[9] $(C_{10}H_{14}O)$	Perilla nankinesis		Liquid, bp.$_{745}$ 237°.
Sabinol[9] $(C_{10}H_{16}O)$	Oil of Juniper		bp. 208°.
Myrtenol[9] $(C_{10}H_{16}O)$	Myrtus cummunis		bp. 222-224°.
Linalool[8] $(C_{10}H_{18}O)$	Sweet orange, Mysore oil	 $\rangle C=CHCH_2CH_2-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH=CH_2$	Insoluble in water, miscible with alcohol, ether, bp.$_{760}$ 198°.
Podocarpic acid[10] $(C_{17}H_{22}O_3)$	Resin of podocarpus cupressinium		Soluble in ether, alcohol, insoluble in water, chloroform , mp.193.5
Sclareol[11] $(C_{20}H_{36}O_2)$	Salvia Sclarea.L.		bp.$_{19}$ 218-226°, mp.104-106°

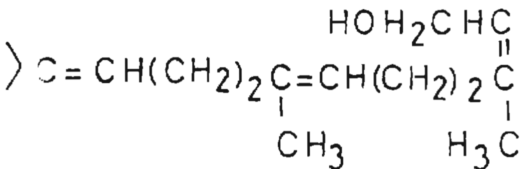
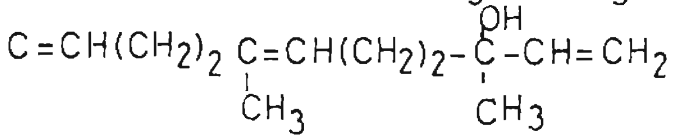
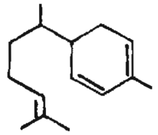
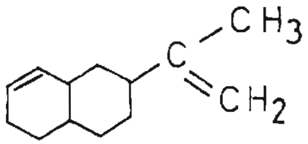
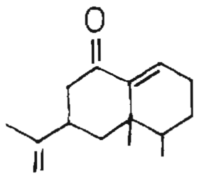
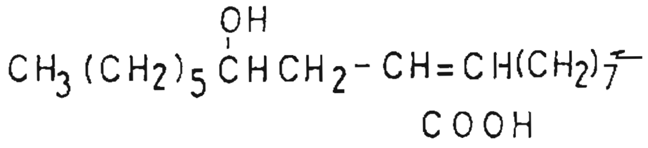
1	2	3	4
Farnesol[7] ($C_{15}H_{26}O$)	Flower oil of rose, Ambrette seed oil	 $\rangle C=CH(CH_2)_2\underset{CH_3}{C}=CH(CH_2)_2\overset{HOH_2CHC}{\overset{\|}{\underset{H_3C}{C}}}$	Liquid, bp.$_{0.55}$ 100°
Neroli diol[8] ($C_{15}H_{26}O$)	Neroli oil	 $C=CH(CH_2)_2\underset{CH_3}{C}=CH(CH_2)_2-\overset{OH}{\underset{CH_3}{C}}-CH=CH_2$	Liquid, pleasant odor, bp.276-277° at 6 mm pressure
Zingiberene[7] ($C_{15}H_{24}$)	Oil of ginger		bp. 134° at 14 mm pressure.
Selinene[9] (C_{15} H_{21})	Celery seed oil		bp.$_{11}$ 128-132°.
Eremophilone[9] ($C_{15}H_{22}O$)	Ermophila mitcheli		bp.$_{15}$ 171°, mp. 41 to 42°.

TABLE 1.2 MONOMERS OF FATTY ACIDS ORIGIN

Name	Source	Structure	Properties
1	2	3	4
Crotonic acid[12] ($C_4H_6O_2$)	Croton oil	$CH_3CH=CHCOOH$	Soluble in water, mp. 71.6°, bp.$_{760}$ 185°.
Oleic acid[12] ($C_{18}H_{34}O_2$)	Olive oil and almond oil	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Insoluble in water, soluble in alcohol, chloroform etc. Colorless liquid, bp. 286°.
Linoleic acid[12] ($C_{18}H_{32}O_2$)	Fatty acid of grape seed, Tobacco seed and sunflower seed oil.	$CH_3(CH_2)_4CH=CH\,CH_2\,CH=CH(CH_2)_7COOH$	Soluble in abs. alcohol, colourless oil, bp.$_{16}$ 230°.
Linolenic acid[12] ($C_{18}H_{30}O_2$)	Linseed oil, hempsed oil and perilla oil	$CH_3CH=CH\,CH_2CH=CH\,CH_2\,CH=CH(CH_2)_7COOH$	Insoluble in water, soluble in organic solvents.
Eleostearic acid[13] ($C_{18}H_{30}O_2$)	Bagilumbang nut oil	$CH_3(CH_2)_3CH=CH-CH=CH-CH=CH(CH_2)_7COOH$	
Ricinoleic acid[12] ($C_{18}H_{34}O_3$)	Castor oil, ergot oil	 $CH_3(CH_2)_5\overset{OH}{C}HCH_2-CH=CH(CH_2)_7COOH$	Soluble in alcohol, chloroform etc., liquid, bp.$_{10}$ 245°.

1	2	3	4
Succinic acid[14] ($C_4H_6O_4$)	Oil, Fungi, turpentine	$\begin{array}{l} CH_2-COOH \\ \vert \\ CH_2-COOH \end{array}$	Odorless, mp.185-187°, bp.235°.
Glutaric acid[14] ($C_5H_8O_4$)	Green sugar beet juice	$HOOC(CH_2)_3COOH$	Soluble in water, freely soluble in Eether, alcohol, bp.$_{760}$ 303-304°.
Adipic acid[14] ($C_6H_{10}O_4$)	Sugar beet	$HOOC(CH_2)_4COOH$	Soluble in alcohol, methanol, insoluble in benzene, mp.152°, bp.$_{760}$ 337.5°
Sebacic acid[15] ($C_{10}H_{18}O_4$)	Castor oil	$HOOC(CH_2)_8COOH$	Soluble in water and alcohol, mp. 134.5°, bp.$_{100}$ 294.5°.
Cinnamic acid[14] ($C_9H_8O_2$)	Natural balsam, cocoa leaves, cinnamol oil	$C_6H_5CH=CHCOOH$	Freely soluble in ether, benzene mp. 133°, bp. 300°
Tartaric acid[15] ($C_4H_6O_6$)	Shizardra Chimnsis, Tamarindus	$\begin{array}{l} COOH \\ \vert \\ (CHOH)_2 \\ \vert \\ COOH \end{array}$	mp. 206°.
Fumaric acid[14] ($C_4H_4O_4$)	Tagestes erecta	$\begin{array}{ll} HOOC- & CH \\ & \Vert \\ & HC-COOH \end{array}$	Insoluble in chloroform, benzene mp. 287°, sublimes at 200°.

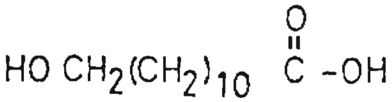
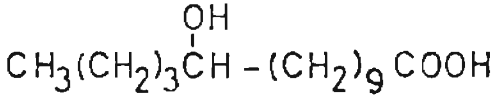
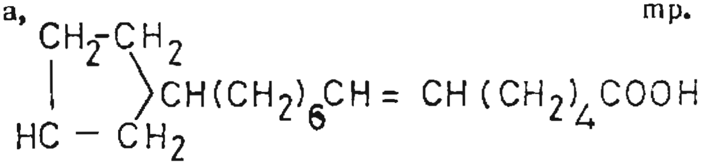
1	2	3	4
Vaccenic acid[12] ($C_{18}H_{34}O_2$)	Vegetable fats	$CH_3(CH_2)_9CH=CH(CH_2)_5COOH$	mp. 43°.
Tariric acid[12] ($C_{18}H_{32}O_2$)	Tariric seed or bitter bush oil	$CH_3(CH_2)_{10}C\equiv C(CH_2)_4COOH$	fp. 50.5°.
Isamic acid[12] ($C_{18}H_{26}O_2$)	Ongokea oil	$CH_2=CH(CH_2)_4C\equiv CC\equiv C-(CH_2)_7COOH$	mp. 39.5°.
Sabinic acid[12] ($C_{12}H_{24}O_3$)	Juniperus Sabina	 $HO\,CH_2(CH_2)_{10}\overset{\overset{O}{\parallel}}{C}-OH$	Soluble in acetone, mp. 39.5°.
Convolvulinolic acid[12] ($C_{15}H_{30}O_3$)	Convolvulacea family	 $CH_3(CH_2)_3\overset{\overset{OH}{\mid}}{C}H-(CH_2)_9COOH$	mp. 63.5 to 64°.
Gorlic acid[12] ($C_{18}H_{30}O_2$)	Seeds of onsoba, gorlid seed		mp. 6°., bp. 232.5°

TABLE 1.3 MONOMERS OF ALKALOID ORIGIN

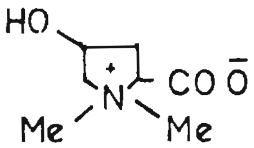
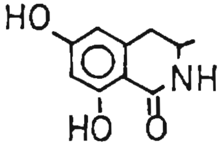
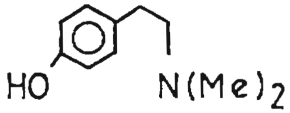
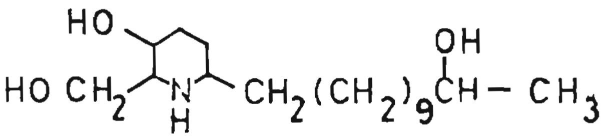
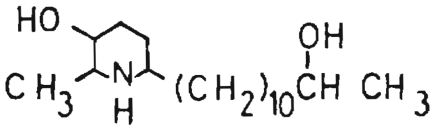
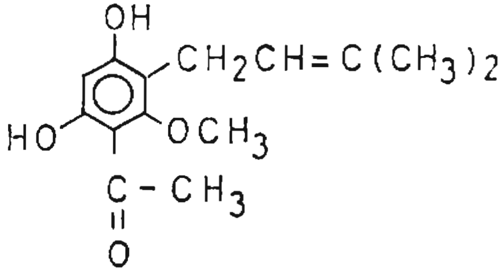
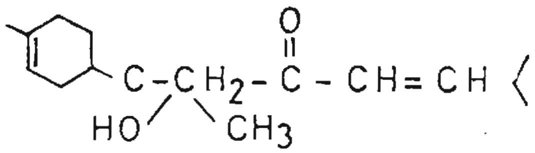
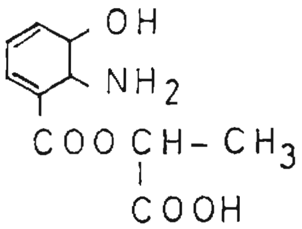
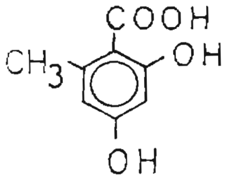
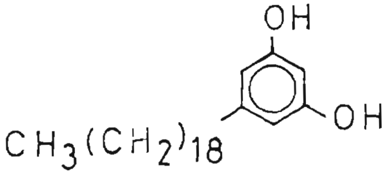
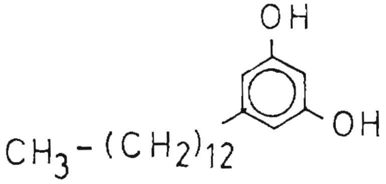
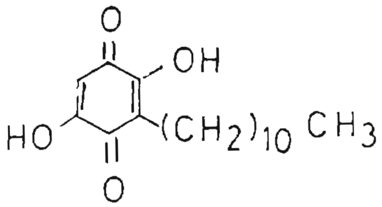
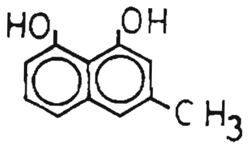
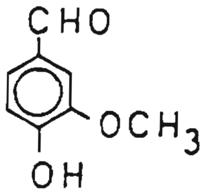
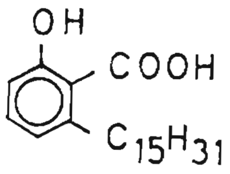
Name	Source	Structure	Properties
Betonicine[16] ($C_7H_{13}NO_3$)	Betonica officinalis.L.		Sweet taste, readily soluble in water or hot alcohol, insoluble in benzene and ether.
Siamin[17] ($C_{10}H_9NO_3$)	Casia Sianea		-
Hordenine[18] ($C_{10}H_{15}NO$)	Anhalonium species		Soluble in alcohol, ether, sparingly in benzene and toluene, bp. 173.4°
Prosopine[19] ($C_{18}H_{37}NO_3$)	Prosopis-afficana. Taub		mp.126°
Carnavaline[20] ($_{18}H_{37}NO_2$)	Cassia-carnaval speg.		mp. 60.7 - 61.2°.

TABLE 1.4 PHENOLIC AND HYDROXY MONOMERS

Name	Source	Structure	Properties
1	2	3	4
Acronylin[22] ($C_{14}H_{18}O_4$)	Acronychia laurifolia.BL		mp. 128-129°
α- bisabolone[23] ($C_{14}H_{24}O_2$)	Chrysanthemum flosulesum.L		Oil, $[\alpha]_D$-20.8°C
Oryzoxymycin[24] ($C_{10}H_{13}O_5$)	S. Venezulae		Amorphous Powder, mp.155°(decomp)

1	2	3	4
O-orsellinic acid[25] ($C_8H_8O_4$)	Chaetomium cochliodes		Soluble in water, alcohol, mp.175°
5-nondecyl resorcinol[26] ($C_{25}H_{44}O_2$)	Wheat bran		mp. 96.5 - 97.5°
5-tridecyl resorcinol[27] ($C_{19}H_{32}O_2$)	Grevillea robusta.A		mp. 82.3°
Embelin[28] ($C_{17}H_{26}O_4$)	Embelia ribes burm.		Soluble in hot organic solvents insoluble in water, mp. 142-143°.

1	2	3	4
3-Methyl naphthalene-1, 8-diol[29] ($C_{11}H_{10}O_2$)	Diopyrosmollis		mp. 140-141°
Vanillin[30] ($C_8H_8O_3$)	Vanilla Plansfolia		Pleasant aromatic odor, soluble in alcohol, ether etc. mp. 80-81°, bp. 285°.
Anacardic acid[31] ($C_{22}H_{36}O_3$)	Anacardium occidantale		-

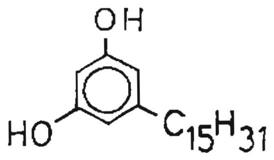
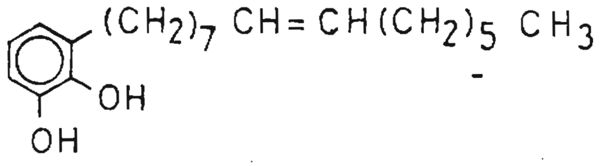
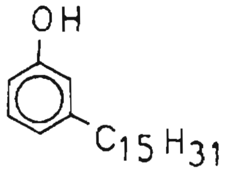
1	2	3	4
Cardol[32] ($C_{21}H_{36}O_2$)	Anacardium occidantale		-
Urushiol[33] ($C_{21}H_{34}O_2$)	Rhus vernicifera		-
Cardanol[34] ($C_{21}H_{35}O$)	Anacardium occidentale		Liquid, bp. 228-235° at 3.4 mm Hg.

TABLE 1.5 MONOMERS OF AMINO ACID ORIGIN

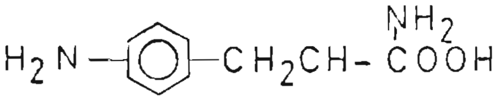
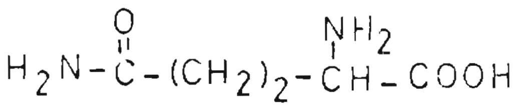
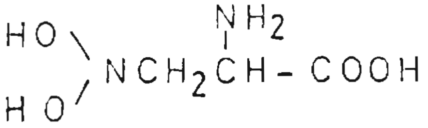
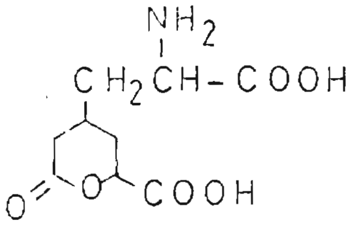
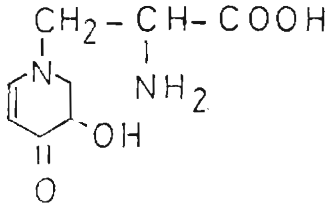
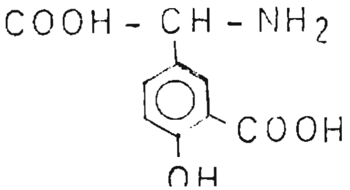
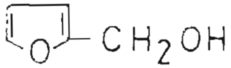
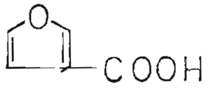
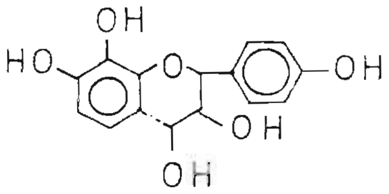
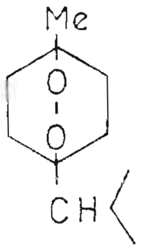
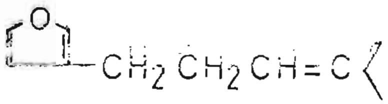
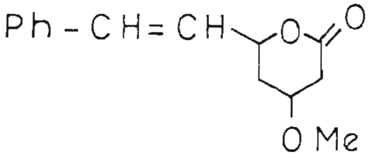
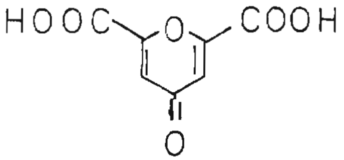
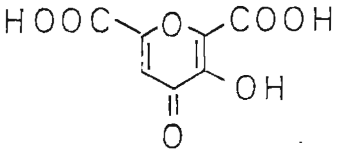
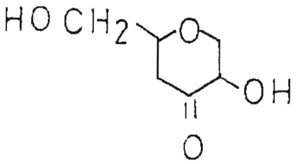
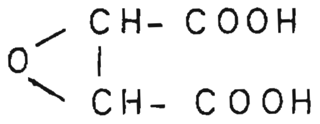
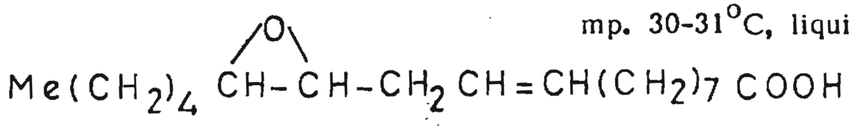
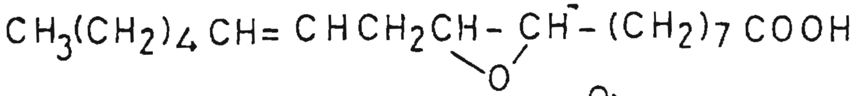
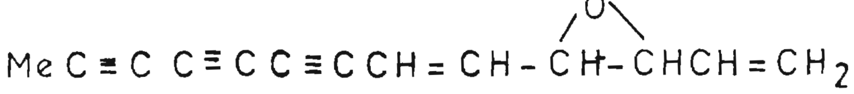
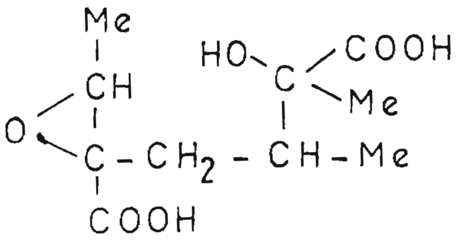
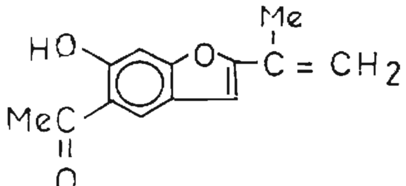
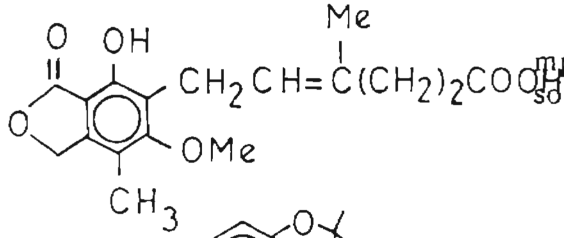
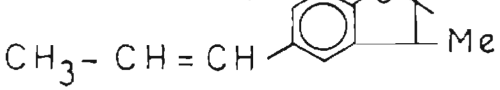
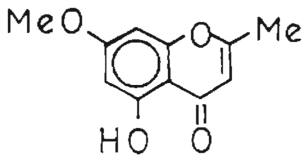
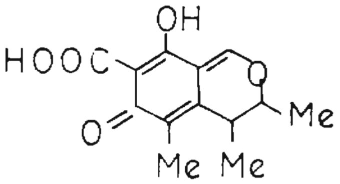
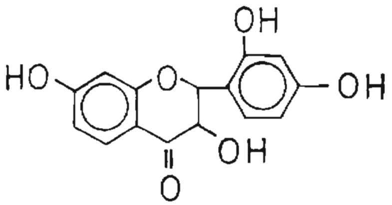
Name	Source	Structure	Properties
1	2	3	4
p-aminophenyl alanine[35] ($C_9H_{12}N_2O_2$)	Vigina vexillata		mp. 260-264° (decomp)
Glutamine[36] ($C_5H_{10}N_2O_3$)	Sugar beet, lemon	 $H_2N-\overset{O}{\overset{\Vert}{C}}-(CH_2)_2-\overset{NH_2}{\overset{\vert}{C}H}-COOH$	Insoluble in methanol, ether, ethanol, dec. 185-186°
Alanosine[37] ($C_3H_8N_2O_4$)	S. alanosinieus		Slightly soluble in water, insoluble in common organic solvents
Stizolobic acid[38] ($C_9H_{13}NO_6$)	Stizolobium hassjoo		mp. 231-3°, decomp. above 270°.
Mimosine[39] ($C_8H_{12}N_2O_4$)	Leucena glauca (wild)		Slightly soluble in water, insoluble in higher alcohols, mp. 236°.
(3-carboxy-4 hydroxy phenyl) glycine[40] ($C_9H_9NO_5$)	Dyer's weed		mp. 250°.

TABLE 16 MONOMERS OF FURAN AND DERIVATIVES

Name	Source	Structure	Properties
1	2	3	3
Furfural[42] ($C_5H_4O_2$)	Enteromorpha, Corncobs		Liquid, soluble in alcohol, ether, bp. $_{760}161.8^{\circ}C$
Furfuryl alcohol[43] ($C_5H_6O_2$)	Oil of cloves		Liquid, faint burning odor, miscible with water, soluble in alcohol, ether, bp. $_{760}170^{\circ}$.
β -Furoic acid[43] ($C_5H_4O_3$)	Eronymus atropurpureus		mp. 133-134°, bp. $_{760}230\text{-}232^{\circ}$. Freely soluble in ether
Teracacidin[43] ($C_{15}H_{14}O_6$)	Tannin, exudates from woody plants		Amorphous
Ascaridole[44] ($C_{10}H_{16}O_2$)	Chenopodium oil		Liquid, unstable, mp. 3.3°, bp.$_{0.2}$ 39-40°, soluble in hexane, pentane

1	2	3	4
Perillene[42] ($C_{10}H_{14}O$)	Perilla citriodora Makino		bp. 186°
Carlina oxide[43] ($C_{13}H_{10}O$)	Carline aeaulis L.		mp. 89°, bp. 168°,/20 mm.
5,6-Dehydro Kawain[43] ($C_{14}H_{16}O_3$)	Aniba firmule, Kawa root		mp. 140°
Chelidonic acid[45] ($C_7H_4O_6$)	Asparagus, Celandine anemone		mp. 262° (decomp)
Meconic acid[43] ($C_7H_4O_7$)	Papaveraceae		Soluble in ethanol, benzene, becomes anhydride when heated to 100-102°C for 20 min.
Kojic acid[46] ($C_6H_9O_4$)	Aspergilli		mp. 153-154°, soluble in water.

1	2	3	4
1,4-cineole[43] ($C_{10}H_{18}O$)	Piper Cubea, Xanthoxyla - rhetea		Colourless liquid, camphor like odor spicy taste, bp.172°, insoluble in water, miscible with alcohol.
Trans-epoxy succinic acid[47] ($C_4H_4O_5$)	Aspergillus - fumigatus		-
Vernolic acid[47] ($C_{18}H_{32}O_3$)	Vernonia - antholmintica, wild.		mp. 30-31°C, liquid at room temp.
Coronaric acid[48] ($C_{18}H_{32}O_3$)	Chrysanthemum - coronarium		
Pontica epoxide[49] ($C_{13}H_{10}O$)	Artemisia including A.pontica,L.		
Jacobine[50] ($C_{10}H_{16}O_6$)	S.Jacobaea.L.		-

1	2	3	4
Euparin[51] $(C_{13}H_{12}O_{3})$	E. Cannabinum		mp. 121-122°, soluble in alcohol, benzene
Mycophenolic acid[43] $(C_{17}H_{20}O_{6})$	Pencillum brevi, compactum		mp. 141°, insoluble in cold wwater, soluble in alcohol.
Anisoxide[43] $(C_{14}H_{18}O)$	Star aniso oil		bp. 141°/11 mm
Eugenin[52] $(C_{11}H_{10}O_{4})$	Eugenia caryophyllata		mp. 120°
Citrinin[53] $(C_{13}H_{14}O_{5})$	Aspergillus terreus		mp. 179°
Morin[43] $(C_{15}H_{10}O_{7})$	Calico yellow		mp. 303-304°.

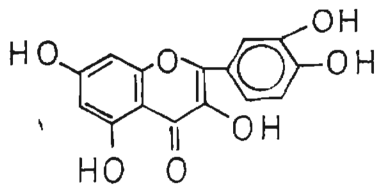
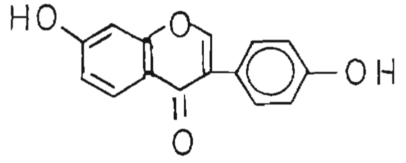
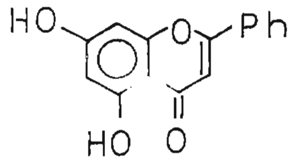
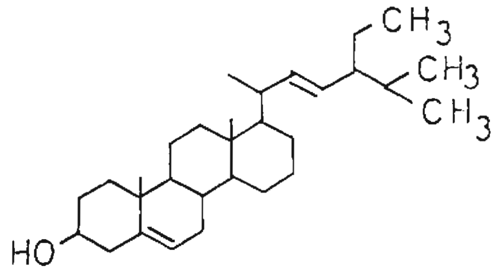
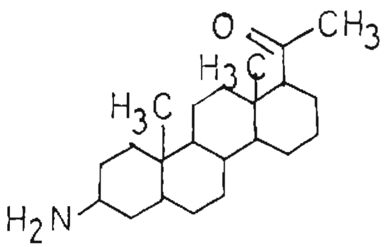
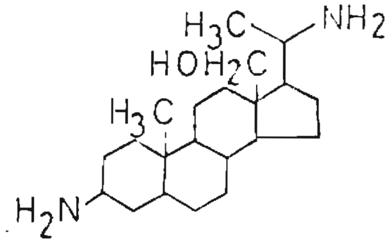
1	2	3	4
Quercetin[43] ($C_{15}H_{10}O_7$)	Aesculus		Soluble in glacial acetic acid
Diadzein[43] ($C_{15}H_{10}O_4$)	Pueria thunbergia, Berth.		Soluble in alcohol, ether, mp.320°.
Chrysin[43] ($C_{15}H_{10}O_4$)	Pinus species		mp. 285°, insoluble in water, soluble in alkali hydroxide.

TABLE 1.7 MONOMERS OF STEROID ORIGIN

Name 1	Source 2	Structure 3	Properties 4
Stigma Sterol[54] $(C_{30}H_{49}O)$	Calaber been, soybeen oil		
Funtumine[55] $(C_{22}H_{35}NO)$	Funtumia latifolia Stapf		mp. 126°, soluble in usual organic solvents.
Holarrhidine[54] $(C_{21}H_{38}N_2O)$	Holarrhena – antidysenterica		

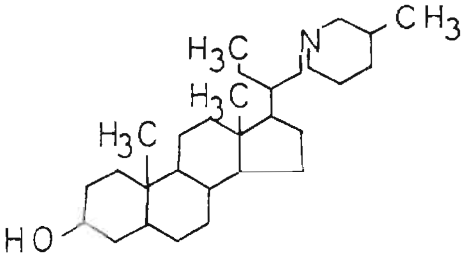
1	2	3	4
Solacongestidine[56] ($C_{27}H_{45}NO$)	Solanium Congestiflorum		-

TABLE 1.8 POLYMERIZATION METHODS USED IN POLYMERIZING NATURALLY OCCURING MONOMERS

Monomer	Polymerization techniques
Myrcene[61]	Polymerized using silica gel, synthetic magnesium or aluminium silicate.
Ocimene[61]	It is polymerized using silica gel, fullers earth, or artificial silicate of metals of group II or III of the periodic table.
Nerol[62]	Polymerized with ethylene oxide to form water soluble perfumes.
Limonene[6]	Polymerized with triisobutylaluminium-monochloride to get low molecular weight polymers.
Terpin[63]	Polymerized by condensation with bis-(cyclohexyloxy) dichlorosilane and gives water repellant coating.
Eugenol[64]	When treated with $SnCl_4$, polymers with molecular weight of the order of 2000 are formed.
Car - 3 - one[65]	Polymerized by mixing with anhydrous $AlCl_3$, when mixture of oligomers and high polymers are formed.
α - Pinene[6]	Polymerized using $AlCl_3$-dibutyltinchloride catalysts.
β - Pinene[6]	Polymers are prepared by initiation with high energy radiation, free radical and cationic catalysts.
Camphene[66]	Polymerized in gasoline solvents in presence of hydrogen fluoride below 30°C.

Monomer	Polymerization techniques
Citronellol[62]	Condensed with ethylene oxide to give water soluble perfumes.
Abietic acid[67]	Esters are prepared by refluxing polyglycerol-diglycerol with rosin and zinc dust and are used in varnishes.
Squalene[68]	Polymerized using acid clay catalyst at 200°C for 30 min. to give 56 to 58% polymer (yield).
Citral[69]	Polymerized catalysts and initiators.
Linalool[62]	Condensed with ethylene oxide to give water soluble perfumes.
Crotonic acid[14]	Co-polymerized with vinyl acetate using peroxide catalyst system.
Oleic acid[70]	Polymerized by heating a mixture of oleic acid, water, sodium hydroxide and acid activated montmorillonite clay at 240°C kept under steam pressure of 135 lb/sq. inc.
Linoleic acid[71]	Polymerized in presence of iron pentacarbonyl or Sn Cl_4. The polymeric fraction contained mainly dimer and a small fraction of a high molecular weight polymer.
Linolenic acid[72]	This acid in the form of its methyl ester can be polymerized by heating at 300°C in presence of hydrogen for 6 to 10 hours.
Eleostearic acid[12]	This acid is polymerized to form elastic gel by heating.
Ricinoleic acid[73]	Used as surface active agent by condensing castor oil with ethylene oxide.

Monomer	Polymerization technique
Succinic acid[14]	Polymerized in combination with a diol.
Glutaric acid[74]	Reacts with xylitol to give poly esters.
Adipic acid[14]	Undergoes polymerization to give artificial resin, plastics and urethane. It is used in the manufacture of nylon-6,6.
Sebacic acid[14]	Polymerized to synthetic resin of alkyd/polyester type, polyester rubbers and synthetic fibers of polyamide type.
Cinnamic acid[14]	Polymerized using uv radiation or thermal co-polymerization with styrene.
Azelaic acid[74]	Reacts with xylitol to give polyesters.
Tartaric acid[75]	Polymerizes in the form of its ester to give thermoplastic resins.
Fumaric acid[76]	Co-polymerized with styrene, vinyl toluene etc., to give rubbers, coatings etc.
Isamic acid[58]	Polymerizes when heated above 250°C. It is used as a drying oil.
Sabinic acid[77]	Gives 11% lactone, 69% dimeric lactone and 20% trimeric lactone when lactonized by boiling in benzene with $PhSO_3H$.
p-aminophenyl alanine[75]	A co-polymer of p-aminophenyl alanine and L-leucine is reported.
Glutamine[79]	A poly amino acid can be obtained by the poly condensation of aromatic amino carboxylic acid in presence of alkaline compounds.

Monomer	Polymerization technique
Furfuraldehyde[41]	Forms thermosetting resins with phenols and used in the manufacture of coated abrasive.
Furfuryl alcohol[80]	This compound, water and sulphuric acid when heated to 60°C give a liquid resin of uniform molecular size.
β -furoic acid[81]	Polymerized by heating with 98% sulphuric acid and a cation exchange resin is obtained.
Teracacidin[43]	When heated with mineral acid a polymeric material is formed.
Ascaridole[82]	1,2 & 1,4 - addition occurs with the formation of polymeric peroxides of dienes.
Vanillin[83]	Polymerized by treating with $HS(CH_2)_6SH$, and $HS(CH_2)_{10}SH$ & reaction is catalysed by hydrochloric acid.
Anacardic acid[31]	Methyl and ethyl, ethers of anacardic acid act as excellent plasticizers for chloroprene rubber and improves the aging and elongation characteristics of cured rubber.
Cardol[32]	Derivatives of cardol are used as anti-oxidants and also monomers.
Urushiol[33]	Salts of thiophosphate esters of urushiol have been found use as lubricants and adhesives.
Cardanol[84]	Cardanol gives vinyl resin which gives films with excellent adhesion, flexibility, resistance to oils, grease, water and chemicals. Cardanol can be polymerized by both addition and condensation techniques and the polymers have a variety of uses as surface coatings, adhesives, sealants, and also has applications in brake-linings, polymer-composites etc.

TABLE 1. 9 POSSIBLE POLYMERIZATION ROUTES FOR NATURALLY OCCURRING MONOMERS WHICH HAVE NOT YET BEEN POLYMERIZED

Monomers	Polymerization techniques
Perillaldehyde	Chain reaction polymerization can be initiated at the double bond in the side chain by normal techniques.
Sabinol	There is a possibility that ring opening polymerization can be carried out as in the case of β - pinene. The presence of -OH group will give hydrophilic character to the polymer.
Myrtenol	Ring opening polymerization is possible.
Podocarpic acid	Condensation polymerization with suitable bifunctional monomers is possible. Polymers with structural rigidity can be obtained from this and can be used for high temperature applications.
Sclareol	Chain reaction polymerization is possible through the double bond in the side chain. Condensation polymerization also can be initiated through the -OH group.
Farnesol	Addition polymerization can be carried out or double bond could be epoxified and epoxy-fatty acid polymers could be prepared. The system could also be considered for interpenetrating network polymer.
Neroli diol	Same as above
Zingiberene	Chain reaction polymerization is a possibility. High molecular weight polymers may be difficult due to steric hindrance but oligomers are possible.
Selinene	Chain polymerization is possible.
Eremophilone	Same as above.
Betonicine	Condensation polymerization is a possibility.
Siamin	Condensation polymerization with aldehydes is possible.
Prosopine	Condensation polymerization is possible. It can also be used as a cross-linking agent.

Monomers	Polymerization techniques
Hordenine	Aldehyde condensation is a possibility.
Carnavaline	Condensation polymerization with diacids, acid chlorides, isocyanates etc., is a possibility.
Vaccenic acid	Chain reaction polymerization is a possibility.
Tariric acid	Same as above.
Convolvulinolic acid	It can undergo self condensation to form polyesters.
Gorlic acid	Chain reaction polymerization is possible.
Acronylin	There is possibility of double bond being opened up for polymerization though there will be steric hindrance.
α -Bisabolone	Chain reaction polymerization is possible.
Oryzoxymycin	Condensation polymerization through -OH and - -NH_2 group with appropriate bifunctional reagents is a possibility and the probability of development of high temperature systems are envisaged.
O-orsellinic acid	It can be used as an cross-linking agent.
5-Nondecyl resorcinol	Condensation polymerization with aldehyde systems can be carried out. Side chain will impart internal plastisization.
5-Tridecyl resorcinol	Same as above
Embelin	Condensation polymerization through OH group is possible.
3-Methyl napthalene-1,8-diol	Condensation polymerization with aldehydes is possible.
Alanosine	Self polymerization is possible. It can also be used as a cross-linking agent due to its multifunctionality.
Stizolobic acid	Same as above
Mimosine	Same as above
(3-Carboxy-4-Hydroxy Phenyl) Glycine	Same as above.

Monomers	Polymerization techniques
Perillene	Chain reaction polymerization is possible though there will be steric hindrance.
Carlina oxide	Addition polymerization is possible.
5,6-Dehydrokawain	It could be polymerized by chain reaction techniques overcoming steric hindrance and rigid polymers could be built up.
Chelidonic acid	Polyester type polymer can be prepared.
Meconic acid	Polyester type polymer can be prepared.
Kojic acid	Condensation polymerization can be carried out.
1,4 cineole	Ring opening with cationic initiators like BF_3, $AlCl_3$, etc., may polymerize the compound.
Euparin	Chain reaction polymerization is possible.
Mycophenolic acid	Addition polymerization is possible and will form oligomers.
Anisoxide	Addition polymerization is possible and will form oligomers.
Anisoxide	Addition polymerisation could be effected but strong steric hindrance will be there.
Eugenin	Condensation polymerization with aldehydes is possible.
Trans-epoxy succinic acid	Epoxide polymers could be prepared.
Vernolic acid	Epoxide polymers could be prepared.
Coronaric acid	Epoxide polymers could be prepared.
Pontica epoxide	Further epoxidation is possible and epoxide polymer can be prepared.
Jacobine	Condensation polymerization will be effected through -COOH group and polyesters with epoxide could be prepared.
Morin	It can be used as a cross linking agent due to its poly-functionality and also could be considered for the development of heat resistant polymers.

Monomers	Polymerization techniques
Quercetin	Condensation polymerization with diacids, acid chlorides, isocyanates, etc., is possible.
Diadzein	Condensation polymerization with diacids, acid chlorides, isocyanates, etc., is possible.
Chrysin	Condensation polymerization with diacids, acid chlorides, isocyanates, etc., is possible.
Stigma sterol	The double bond in the side chain can be opened up and polymerized. Possibility of development of rigid polymers due to condensed ring systems.
Funtumine	This could be suitably modified to produce diamine functional groups and it can either be used as curing agents or in the development of polyamides.
Holarrihidine	This could be used as a monomer for polyamide system and can be used as curing agents.
Solacongenstidine	The presence of -OH group allow ready modification of monomer and incorporation into polymer structure.

TABLE 1.10: PHENOLIC COMPOSITION (%) OF NATURAL AND TECHNICAL CNSL

Component	Natural CNSL	Technical CNSL
Cardanol	1.20	62.86
Cardol	11.31	11.25
2-Methyl cardol	2.04	2.08
Anacardic acid	64.93	-
Polymer and minor materials	20.3	23.8

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CHAPTER 2

OLIGOMERIZATION OF CARDANOL OVER ACID CATALYSTS

CHAPTER 2

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2.1 Introduction

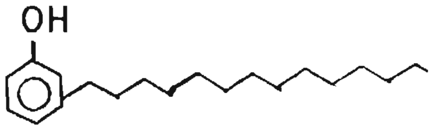
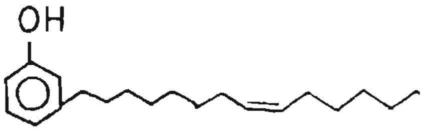
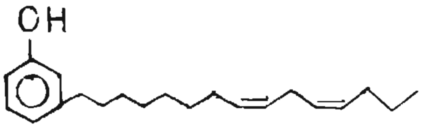
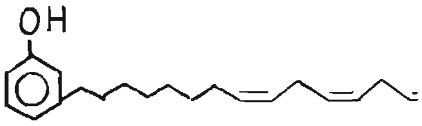
Cardanol is a phenolic derivative with a C_{15}–side chain in the meta position and is obtained from cashewnut shell liquid (CNSL) by vacuum distillation at 3.4 mm Hg (B.P. 228 - 235°C)[1]. CNSL contains about 90% of its weight cardanol. The physical properties of cardanol are tabulated in Table 2.1.

TABLE 2.1 PHYSICAL PROPERTIES OF CARDANOL

B.P. °C	228-235°C (3.4 mm Hg)
Colour (Lovibond, 1 cm cell)	Red (1.0 - 3.0)
Freshly distilled	Yellow (1.5 - 3.5)
Viscosity 30°C cP	45 - 52
Refractive index	1.509

Cardanol is a mixture of four components differing in the degree of unsaturation at the side chain. Table 2.2 shows the structure, molecular weight, and % composition of each component of cardanol[2]. The % composition, however, may vary depending upon the source, method of extraction, etc.

TABLE 2.2 CHEMICAL COMPOSITION OF CARDANOL

Component	Molecular weight	%	Molecular structure
Cardanol with saturated side chain	304	5.4	
Cardanol with one double bond in the side chain	302	48.5	
Cardanol with two double bonds in the side chain	300	16.8	
Cardanol with three double bonds in the side chain	298	29.3	

Structural elucidation of cardanol was carried out using NMR by P.H. Gedam[3] et al and extensive literature is available on the separation of the components of cardanol which is described in detail in the previous chapter.

Cardanol has the phenolic ring and the side chain double bonds as functional groups and through either of which it could be polymerized. Cardanol is reported to be polymerized using anhydrous aluminium chloride, anhydrous ferric chloride, anhydrous stannic chloride etc. and further the resin is reported to be hardened by condensation reaction with para formaldehyde. This material could be used as a condensate for filling[4]. Kinetics of alkaline catalyzed formaldehyde condensation polymerization of cardanol had been studied recently by Misra et al[5], and the dimerization through the side chain double bonds had been investigated by J.H.P. Tyman[6].

Cardanol could be converted into high value polymers or suitable products and is the subject of numerous patents[7]. Being a phenolic derivative with a C_{15} side chain in the meta position, this molecule provides possibilities of polymerization through the phenolic ring. Polymerization through the double bonds of the side chain, of course, may not yield products with high degree of polymerization. However, phenol-formaldehyde products reported from cardanol do not give good mechanical properties due to the presence of a long substitution at the phenolic ring. Possibility exists to improve the mechanical properties of cardanol-formaldehyde by involving the long side chain also in the polymerization process. This could not be achieved in cardanol formaldehyde condensation step and hence had to be performed by independent steps. Polymerization of cardanol through side chain double bonds, although, cannot proceed to very high molecular weight product, could yield oligomers. This product on further polymerization could be expected to give improved mechanical properties.

Oligomerization of cardanol had already been attempted using acidic catalysts by J.H.P. Tyman[6]. He reported that a preliminary acidic polymerization of the side chain had been carried out with diethyl sulphate or dimethyl sulphate, and the semi-polymerized material is further condensed with formaldehyde. Polymerization of CNSL using 25% solution (v/v) of concentrated sulphuric acid in diethyl sulphate was used to find out the gel time of CNSL[8]. It is reported that monoalkyl sulphate, dialkyl sulphate, etc. can also be used for the polymerization of cardanol besides sulphuric acid. Examples of dialkyl and monoalkyl acid sulphates suitable for the oligomerization of CNSL/cardanol are dimethyl sulphate, diethyl sulphate, dibutyl sulphate and dipropyl sulphate[9].

Another catalyst that can be used for oligomerization is boron trifluoride-etherate (BF_3/Et_2O) complexes. This is often used for the polymerization of olefins, diolefins and vinyl ethers belonging to the class of Brönsted acid/Friedel-Crafts acids initiating systems. Most investigations have been carried out with the reasonably stable BF_3/Et_2O complex, but other etherates such as $O\text{-}n\text{-}Bu_2$ have also been used occasionally[10]. Though there are a large number of polymerization reactions induced by these complexes, there were only two reports that concern the chemistry of these reactions. Worsfold and Bywater investigated the polymerization of α-methyl styrene[11] and Giusti et al studied that of styrene using BF_3/Et_2O in the presence and absence of water[12]. The data obtained by these groups indicate that although BF_3/Et_2O may be active, BF_3/H_2O is probably a much more active initiating system. But many scientists found the use of relatively less reactive but conveniently applicable BF_3/Et_2O complex more advantageous than the highly reactive BF_3/H_2O system.

A systematic study on the nature and kinetics of oligomerization of cardanol through the side chains using a variety of acid catalysts and other cationic initiators is attempted in this chapter. Initiators chosen for oligomerization are diethyl sulphate-sulphuric acid (3:1), diethyl sulphate-phosphoric acid (3:1) and boron trifluoride-etherate.

2.2 Experimental

2.2.1 Materials

Cardanol: Cardanol was obtained from M/s. Satya Chemicals, Madras, India, and was purified by distillation under vacuum at 3.4 mm Hg and the fraction distilled at 228-235°C was collected.

Boron trifluoride etherate (BF_3-Et_2O): BF_3-Et_2O (Fluka AG) was used after purification by distillation under vacuum and the fraction at 65°C was collected (at 3-4 mm Hg).

2.2.2 Methods

2.2.2.1 Synthesis

2.2.2.1.1 Oligomerization using diethylsulphate-sulphuric acid (DES-H_2SO_4) catalyst system

A 25% solution (v/v) of sulphuric acid in diethyl sulphate was prepared. In a typical procedure 50 g (0.166 mole) of cardanol was mixed with 3 ml of this reagent (containing 0.014 mole of sulphuric acid and 0.017 mole of diethyl sulphate) and taken in a 3-necked flask fitted with a mechanical stirrer, N_2-inlet and a reflux condenser. The whole assembly was kept in a thermoregulated bath kept at 180°C and the mixture was stirred for 1/2 hr. After the reaction, the monomer and the catalysts were washed off with methanol and the polymer was dried and weighed. The experiment was repeated by varying the temperature, reaction time and catalyst concentration and the conditions were optimized with respect to maximum yield.

2.2.2.1.2 Oligomerization using diethyl sulphate - phosphoric acid ($DES-H_3PO_4$) catalyst system

Since phosphoric acid was not soluble in diethyl sulphate, they were added separately and the experiment was carried out as in the case of $DES-H_2SO_4$ system.

2.2.2.1.3 Oligomerization using boron trifluoride-etherate (BF_3-Et_2O)

20 g cardanol (0.066 mole) was mixed with 0.6 ml (0.0047 mole) of BF_3-Et_2O and the reaction was carried out as in the case of $DES-H_2SO_4$ catalyst system by heating and stirring the reaction mixture at 80°C for 1 1/2 hrs and the product was also worked as in the previous cases.

2.2.2.2 Physical and chemical characterization

2.2.2.2.1 Viscosity[13]

Relative viscosity (η_r) of oligomerized samples using different catalyst systems were measured using Ubbelholde viscometer at 45°C using toluene as the solvent. Relative viscosity and the intrinsic viscosity $[\eta]$ were calculated using the following equation.

η_r = t/t_o where is the time (sec) of flow for the solution and t_o is that for the solvent.

$\eta_{sp/c}$ (specific viscosity) = $t - t_o/t_o$

$\eta_{sp/c}$ was plotted against C where C is the concentration of the solution in g/dl and the graph was extrapolated to $[\eta_{sp/c}]_{C=0}$, the intercept of which gives the value of $[\eta]$

2.2.2.2.2 Determination of hydroxyl value[14]

Hydroxyl value is defined as the number of milligrams of potassium hydroxide required to neutralize 1 gram of sample. It was determined by acetylation method.

Around 2 g of polymer was weighed and 20 ml of acetylating mix (120 ml acetic anhydride mixed with 880 ml anhydrous pyridine) was added. The flask was heated under reflux on a water bath for an hour. 25 ml of benzene was added, flask was stoppered and vigorously shaken. 100-150 ml water was added and titrated against sodium hydroxide (0.5 N).

Hydroxyl value was calculated using the following equation:

$$\text{Hydroxyl value} = 56.1\,(v_1 - v_2)\,n/m$$

where v_2 and v_1 are the volumes (ml) of 0.5 N potassium hydroxide used for the titration of sample and blank respectively.

n - normality of potassium hydroxide

m - weight of the polymer sample, g

2.2.2.2.3 Determination of iodine value[14]

Iodine value is defined as the number of centigram of iodine absorbed per gram of the sample and was determined by Wij's method.

To determine iodine value by Wij's method, a small portion of the material was slowly heated to 205 ± 5°C on an electric hot plate with continuous stirring till the foaming cease. Then it was cooled and filtered. 0.1 to 0.14 g of filtered material was accurately weighed into an iodine flask. 20 ml of Wij's solution was pipetted into the flask and 20 ml of mercuric acetate was added. The flask was stoppered and swirled to ensure intimate mixing for 1 minute and was allowed to stand in the dark for 2 minute. A duplicate was run side by side with blank determination. 50 ml of potassium iodide solution was added followed by 100 ml water, and was titrated with sodium thiosulphate solution. Iodine value was calculated using the following equation:

$$\text{Iodine value} = 12.69\,(v_1 - v_2)\,n/m$$

where v_2 and v_1 are volumes (ml) of 0.01 N sodium thiosulphate used for the titration of the sample and blank respectively.

n - normality of sodium, thiosulphate solution

m - weight of the polymer sample, g

2.2.2.4. Spectral characterization

Infrared spectra (IR): The IR were recorded as a neat film (liquids) or as nujol mull or KBr pellets (solids) on a Perkin-Elmer Model 2993 B Infrared spectrophotometer.

^{1}H NMR spectra: ^{1}H NMR spectra were recorded in a JEOL FX - 90 Q spectrometer.

Mass spectra: Mass spectra were recorded on a VG MICROMASS 70-70 H instrument with 2035 data system.

2.2.2.5 Gel permeation chromatogram (GPC)

GPC were recorded on a Waters 244 instrument fitted with a 6000 A pump system and a column combination of 100, 500 Å (micro styragel) with tetrahydrofuran as solvent at a flow rate of 1 ml/minute. A Differential Refractometer R 40 with sensitivity 8 X is used as the detector.

2.3 Results and Discussion

The oligomerization of cardanol was studied as described in the experimental. Reaction of cardanol with catalysts, DES-H_2SO_4, DES-H_3PO_4 and BF_3-Et_2O at various temperatures gave rise to an increase in viscosity indicating oligomerization. The intrinsic viscosity was measured in toluene at 45°C and the values are tabulated in Table 2.3.

The optimum reaction conditions of oligomerizations are given in Table 2.4. The viscosity comparison was carried out at 160°C rather than at the optimum temperature because oligomerization using BF_3-Et_2O gave a gel productat 180°C.

TABLE 2.3 OLIGOMERIZATION CONDITIONS OF CARDANOL

Product	Catalyst	Temp. ^{o}C	Duration of oligomerization (mts)	$[\eta]$ (dl/g)
I	Nil.	30	30	0.005
II	Nil	160	30	0.009
III	DES-H_2SO_4	160	20	0.032
IV	DES-H_3PO_4	160	13	0.021
V	BF_3-Et_2O	160	15	0.01

TABLE 2.4 OPTIMUM REACTION CONDITIONS FOR MAXIMIUM YIELD

Catalyst	Time (min)	Temp. ^{o}C	Catalyst conc. (%)
DES-H_2SO_4	30	180	6
DES-H_3PO_4	20	180	10
BF_3-Et_2O	90	80	3

The products of oligomerization were analyzed by GPC and the GPC of products I, II, III, IV and V (viz. Table 2.3) are given in Fig. 2.1. Fig. 2.1 indicates that cardanol with a molecular weight around 300 has oligomerized into dimer, trimer, tetramer and higher oligomers with molecular weights around 600, 900, 1200 and $>$ 1200. The % composition computed from the GPCs are given in Table 2.5.

TABLE 2.5 % COMPOSITION OF CARDANOL OLIGOMERS

Product	Monomer (%)	Dimer (%)	Trimer (%)	$\geqslant$Tetramer (%)
I	100	-	-	-
II	94.13	2.68	3.19	-
III	9.9	9.3	21.41	59.39
IV	21.07	35.5	17.11	26.3
V	53.72	43.02	3.25	-

The higher oligomer content in the case of product III (using DES-H_2SO_4) in comparison to product IV (using DES-H_3PO_4) is also reflected in the $[\eta]$ measurements viz. 0.032 and 0.021 respectively.

Spectral Analysis

Figures 2.2, 2.3, 2.4, 2.5 and 2.6 show the IR spectra and figures 2.7, 2.8, 2.9, 2.10 and 2.11 show the NMR spectra of products I, II, III, IV and V respectively. The comparison of IR spectra indicate the loss of unsaturation (peak at 1630 cm^{-1}) from cardanol on oligomerization.

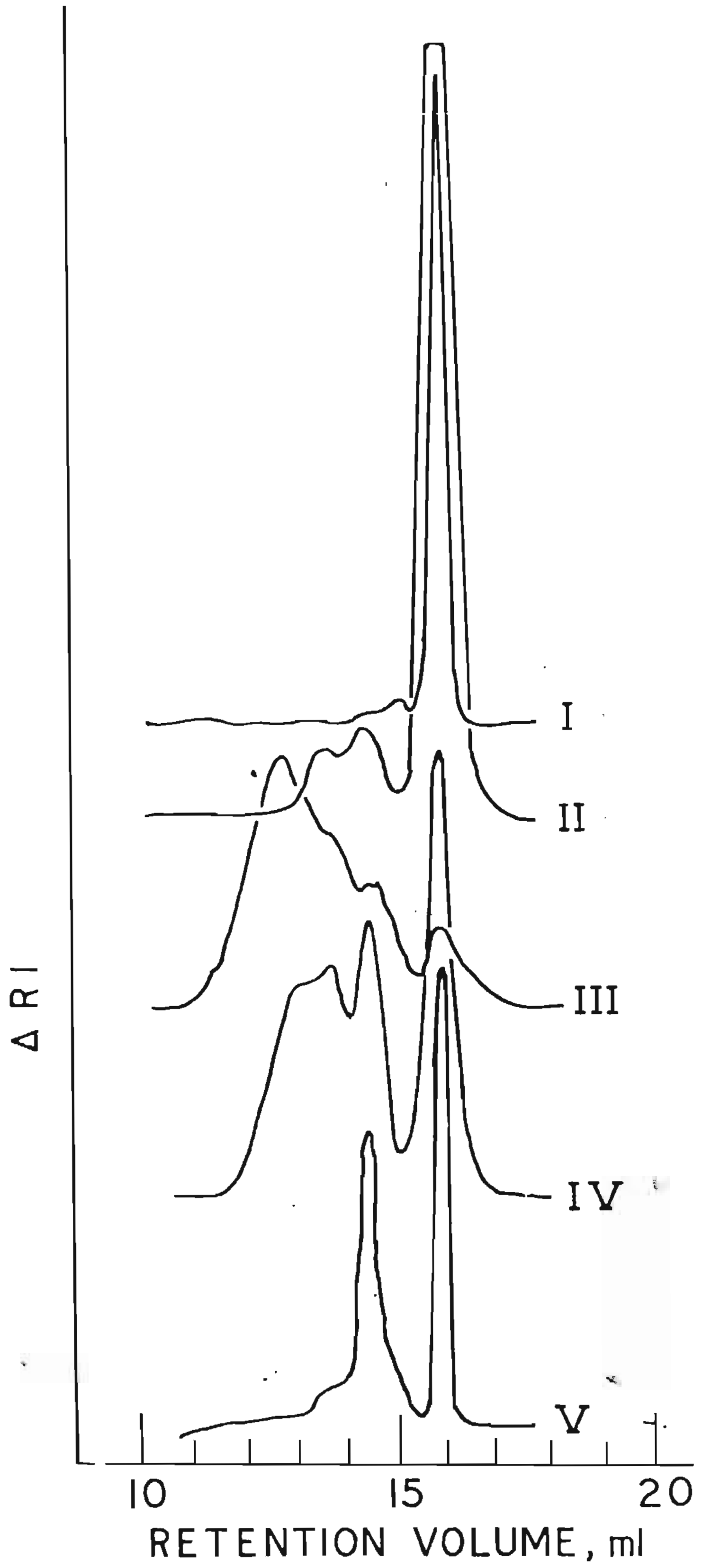


Fig. 2.1 GPC of products I, II, III, IV & V

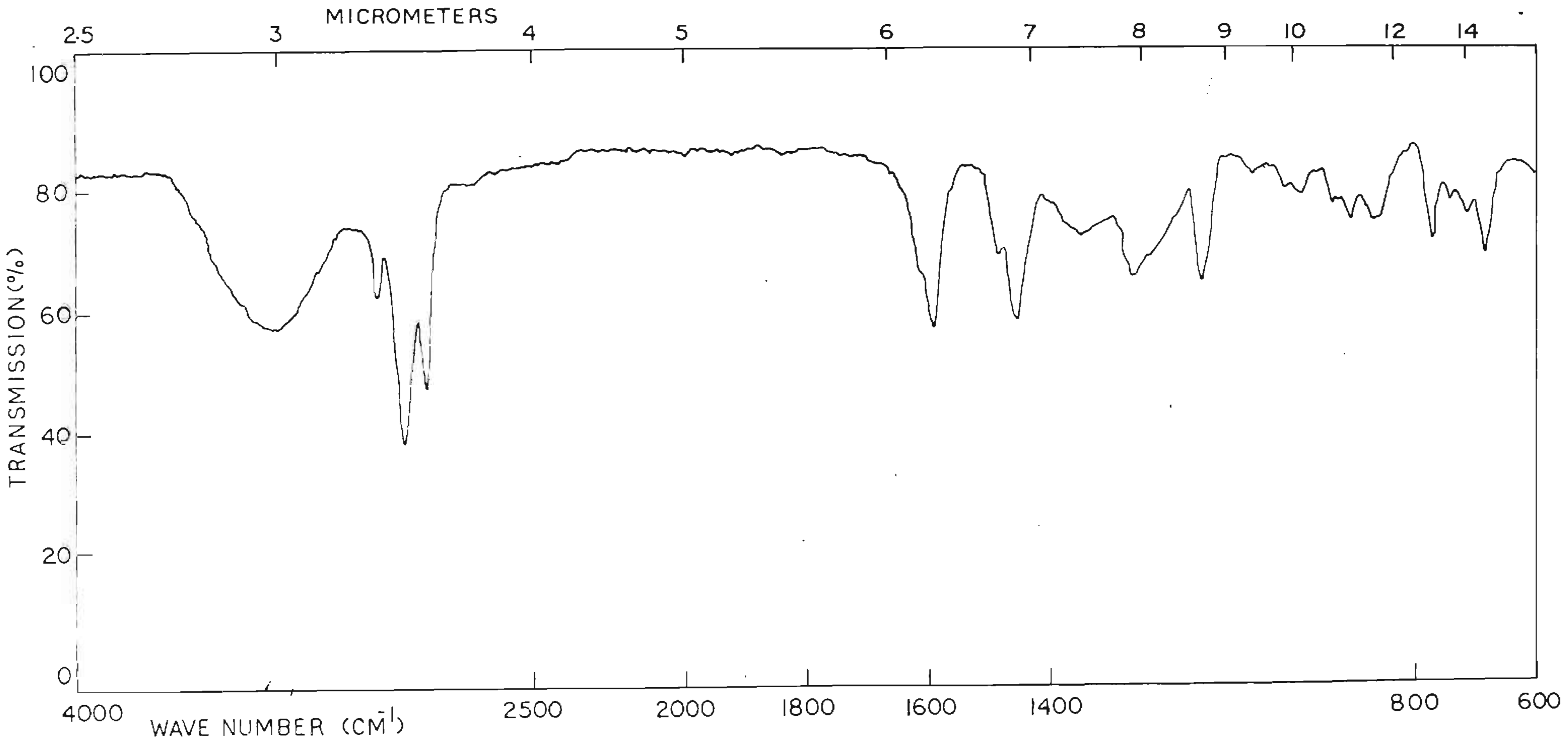


Fig 2.2. IR of product I

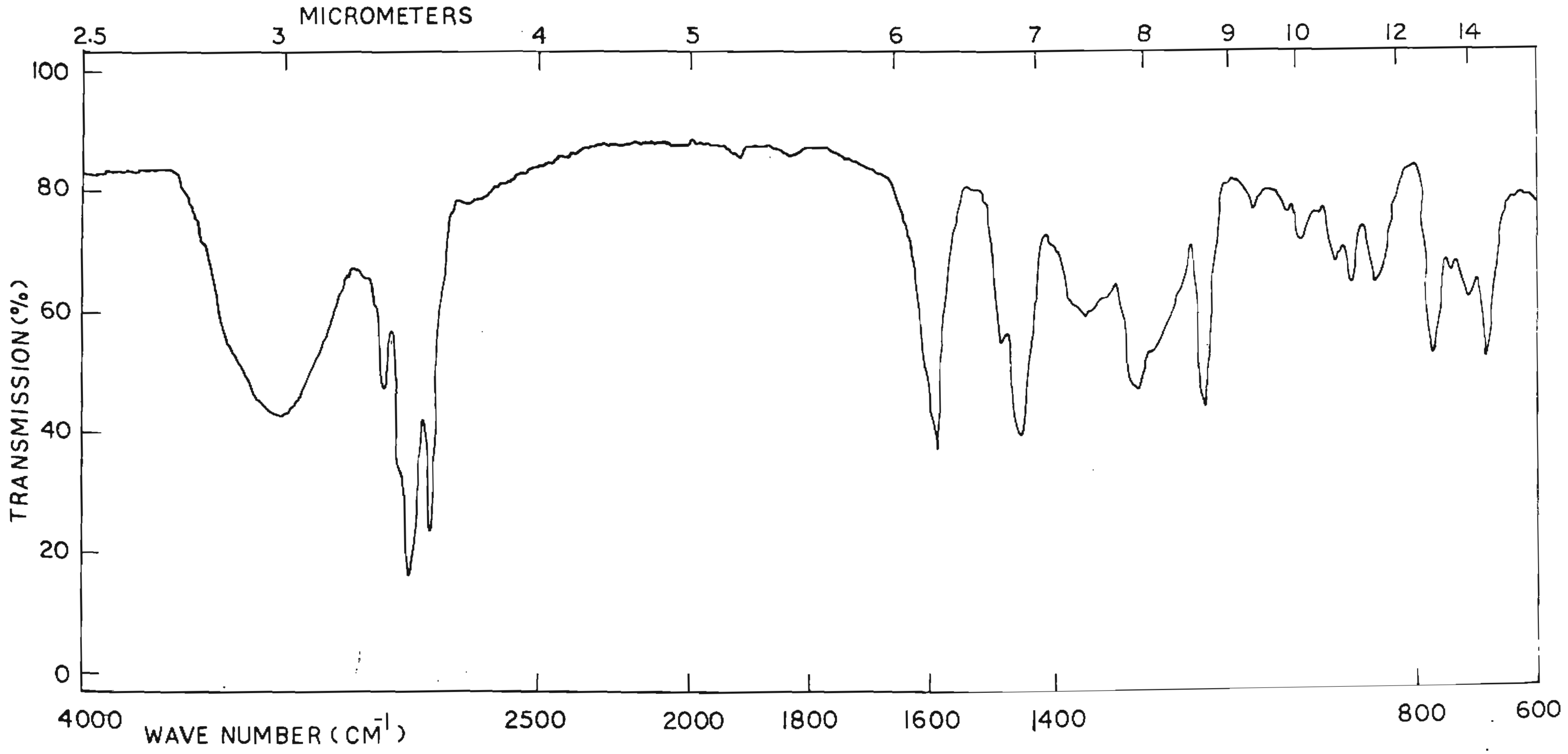


Fig 2.3. IR of product II

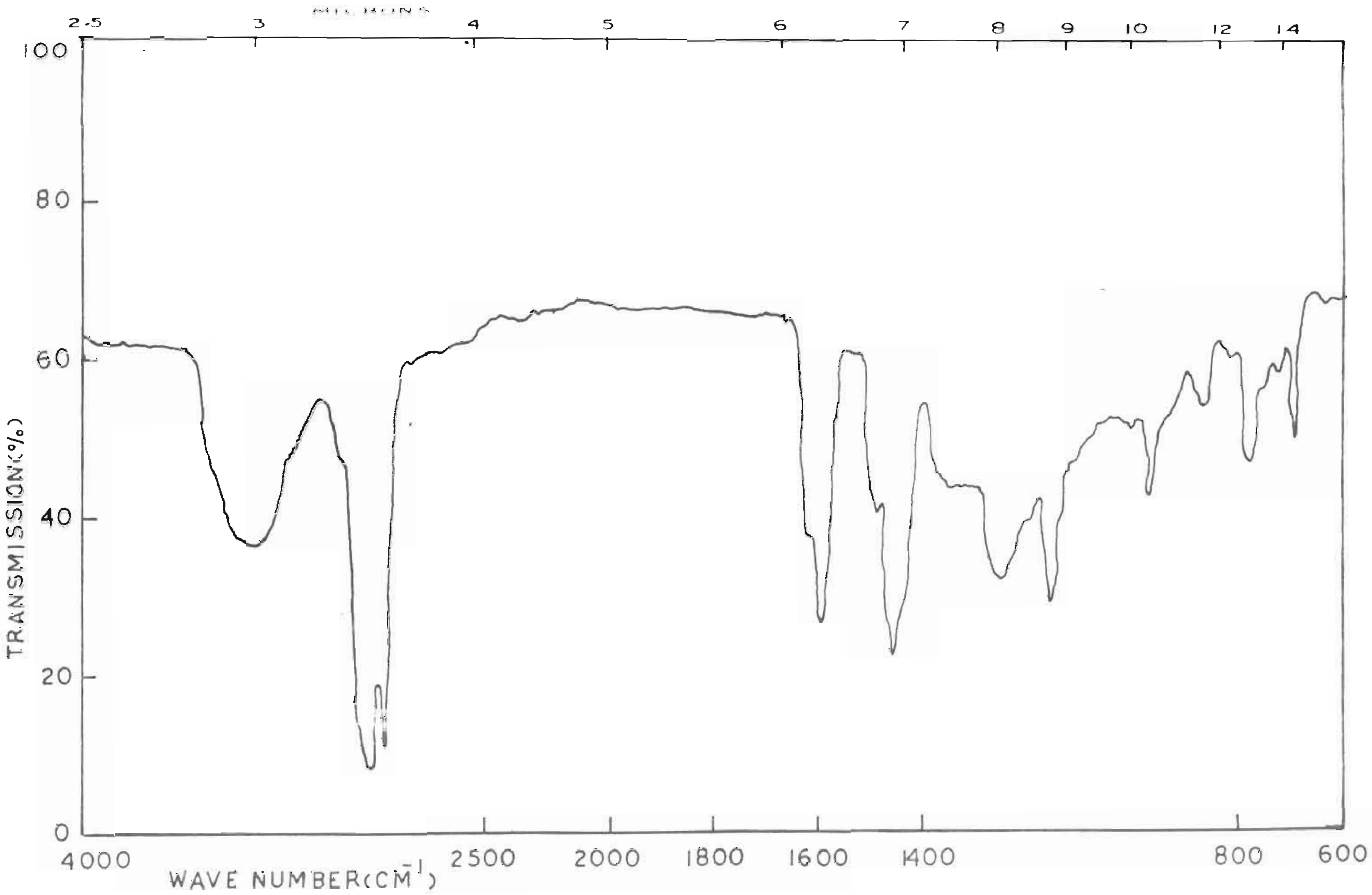


Fig 2.4 IR of product III

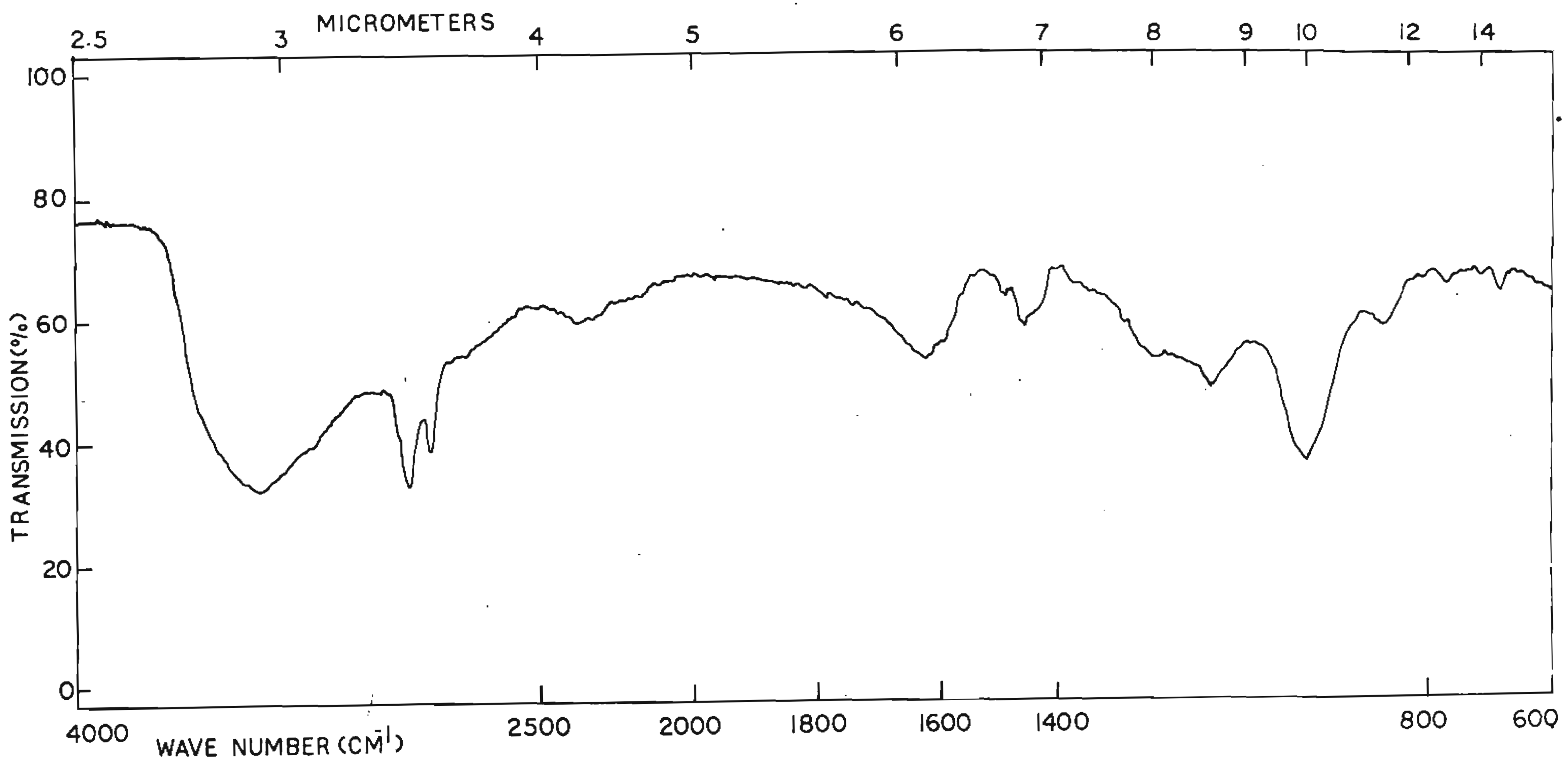


Fig 2.5. I R of product IV

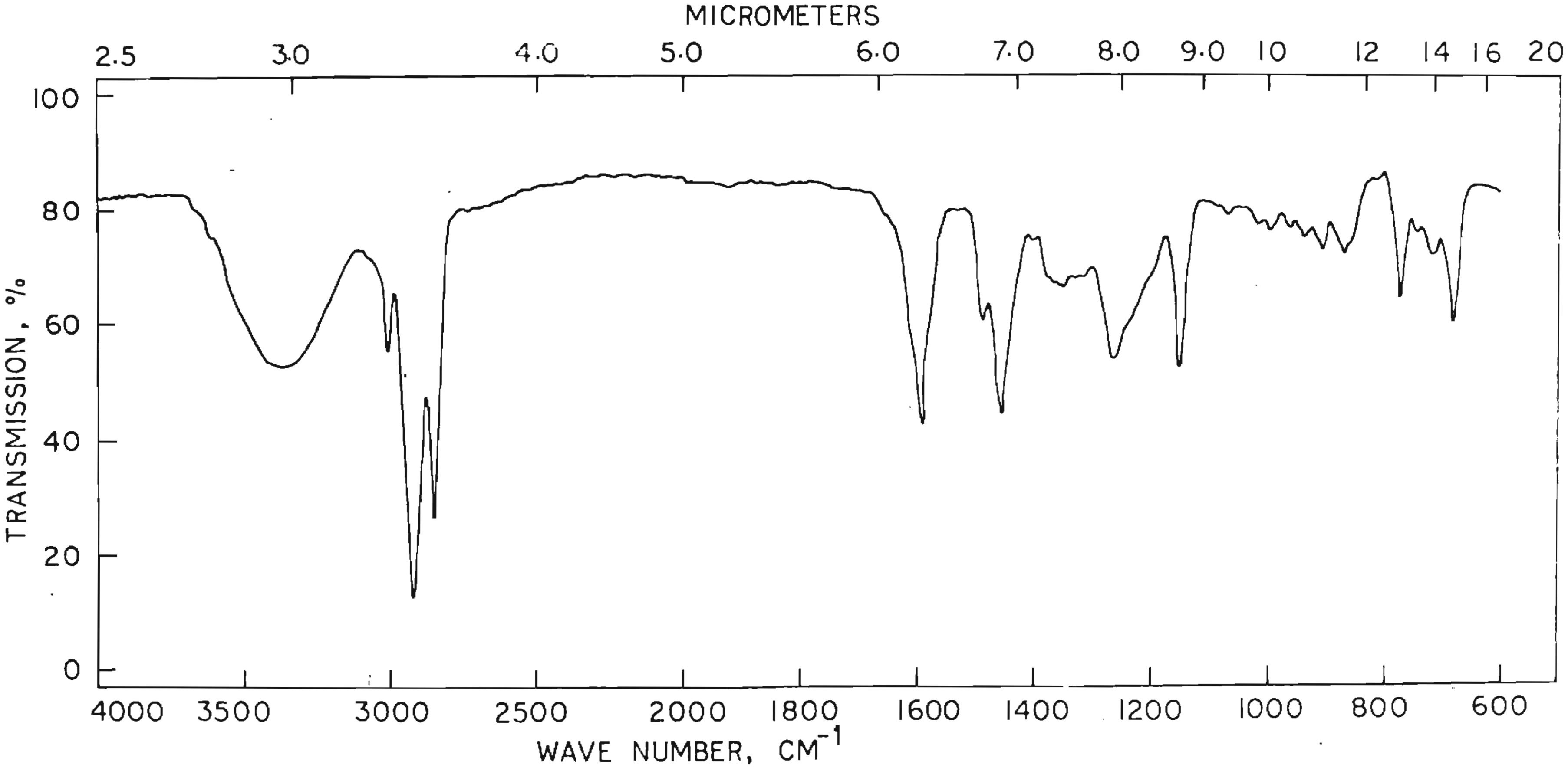


FIG. 2.6. IR OF PRODUCT V

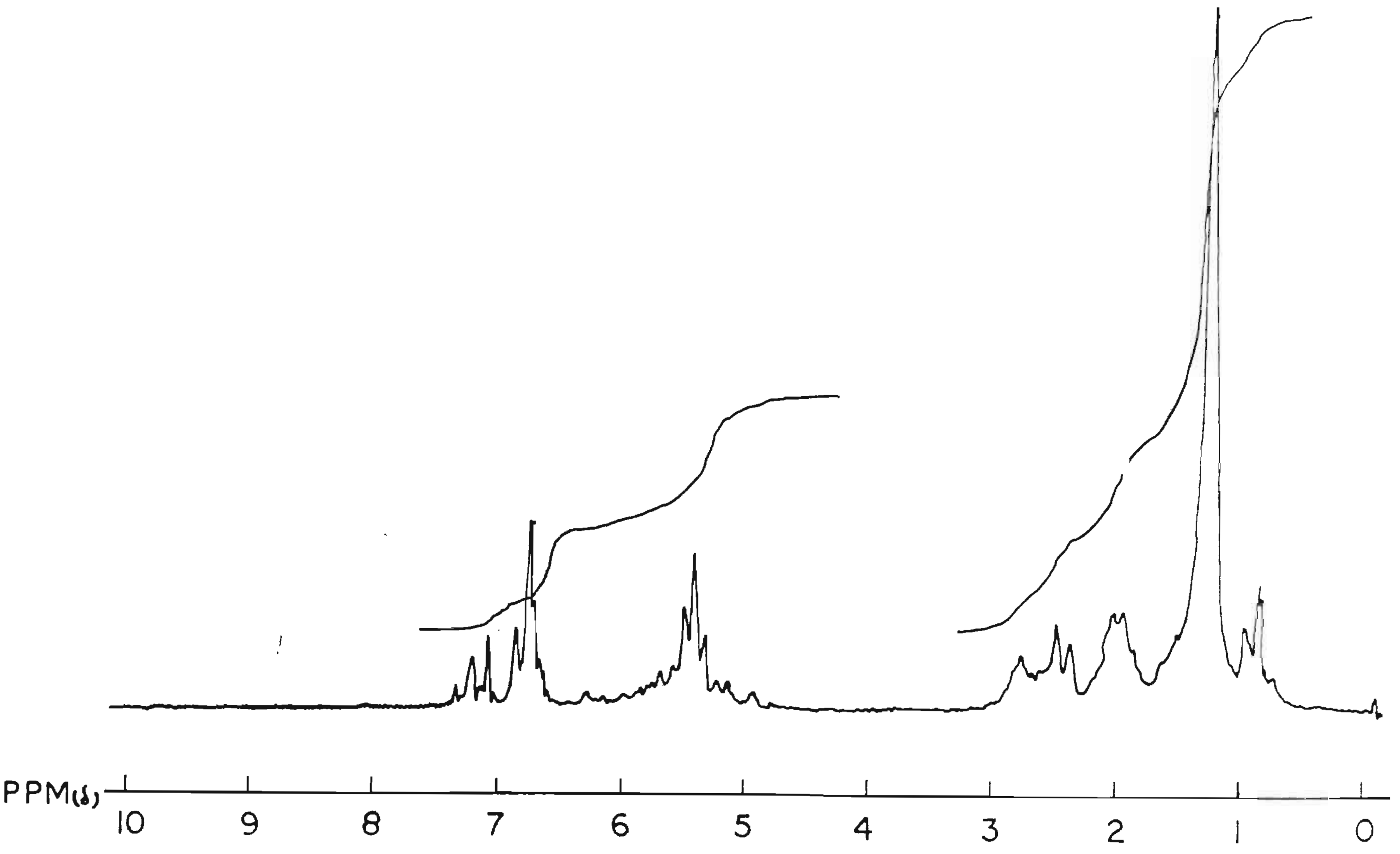


Fig 2.7. NMR of product I (Solvent CCl_4)

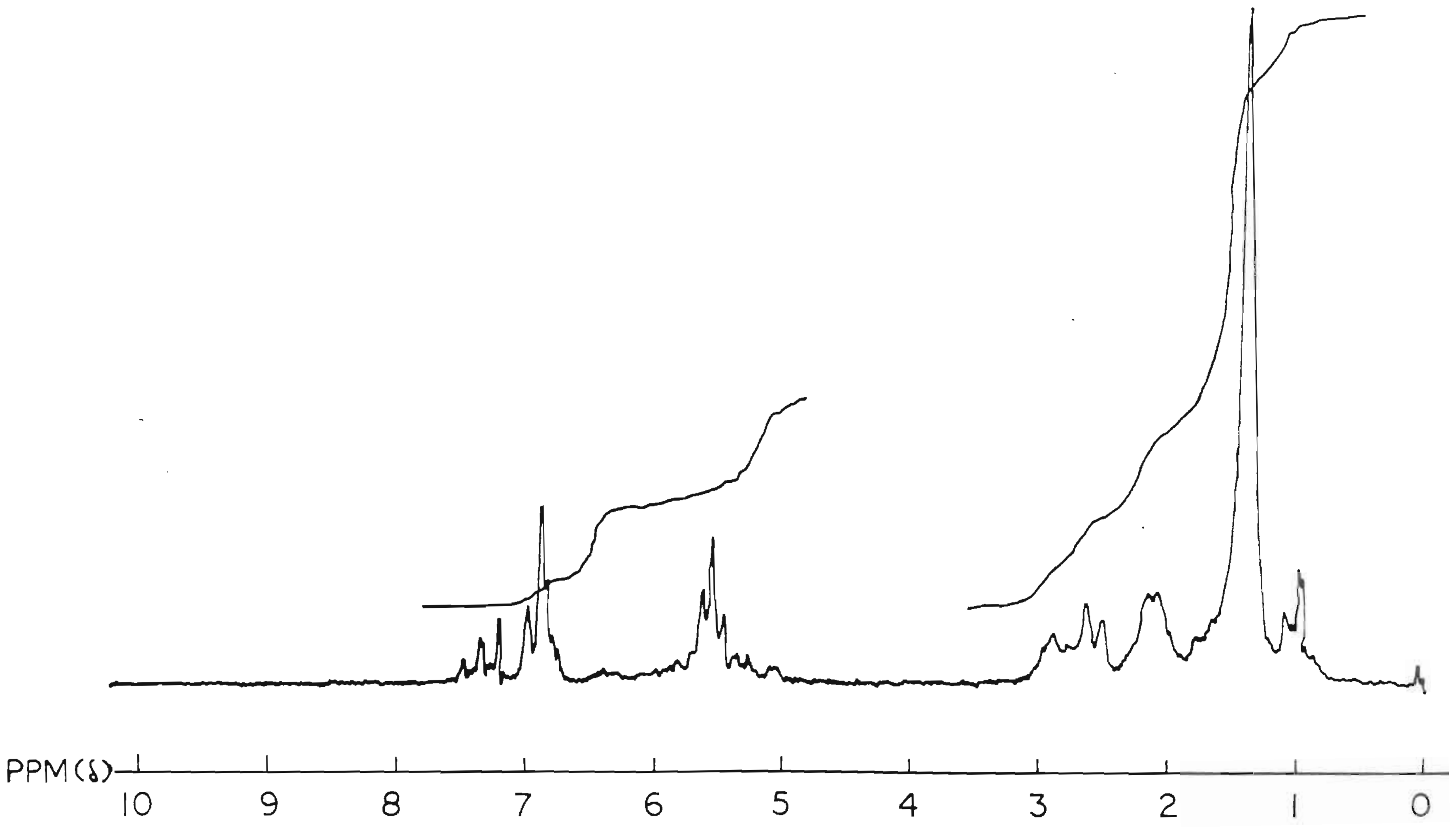


Fig 2.8. NMR of product II (Solvent CCl_4)

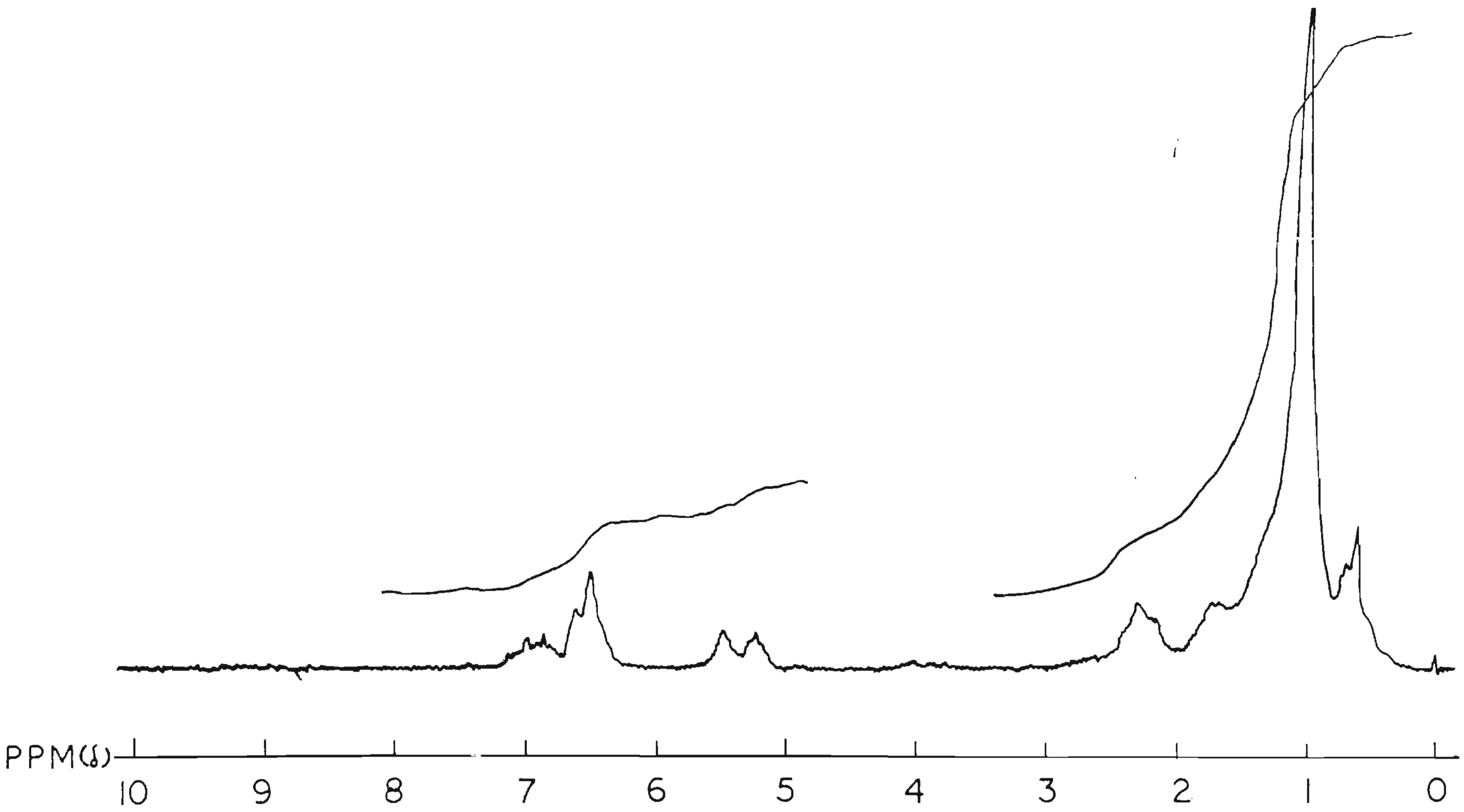


Fig 2.9. NMR of product III (Solvent CCl_4)

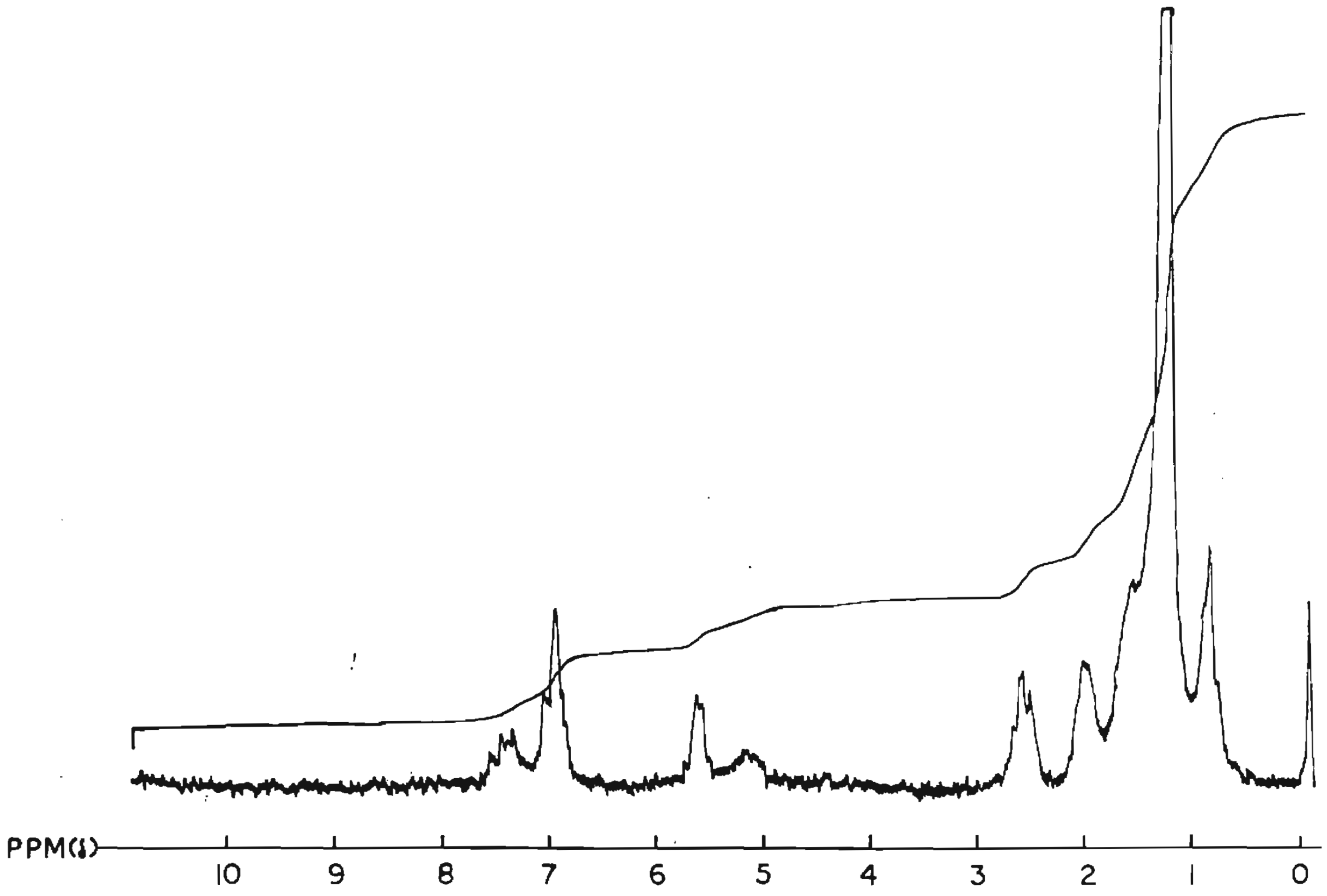


Fig 2.10. NMR of product IV (Solvent CCl_4)

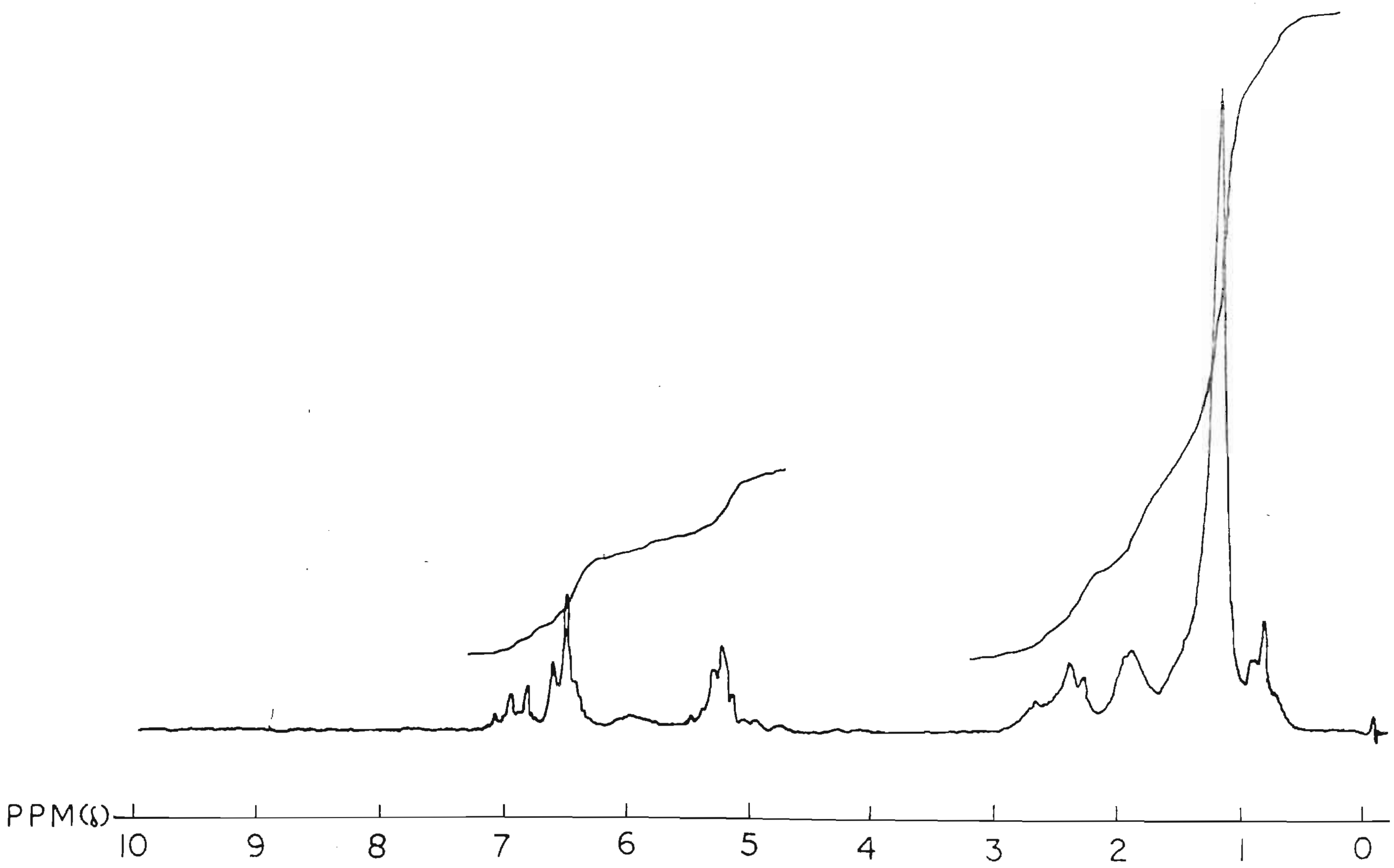


Fig 2.11. NMR of product V (Solvent CCl_4)

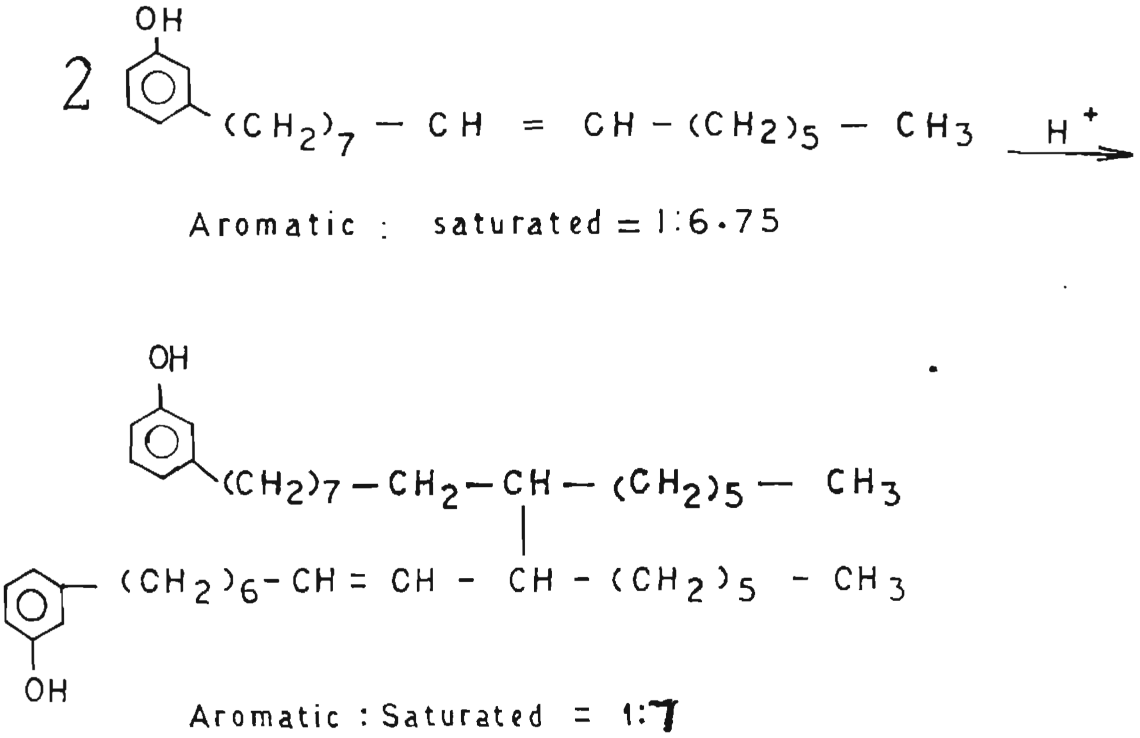
The decrease in 1630 cm^{-1} peak intensity is, however, expected as the oligomerization takes place through the double bonds of cardanol. Table 2.6 shows the assignment of peaks in the IR of cardanol.

TABLE 2.6 ASSIGNMENT OF PEAKS IN THE IR OF CARDANOL

Peak (cm^{-1})	Assignment	Intensity
630	vinyl	W
690	$-CH_2\ CH_2\ CH_2\ CH_2-$	m
740	Phenolic	W
765	vinyl	W
770		m
895	terminal	W
907	double bond	W
995	vinyl	W
1015 1048	aromatic	W
1050	C-O stretching	W
1115	O-H stretching of phenol	m
1345	C-H bending	m
1455	asymmetric bend of -OH scissoring vibration of methylene	S
1450	$-CH_2$ bending of aliphatic attached to aromatic	S
1600 1635 1685	vinyl	W

The resonance due to the unsaturated protons (5.5 δ) in ^1H NMR is also observed to decrease with respect to saturated protons (0.9-2.5 δ). The ratio of the integration of unsaturated protons to saturated protons resonances decrease from a value of 1 : 6.75 to 1 : 20 in the case of DES-H_2SO_4 and DES-H_3PO_4 catalyst systems for samples III and IV (Fig. 2.9, 2.10). The decrease in unsaturated protons is, however, marginal in the case of BF_3-Et_2O catalyst and this is also reflected in the % composition of the oligomers (high monomer content). The intrinsic viscosity measurements also indicate low conversion for product V (Table 2.3). It appears that the oligomerization is probably more favoured in the presence of catalysts with high proton concentration which donate protons during oligomerization. This is evident from higher viscosity and greater % of higher oligomers in the case of DES-H_2SO_4 catalyst system.

The oligomerization reaction over the acidic catalysts could be represented as follows (Scheme 2.1).



Scheme 2.1

There exists two more possible mechanisms for the oligomerization. One mechanism involves the formation of a 4-membered carbon ring from two separate cardanol molecules each having a double bond as shown in Fig. 2. 12 In that case the oligomerization should stop at the dimer stage. However, GPC analysis of the products shows a mixture of dimer, trimer and higher oligomers. Hence, the possibility of this reaction could be ruled out.

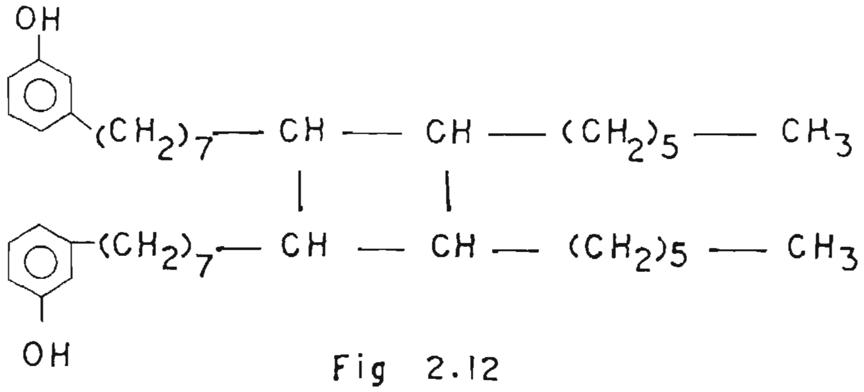
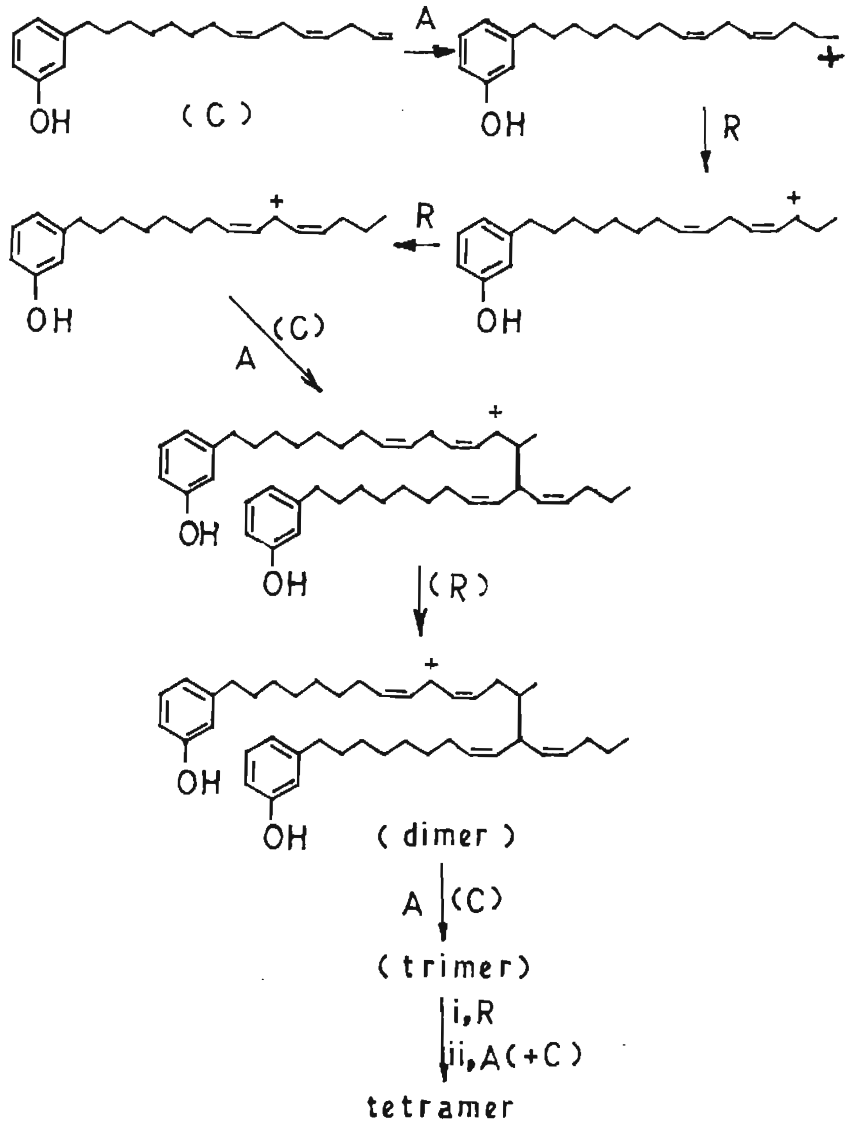


Fig 2.12

The absence of IR absorption peaks at 960 cm^{-1} and 1000 cm^{-1} in the oligomerized product also suggest the absence of this mechanism during oligomerization.

Tyman proposed an acidic polymerization involving allylic carbonium ion formation from the more reactive double bonds of the triene (Scheme 2.2)[7].

In all cases the oligomerization also changes the aromatic and saturated resonance integral ratio marginally from 1 : 6.75 to 1 : 7. The integrals of aromatic proton resonances and the saturated proton resonance for samples I, II, III, IV and V are given in Table 2.7.



(C) = Cardanol

A = Addition

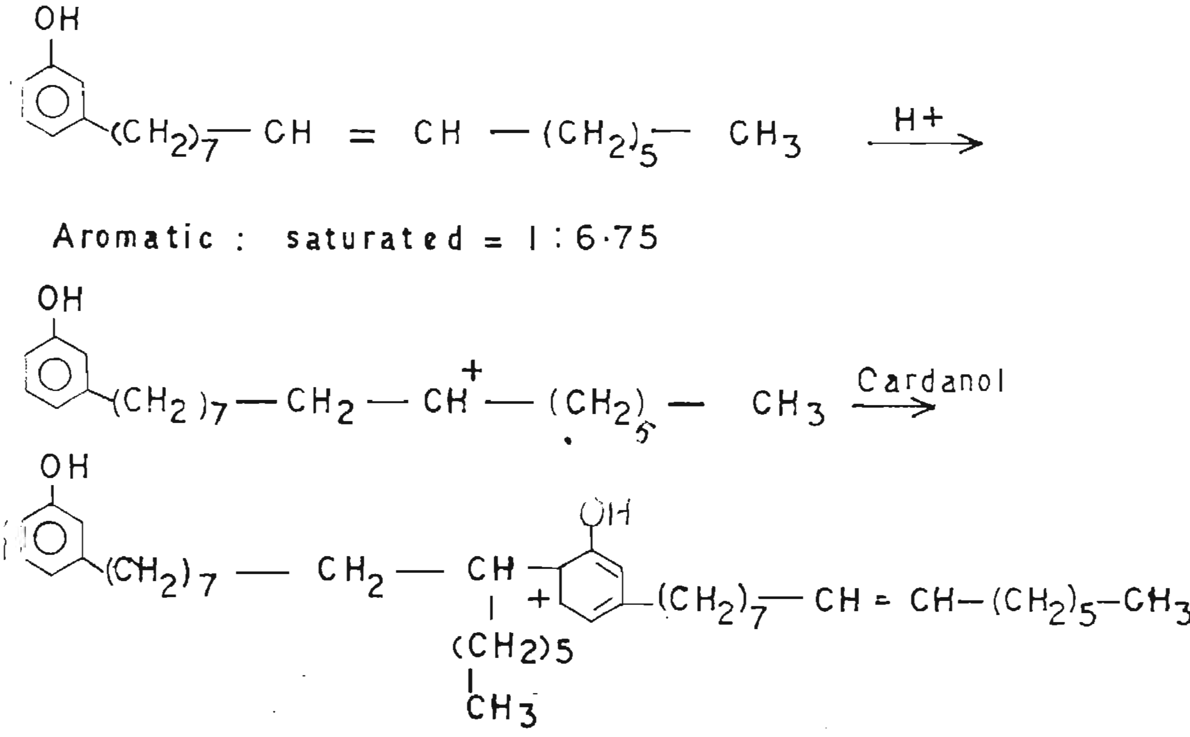
R = Rearrangement

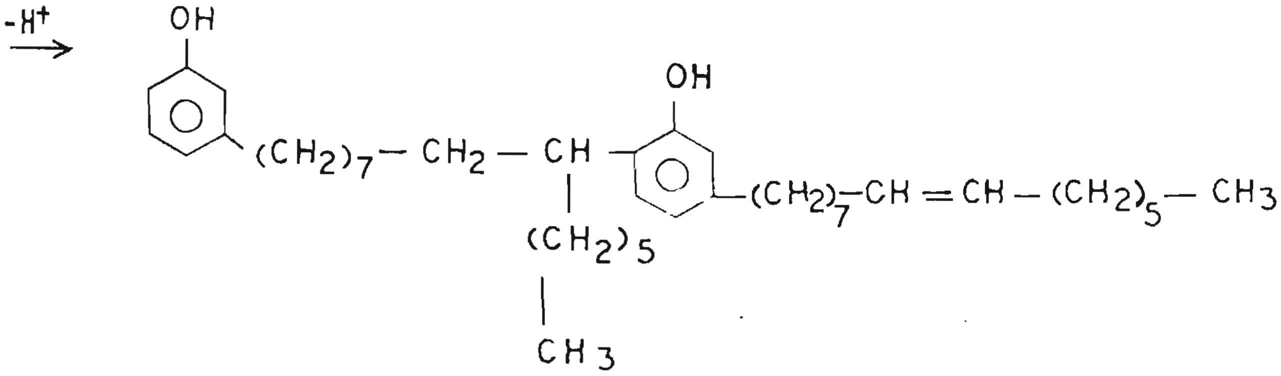
Scheme.. 2.2

TABLE 2.7 AROMATIC AND SATURATED RESONANCE INTEGRALS OF CARDANOL OLIGOMERS

Product	Aromatic	Saturated	Aromatic : Saturated
I	12	75	1 : 6.25
II	23	140	1 : 6.08
III	16	134	1 : 8.3
IV	19	133	1 : 7
V	23	163	1 : 7.08

The ratio of aromatic to saturated protons integrals is higher than the expected 1 : 7 in the case of product III. This implies that loss of aromatic protons during the oligomerization reaction is possibly a side reaction. The catalyst system employed is highly acidic in nature and Friedel - Crafts type alkylation of the aromatic ring of cardanol is a possibility. This could lead to reduction in aromatic protons ratio with respect to that of saturated protons. This is illustrated in the following scheme (Scheme 2.3).





Scheme 2.3

The reduction in aromatic protons with respect to saturated protons in the case of product III is possibly due to the Friedel-Crafts type alkylation reaction. Acid catalysed polymerization of cardanol was investigated by Stuart Mark Kaback in 1960 and he had reported a Friedel-Crafts type alkylation of the phenolic rings by a comparison of the IR spectra of cardanol and polycardanol[15]. The molecular weight of the product obtained is identical with the double bond oligomerized one and hence is not possible to distinguish the alkylated product from GPC analysis.

However, the Friedel-Crafts type alkylation and the subsequent loss of aromatic protons is also expected in the case of DES-H_3PO_4 catalyst system (Product IV). Contrary to the expectation, the ratio of aromatic protons to saturated proton remain 1 : 7. In addition, the overall conversion to oligomers is also observed to be less in this case as compared to DES-H_2SO_4 catalyst system (Table 2.5). But this can be explained by the difference in the dissociation constants of sulphuric acid and phosphoric acid. The dissociation constants of sulphuric acid and phosphoric acid at 25°C are 1.20×10^{-2} and 6.23×10^{-8} respectively.

The -OH content of the samples were followed for the oligomerization reaction at different temperatures and the values are tabulated in Table 2.8.

TABLE 2.8 HYDROXYL VALUE OF THE CARDANOL OLIGOMERS AT VARIOUS TEMPERATURES

Catalyst	Temp. °C	-OH value, mg KOH/g
DES - H_3PO_4	30	180
"	100	156.2
"	120	118.3
"	140	91.0
"	160	36.5
DES - H_2SO_4	30	180
"	100	126.5
"	140	123.5
"	160	107.5
"	180	106.4

The hydroxyl value reduces from 180 to as low as 36.5 in the case of DES-H_3PO_4 system and indicates a comparatively marginal reduction for the DES-H_2SO_4 system. Thus most of the phosphoric acid is consumed for the esterification reaction. The phosphorylation of cardanol using phosphoric acid is already reported[14]. So, effective hydrogen ion concentration for oligomerization is quite low in the case of DES-H_3PO_4 and hence explains the low conversion to higher oligomers and low viscosity in the case of DES-H_3PO_4 catalyst system.

In the case of BF_3-Et_2O catalyst system also low double bond oligomerization and low Friedel-Crafts alkylation is observed.

Kinetics of oligomerization

The kinetics of the oligomerization reaction was studied with DES-H_2SO_4 catalyst system at 50°C. The monomer concentration was estimated from the GPC at different intervals of reaction time. Plot of log a_o/a_o-x (where a_o = initial concentration of monomer and x = amount of monomer reacted at any time) Vs time is given in Fig. 2.13. A straight line plot is obtained which indicates that oligomerization follows a first order kinetics and rate constant at this temperature is estimated to be, $k = 6.6 \times 10^{-5}\ S^{-1}$.

The composition and the comparison of the trend in the formation of dimer, trimer and $\geq$ tetramer species at 50°C is shown in Fig. 2.14. In Fig. 2.14 it appears that monomer concentration decreases as time passes and correspondingly dimer, trimer and $\geq$ tetramer concentration increases. The decrease of monomer concentration and increase in dimer, trimer and higher oligomers concentration attain a plateau after 30-40 minutes of the reaction and reaches a saturation equilibrium during this period. The rate of formation of dimer, trimer and higher oligomers follow an almost identical trend and this suggests a chain mechanism for the oligomerization reaction. In fact, as dimer is the first product of the reaction between two monomers, at least during the initial stages of

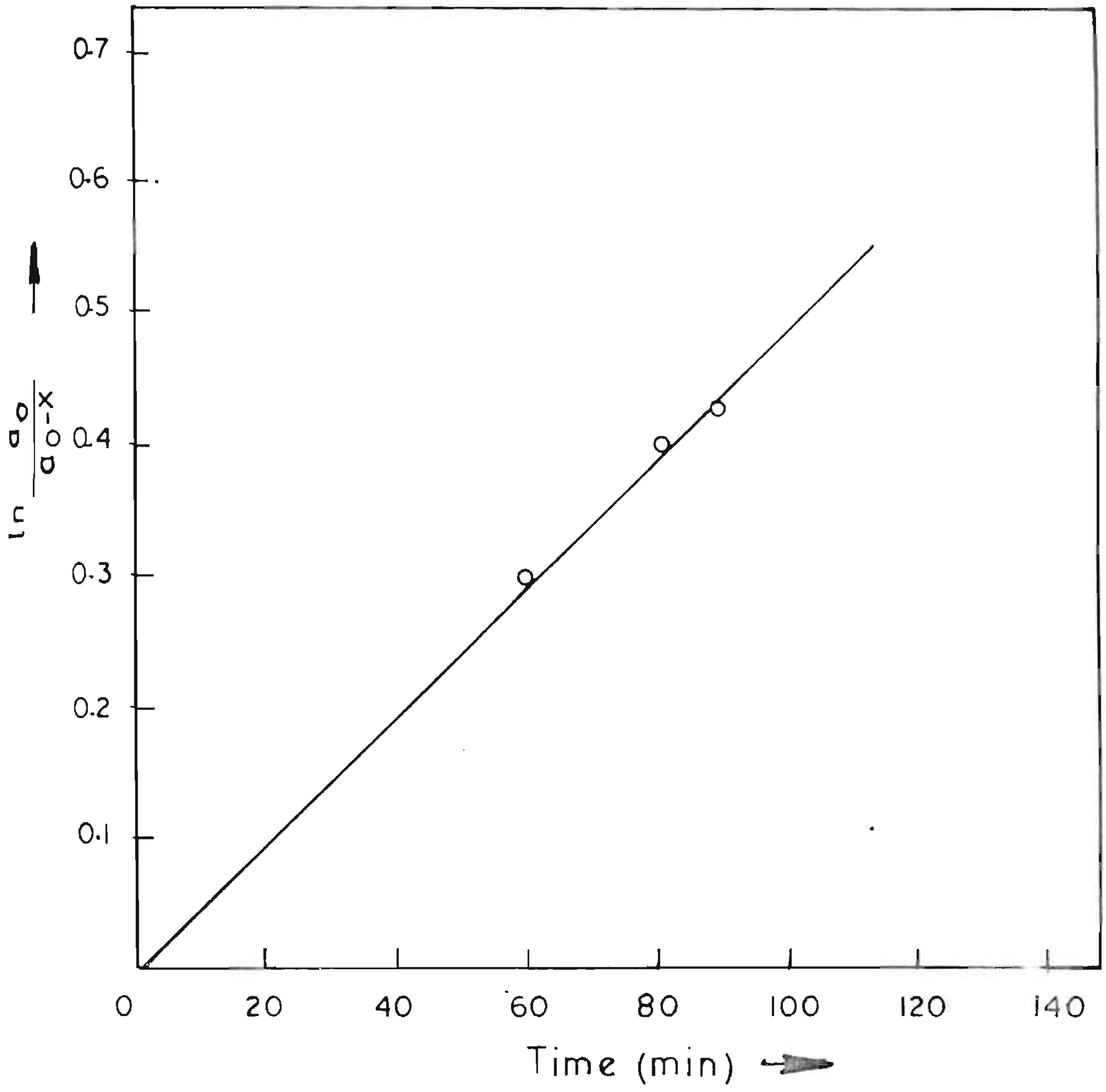


Fig 2.13 Plot of $\ln \frac{a_0}{a_0 - x}$ Vs time (min) for oligomerization of Cardanol over DES-H_2SO_4 Catalyst system.

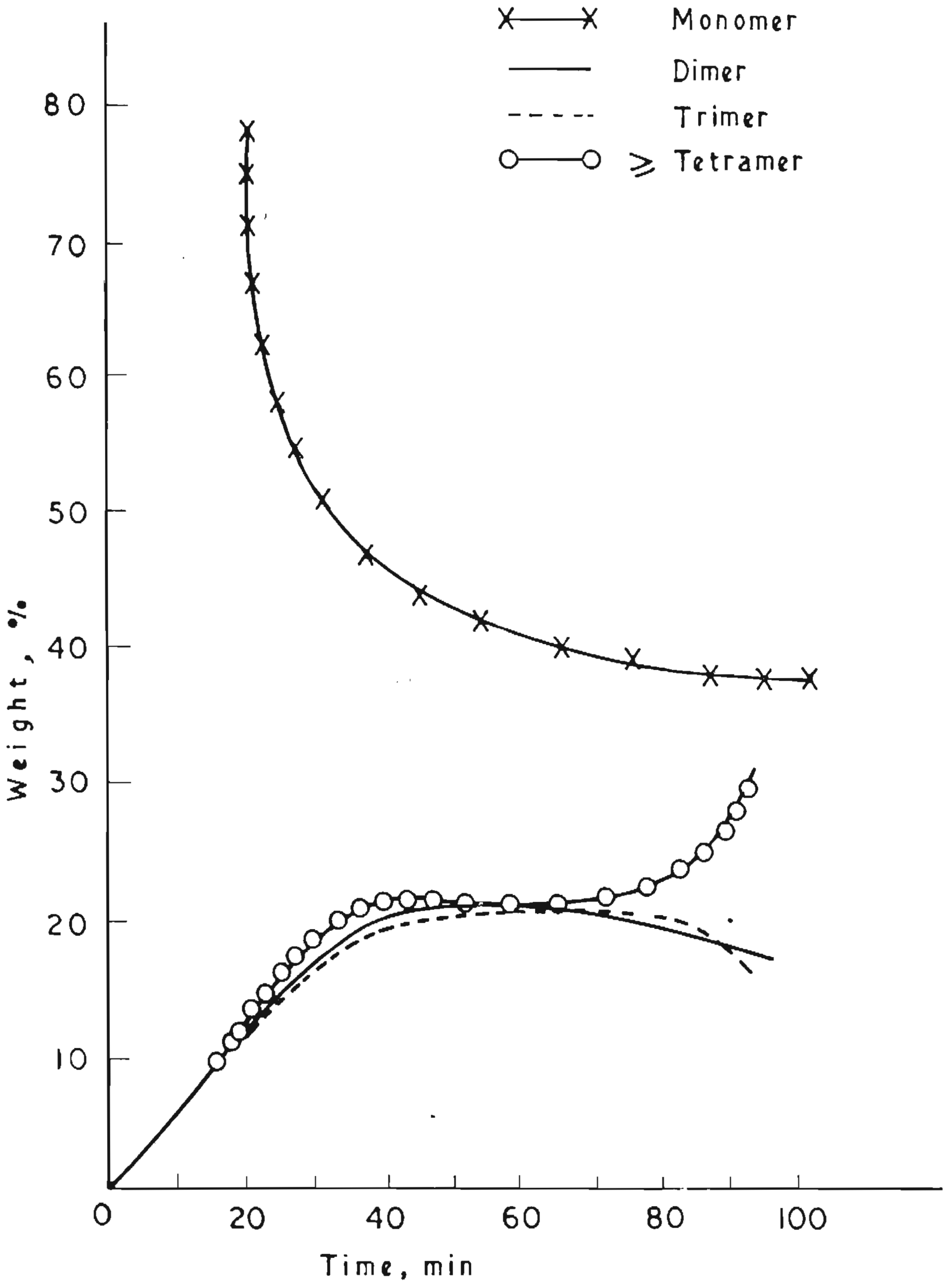
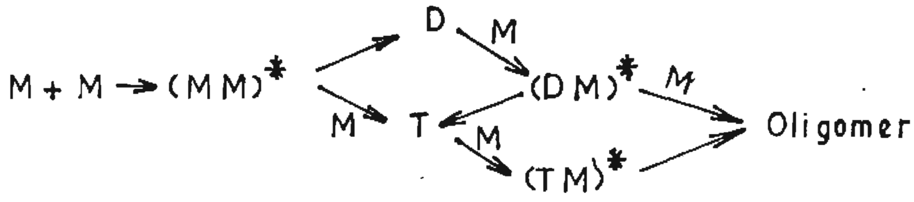


Fig. 2.14. Plot of weight (%) Vs time (min) of monomer, dimer, trimer & ≥ tetramer species for DES-H_2SO_4 catalyst system. at 50°c.

reaction, a higher concentration of dimer is expected. Contrary to that the dimer, trimer and higher oligomers are formed to the same weight percentage at any time during the reaction. This is possibly explained by the following kinetic scheme for the reaction (Scheme 2.4).



Scheme 2.4

The active intermediate $(MM)^*$ when formed as a fast step could either convert itself into a dimer and could react with another monomer leading to a trimer. Similar is the case with a $(DM)^*$ active intermediate which can form either a trimer or a tetramer. The composition of the dimer, trimer and higher oligomers could thus be decided by the stability and half-life of the active intermediates, $(MM)^*$, and $(DM)^*$, etc. It may be noted that although weight percentages of dimer, trimer, etc. are almost the same at any time, the mole percentages would vary where the dimer content is high.

The first order kinetics at 50°C can be explained by the following scheme (Scheme 2.5).

$$M + H^+ \xrightarrow{k_i} MH^+$$

$$MH^+ + nM \xrightarrow{k_p} M_{n+1}H^+$$

$$M_{n+1}H^+ \xrightarrow{k_t} P$$

$$-\frac{dM}{dt} = k_p [MH^+][M]$$

Assuming steady state

$$k_i [M][H^+] = k_t [MH^+]$$

$$[MH^+] = \frac{k_i [M][H^+]}{K_t}$$

$$-\frac{dM}{dt} = \frac{k_p k_i}{k_t} [M]^2 [H^+]$$

Scheme 2.5

The reaction is second order with respect to the monomer concentration whereas the results at 50°C indicate a first order kinetics with respect to monomer. This could be explained if the termination takes place in a transfer of H^+ into a monomer (Scheme 2.6).

$$M_{n+1}H^+ + M \xrightarrow{K_{tr}} P + MH^+$$

When $K_{tr} > K_t$

$$k_i [M][H^+] = k_{tr} [M][MH^+]$$

$$[MH^+] = \frac{k_i}{k_{tr}} \frac{[M][H^+]}{[M]}.$$

$$-\frac{dM}{dt} = \frac{k_p k_i [H^+][M]}{k_{tr}}.$$

Scheme 2.6

Hence at 50°C, in the case of DES-H_2SO_4 system, the termination of oligomerization takes place through transfer.

Thus, when $k_{tr} \gg k_t$, the rate is proportional to $[M]$, indicating first order with respect to monomer concentration.

The product composition plots for DES-H_3PO_4 catalyst system at different temperature for a fixed reaction time (20 minutes) is shown in Fig. 2.15. Monomer content is decreasing and higher oligomers are increasing. The increase of dimer and higher oligomers follow almost in identical pattern.

2.4 Conclusions

1. Oligomerization of cardanol using acidic initiators takes place both through the double bonds as well as through the aromatic rings.

2. The conversion to higher oligomers is higher in the case of DES-H_2SO_4 catalyst system when compared with DES-H_3PO_4 and BF_3-Et_2O catalyst systems.

3. Oligomerization follows a first order kinetics for the oligomerization studied (50°C, DES-H_2SO_4).

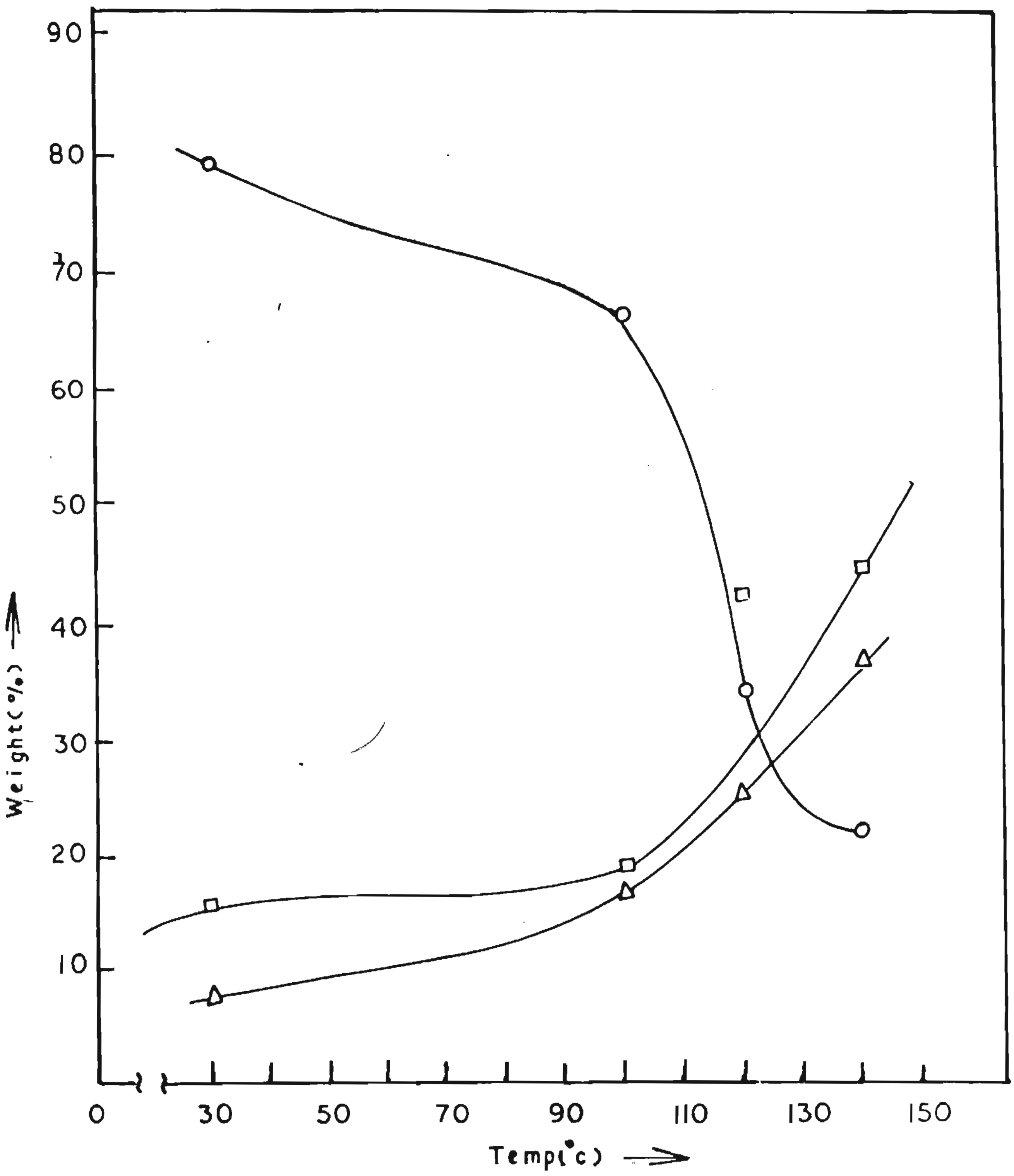


Fig 2.15. Plot of weight (%) Vs ,temp(°c) of monomer dimer & higher oligomer species for oligomerization of cardanol DES-H_3PO_4 catalyst system at a fixed reaction time (20 minutes)

○–○ Monomer ; △–△ Dimer ; □–□ Higher Oligomers.

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CHAPTER 3

SYNTHESIS AND MECHANICAL PROPERTIES OF INTERPENETRATING NETWORKS OF CARDANOL-FORMALDEHYDE AND POLY(METHYLMETHACRYLATE)

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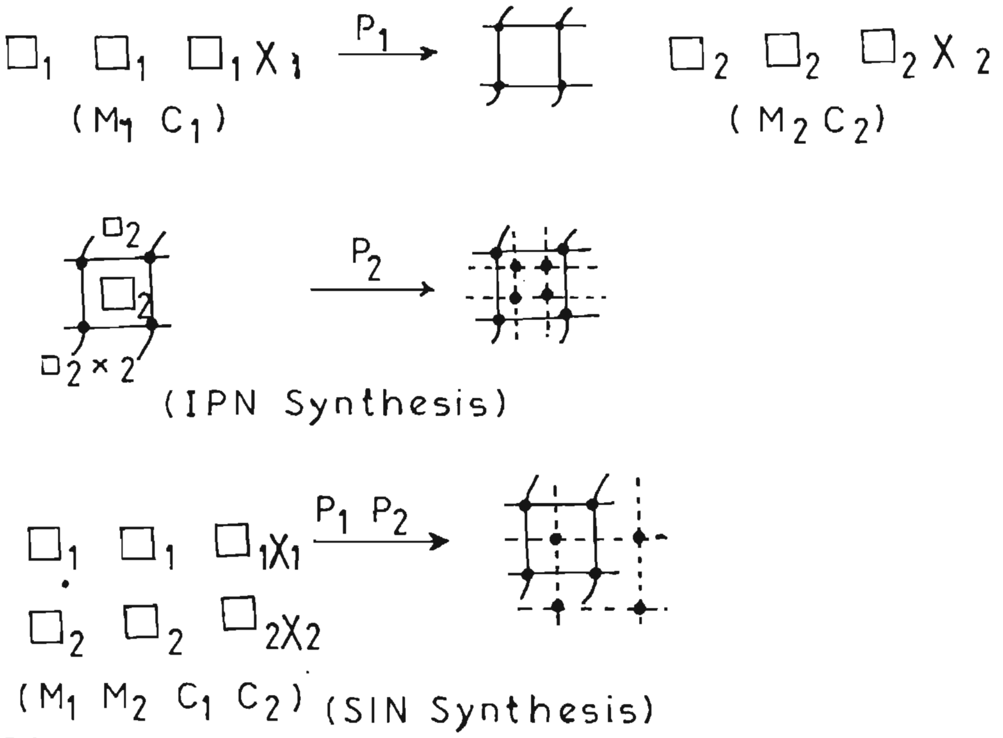
3.1 Introduction

Structural and chemical variations on monomer and thereby polymer chains were common to polymer chemistry for tailor making materials of varying mechanical properties. Synthesis of copolymers involving more than one type of monomers provided lot of flexibility in achieving suitable properties for polymers. Blending of miscible polymers to modify the properties is also common. Although first prepared by Millar in 1960, interpenetrating polymer networks for property modifications gained fairly increased research attention only from the early seventies[1]. Their unique supermolecular structure was shown to yield many materials with new properties as well as outstanding physical and mechanical behaviour[1].

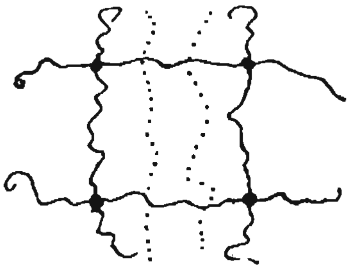
Interpenetrating networks (IPNs) constitute a novel arrangement of polymer chains in space. IPN can be defined as a combination of two polymers in network forms, at least one of which is synthesized and/or crosslinked in the immediate presence of the other[2,3,4]. An IPN can be distinguished from simple polymer blends, blocks and grafts in two ways, (1) an IPN swells but does not dissolve in solvents, (2) creep and flow are suppressed[1]. Millar made the first serious scientific study of IPNs and he used polystyrene/polystyrene IPNs as models for ion-exchange resin materials[5,6]. Later Sperling and Frisch began their work on IPNs. The first IPN known was synthesized by Aylsworth in 1914 which was a mixture of natural rubber, sulphur and partly reacted phenol-formaldehyde resin[7].

There are two types of IPNs, (1) the sequential IPN begins with the synthesis of a cross linked polymer I. Monomer II, plus its own cross-linker and initiator are swollen into polymer I and polymerized in situ, (2) simultaneous interpenetrating networks, SINs, begin with a mutual solution of both monomers and their respective crosslinkers which are then polymerized simultaneously by noninterfering modes such as stepwise and chain polymerization[8] (Scheme 3.1).



Scheme 3.1
Solid lines represent network I, dotted lines network II, heavy dots represent crosslink sites.

When only one of the polymers is crosslinked, the product is called a semi - IPN structure[9]. If the polymerizations are sequential in time, four semi IPNs may be distinguished (Scheme 3.2).



Scheme 3.2

If polymer I is crosslinked and polymer II is linear, the product is called a semi-IPN of the first kind or semi-I. If polymer I is linear and polymer II is crosslinked, a semi-II results. The remaining two compositions are materialized by inversing the order of polymerization. For simultaneous polymerizations, only two semi-IPNs may be distinguished. Yenwo synthesized a sequential IPN from castor oil and polystyrene[10,11]. Castor oil has three hydroxyl groups per molecule which were used to form the polyurethane. The urethane elastomers were swelled with styrene and its initiators and polymerization of styrene was carried out by UV radiation. The corresponding castor oil polyester/polystyrene SINs were synthesized by Devia et al[12,13] who prepared castor oil - sebacic acid polyester/polystyrene SINs.

The chief disadvantage of sequential IPN is its thermoset nature which makes processing difficult[1].

A third mode of IPN synthesis takes two latexes of linear polymers, mixes and coagulates them and crosslinks both components simultaneously. The product is called an interpenetrating elastomeric network, IEN.[1]

Thus IPNs can be classified as polymeric catenanes if we envision a crosslinked polymer network to be composed of many macrocycles of varying sizes. The various techniques of preparing IPNs (sequential polymerization, simultaneous polymerization, etc.) can be viewed as statistical methods where a cyclization (crosslinking) of one component occurs in the presence of the other already cyclized component (crosslinked polymer networks)[14].

Many authors consider IPNs as polymer/polymer composites where one of the networks function as a filler to the already formed polymer network[15]. If the synthetic mode yield two networks, then the extent of continuity of each network is to be considered. If both networks are continuous throughout the sample and the material is phase separated, the phases must interpenetrate in same way. Thus IPN compositions are thought to contain two continuous phases[16]. Most of IPNs reported so far involve heterogeneous systems, usually one phase rubbery and the other phase glassy. The morphology of IPNs depends on the method of synthesis, compatibility of the polymer system employed and on the relative rates of formation of each network[14]. IPNs reported so far can be classified as having large domain structures with domain sizes of a few microns[17], intermediate structures with sizes around 1000 A^o, fine structures with sizes around 100 A^o [18] and no resolvable domain structure at all[19]. The nature of interpenetration vary systematically with morphology.

The major problem pending in the study of IPNs is that there is no general method to prove the existence of interpenetration and to measure the quantitative level of interpenetration. Equilibrium swelling and the apparent crosslink density measurements can be used only when the IPN system is homogeneous[20]. In heterogeneous systems, the compression modulus depends largely on the morphology and the preference of the swelling solvent to one component network will generate cases where the swelling of the dispersed phase is restricted, therefore making the measurement of apparant cross-link density at best gross approximation[14].

The measurement of the shift in glass transition temperature can also be useful if the IPN system consists of a one component network such as Millar's polystyrene/polystyrene sequential IPNs[5]. If the IPN system employs two different polymer networks, the shift of glass transition temperature should be compared to that of its topological isomers (both networks cross-linked but not interlocking). But topological isomers are difficult to obtain because of the insoluble and infusible nature of cross-linked polymer networks. One alternative is to compare the shift of glass transition of IPNs with its corresponding pseudo-IPN s (one polymer cross-linked and the other polymer linear) and linear poly blends (both polymers linear) provided the cross-link densities of the IPNs are small. A similar approach would be to compare morphology of IPN s to that of corresponding pseudo IPN s and linear polyblends by electron microscopy. This will be qualitative but quantitative analysis would be difficult. Mechanical property measurements could also be used for providing the existence of interpenetration if a fair comparison of IPN s with the corresponding pseudo IPN s and with linear polyblends is possible. The existence of interpenetration has been generally shown based on a combination of effects described above[14].

The interpenetration could be expected to be better if the two chains are allowed to grow at comparable rates. This could happen because the restrictions of placing two polymer chains in juxta position do not exist in the case of mutually soluble monomers and when they independently consume the monomers at almost equal rates, improved interpenetration could result in comparison to a system where one of the polymer chains is almost grown and second monomer polymerizes at a slower rate[21].

The properties of a polymeric system will be improved on interpenetration with another polymer since the mutual dispersion of phases provide a synergistic effect. This could be achieved by selecting the proper combination of polymer system and arriving at actual conditions[21]. Interpenetration of an elastomer into a plastic component will improve the toughness because (1) energy absorption by the elastomeric particles, (2) energy absorption by yielding of the continuous phase ductility enhanced by strain induced dilatation near elastomeric occlusion, and (3) stress distribution and relief, etc.[22] V.G. Kumar et al reported the synthesis of castor oil - polyurethane - polystyrene divinyl benzene simultaneous IPN networks in 1987. They had shown that there is marginal increase in tensile strength and crosslink density from castor oil polyurethane to castor oil polyurethane-polystyrene IPNs. For eg. castor oil polyurethane showed a tensile strength of 13.6 kg/cm^2 and % elongation of 105 whereas the corresponding values of the IPN were (60 castor oil polyurethane/40 polystyrene) 26.2 kg/cm^2 and 155 respectively[21].

Klempner et al reported an IEN pair which exhibited synergistic/non-synergistic tensile strength depending on composition. The polymer pair was a poly (urethane-urea) and a polyacrylate. As polyacrylate was added to poly (urethane-urea) the tensile strength initially decreased reaching a minimum near 20% polyacrylate and reached a maximum at 75% polyacrylate which is actually above the tensile strength of either component at which there is maximum chain entanglement[23].

An epoxy/poly (n-butyl acrylate) SIN was reported by Touhswent et al with different compositions. It was shown that each SIN was tougher than the parent epoxy, absolute tensile strength was higher and the area under the stress-strain curve was increased[24].

Kim et al studied the engineering properties of polyurethane/PMMA SINs and had shown that tensile strength reached a maximum with polyurethane 85/PMMA 15 SIN, which shows significant synergistic behaviour[25].

Interpenetration of one polymer into another polymer is expected to show an increase in the mechanical properties, compared to the individual polymer chains. The changes depend on the type of polymer networks used, the extent of interpenetration and the conditions at which the two networks are allowed to grow. In general, when an elastomeric network such as polyurethane or natural rubber is allowed to interpenetrate a chain of rigid polymer like poly(methylmethacrylate) (PMMA) or polystyrene, then, the IPN is supposed to have synergistic behaviour resulting in a product having much better properties viz. higher tensile strength, % elongation, etc.[1] But when both the systems are of rigid type, the properties of the IPN, very drastically leading to poorer mechanical properties than the individual polymers.

Thus blending by cosynthesis of two different polymer networks provide a promising tool for achieving mutual improvement in physical properties.

Cardanol is a substituted phenol, having a long side chain in the m-position. The presence of both phenolic group and double bonds in the side chain could be made use of for making interesting materials. The double bonds in the side chain could be opened up to yield oligomers/polymers which have long hydrocarbon side chain and which may be expected to give flexible products. The benzene ring of cardanol could be reacted with formaldehyde to give phenol-formaldehyde type products. Since cardanol has both ortho and para positions vacant, the condensation with formaldehyde is expected to lead to a network of thermosetting resin. The product can be allowed to form IPNs in presence of vinyl monomers such as methylmethacrylate and which are expected to have interesting mechanical properties. The lack of close packing and the increased free volume between the polymer chain could be advantage in synthesising IPNs with other polymer networks. Ellis had shown that cardanol self polymerizes in the presence of acid/alkaline catalyst and reacts with formaldehyde to form different types of phenolic resins[26].

In a catalyzed mixture of phenol and formaldehyde, the mole ratio of phenol to formaldehyde determines the type of phenolic resin obtained. When the mole ratio of phenol to formaldehyde is 1 : 1.2, the system contains ingredients and functionality needed to produce a thermosetting resin. This is termed as one step resin or resol. If the reaction mixture contains acid catalysts, one gets the unctrollably highly cross linked thermosetting resins and if it contains alkaline catalysts, then the setting becomes manageable and a controllable one step resin results. When the mole ratio value of phenol to formaldehyde is 1 : 0.8, a thermoplastic resin results, provided the initial mole ratio of phenol to formaldehyde is maintained. When the catalyst is acidic, a thermoplastic resin results which becomes thermosetting by further crosslinking with hexamethylenetetramine (HMTA). This is called a novolac resin. When the catalyst is alkaline, highly ortho- substituted novolac resin is formed[27]. In the present work, cardanol-formaldehyde systems are synthesised using the standard techniques for the preparation of phenol-formaldehyde resins. Usually novolacs are prepared using acid catalysts. But in the case of cardanol-formaldehyde reaction, which when carried out in the presence of oxalic acid, does not seem to proceed. But it had been reported that cardanol forms both novolac and resol resins in presence of alkaline catalysts depending upon the mole ratio[28]. Hence basic catalyst was used in synthesizing novolac as well as resol resins at cardanol - formaldehyde ratios of 1 : 0.8 and 1 : 1.2 respectively.

The present chapter describes the synthesis and mechanistic evaluation of cardanol-formaldehyde resins prepared under different conditions viz. with mole ratio of cardanol to formaldehyde less than one/more than one. Attempts had been made to obtain novolac resins by using varying quantities of HMTA and the properties are compared with resol resins. In addition, the variation in mechanical properties by first oligomerizing cardanol through the side chain (Chapter 2) and further condensing with formaldehyde is also described. Experiments have also been conducted to interpenetrate PMMA chain into the cardanol-formaldehyde network and the results are presented.

3.2 Experimental

3.2.1 Materials

Methylmethacrylate (MMA)

The following procedure was used for the purification of MMA (KOCH-LIGHT Laboratories, England). MMA was washed with 10% aqueous sodium hydroxide to remove the inhibitor. The monomer was then washed with distilled water till all the base had been removed. It was then dried over anhyd. Na_2SO_4 and then distilled.

$\alpha - \alpha'$ Azoisobutyranitrile (AIBN)

AIBN (Merck - For synthesis) was purified by crystallization from methanol.

All other reagents and solvents were of the AR grade and used without further purification.

3.2.2 Methods

3.2.2.1 Synthesis

3.2.2.1.1 Cardanol-formaldehyde (Resol) prepolymer[29] (I)

250 g (0.825 mole) of cardanol, 101.9 ml (1.249 mole) of 37% aqueous formaldehyde and 3.9 g (0.012 moles) of barium hydroxide octahydrate are mixed thoroughly in a reaction kettle fitted with a mechanical stirrer and reflux condenser. The reaction mixture was heated at 70°C for 3 1/2 hours. The resulting resin was freed from unreacted formaldehyde (if any) and barium hydroxide by washing with water. The product was dried at 70°C and powdered. This product (I) served as the prepolymer for the synthesis of cardanol-formaldehyde (resol) as well as cardanol-formaldehyde (resol) - PMMA semi-IPNs.

3.2.2.1.2 Cardanol-formaldehyde (Resol)

6 g of the cardanol-formaldehyde (resol) prepolymer (I) was compressed in a M.S. closet mould into rectangular bars of 100 mm x 13 mm x 4 mm size using a hydraulic press at 140°C for 1 1/2 hrs at 33.3 kg/cm^2 and then subjected to postcuring at 170°C for 1 hr.

3.2.2.1.3 Cardanol-formaldehyde (novolac) prepolymer (II)[29]

250 g (0.825 mole) of cardanol, 54 ml (0.66 mole) of 37% aqueous formaldehyde and 20 ml of 4 N sodium hydroxide were taken in a reaction kettle fitted with a mechanical stirrer and reflux condenser. The reaction mixture was heated under constant stirring at 100°C for 4 hrs. The product was washed with 10% hydrochloric acid and then with water and dried at 70°C. The product was powdered.

This powder served as the starting material for cardanol-formaldehyde (novolac) and its semi-IPN with PMMA.

3.2.2.1.4 Cardanol-formaldehyde (novolac)

160 g (0.201 mole) of cardanol-formaldehyde (novolac) prepolymer(II) was mixed thoroughly with 4.8 g (0.034 mole) (3%) of hexamethylenetetramine (HMTA) and kept in an oven at 120°C for 1 1/2 hrs. The partially cured product was powdered and passed through ASTM 34 sieve.

5.2 g of this material was mixed with 0.104 g (0.0007 moles) (2%) of HMTA and cold pressed in MS closet mould into rectangular bars of 100 mm x 13 mm x 4 mm size using a hydraulic press. The cold pressed samples were again compressed after placing them in the mould at 120°C for 1/2 hr at approximately 33.3 kg/cm^2. The samples were then subjected to post curing at 170°C for 1 hr. A series of specimens were prepared by varying the % of HMTA added.

3.2.2.1.5 Cardanol formaldehyde (resol) - PMMA semi-IPN

The cardanol formaldehyde (resol) prepolymer (I) powder (10 g) was mixed with varying amounts of methylmethacrylate (MMA) and $\alpha-\alpha'$azoisobutyronitrile (AIBN), (1% by weight of MMA) and stirred thoroughly in a reaction kinetic under nitrogen. The temperature was maintained at 70°C for 1 1/2 hrs. The product was powdered and the particle size was adjusted to pass through ASTM 34 sieve.

The powder was compressed into rectangular bars using a hydraulic press at 140°C for 1 1/2 hrs and post cured at 170°C for 1 hr.

3.2.2.1.6 Cardanol-formaldehyde (novolac) - PMMA semi-IPN

The cardanol formaldehyde (novolac) prepolymer (II) powder 10 g (0.0125 mole) was mixed with 0.5 g(0.0035mole)(5%)of HMTA,90 g (0.9 mole) of MMA and 0.9 g (0.0055 mole) of AIBN and stirred thoroughly in a reaction vessel under nitrogen. The temperature was maintained at 70°C for 1 1/2 hrs. The product was powdered and the particle size was adjusted to pass through ASTM 34 sieve.

The powder was compressed into rectangular bars using a hydraulic press at 120°C for 1 1/2 hrs and postcured at 170°C for 1 hr.

3.2.2.1.7 Oligomerization of cardanol

Oligomerization of cardanol using diethyl sulphate-sulphuric acid, diethyl sulphate - phosphoric acid and boron trifluoride-etherate is described in the experimental section of Chapter 2.

3.2.2.1.8 Oligomerized cardanol-formaldehyde (Resol)

250 g (0.825 mole) of oligomerized cardanol, 101.9 ml (1.249 mole) of 37% aqueous formaldehyde and 3.9 g (0.012 mole) of barium hydroxide octahydrate were mixed together in a reaction kettle fitted with a stirrer and reflux condenser. The reaction mixture was heated at 170°C for 2 hrs. The resin was washed with water to remove uncreacted formaldehyde barium hydroxide, etc. and dried at 70°C. Then the temperature was raised to

120°C and resin was kept at that temperature for 11 hrs. The resin was then rolled into thin sheets using a two roller mill. It was then cut into rectangular bars and they were kept in a MS closet mould and hot pressed at 120°C for 1 1/2 hrs and postcured at 170°C for 1 hr.

3.2.3 Characterization

3.2.3.1 Electron Microscopic studies

Scanning Electron Microscopic photographs were taken using a JEOL' 35 C microscope.

3.2.3.2 Mechanical properties

3.2.3.2.1 Tensile strength[30]

The tensile strength of test specimen were measured using an Universal Testing Machine (Instron Model 1195) and adhesively bonded neoprene rubber tabs were used at the gripping position to avoid breaking at the grip. Measurements were carried out at a cross head speed of 50 mm/min. and the gauge length was 100 mm. The ultimate tensile strength (UTS) and elongation at break were calculated using the formula

$$\text{UTS} = \frac{\text{Breaking load}}{\text{area of cross-section}}$$

$E\ \% = \frac{L}{L_o} \times 100$ where L_o is the initial length and L is the extended length at break and E% is the percentage elongation. Initial modulus was calculated from the initial portion of the load-elongation curve using the formula

$$\text{Initial modulus} = \frac{\text{Initial stress}}{\text{Initial strain}}$$

3.2.3.2.2 Hardness

Shore A and Shore D hardness were measured using Hardness Tester of Model - SHR - A - Gold and SHR - D - Gold respectively. The specimens having the dimensions of 50 x 13 x 4 mm were used for the measurement. The hardness was read directly from the dial.

3.3 Results and Discussion

3.3.1 Mechanistic studies

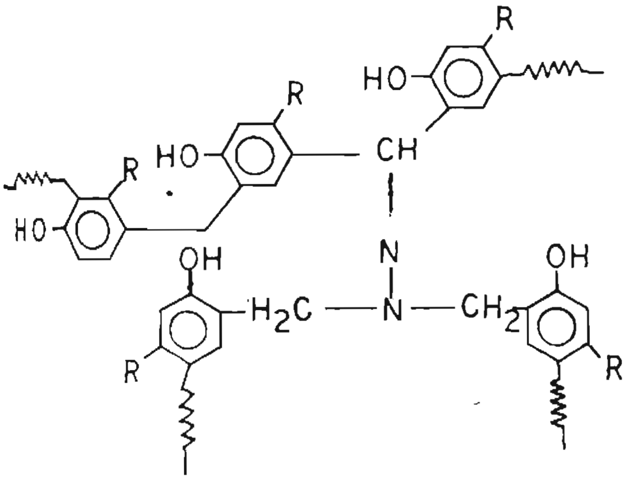
3.3.1.1 Cardanol-formaldehyde polymers (novolac and resol)

Formaldehyde condensation polymers of cardanol were synthesized in the novolac and resol forms. In the case of novolac, the polymer was synthesized in presence of varying percentages of HMTA as crosslinking agent, whereas resol was a simple condensation product of cardanol and formaldehyde. The synthetic procedures are described in the experimental part. The mechanical properties of the samples are compared in Table 3.1.

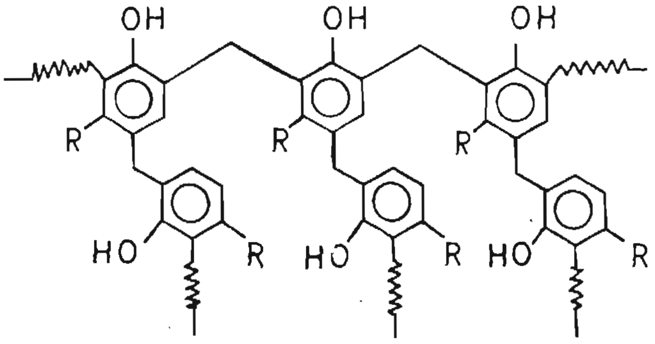
TABLE 3.1 MECHANICAL PROPERTIES OF CARDANOL-FORMALDEHYDE POLYMERS (NOVOLAC AND RESOL)

System	Total % of HMTA added	UTS kg/cm^2	% Elongation	Hardness	
				Shore A	Shore D
Cardanol-formaldehyde (novolac)	3.5	44.4	19.4	87.5	45
	4.0	52.6	10.8	91.5	36
	5.0	33.4	9.9	91.5	44.5
	6.0	33.14	5.2	92	38
	7.0	18.7	4.0	92	46.5
Cardanol-formaldehyde (resol)	-	26.3	2.9	92	57.5

Phenol-formaldehyde has much higher tensile strength reported (340 - 689 kg/cm^2) [31] and although the comparison of the mechanical properties with that of phenol-formaldehyde, has to consider the difference in synthetic condition and procedures, the values for cardanol-formaldehyde novolacs and resols appear to have poorer mechanical properties. The structure of cardanol-formaldehyde (novolac and resol) are represented as follows (Fig. 3.1).



(R = C_{15} H_{25}, C_{15} H_{27}, C_{15} H_{29})
Cardanol-formaldehyde (novolac)



(R = C_{15} $H_{\cancel{28}}$, C_{15} H_{27}, C_{15} H_{29})
25
Cardanol-formaldehyde (resol)

Fig. 3.1

The presence of C_{15} H_{25}, C_{15} H_{27}, C_{15} H_{29} or C_{15} H_{31} side chain on the aromatic nucleus in the case of cardanol could be expected (1) to provide steric hindrance for the aromatic nucleus to come specially close together to condense with formaldehyde and thus, would lead to lower build up of molecular weight in comparison with phenol-formaldehyde, (2) the presence of such a long substitution could also impart strain on the $-CH_2$ bridge linkages between the aromatic nuclei leading to weakening of bonds and (3) the long side chain could reduce the intermolecular interaction and thereby bring down the strength of the polymer. The poor mechanical properties of cardanol-formaldehyde in comparison to phenol-formaldehyde could thus be explained.

Table 3.1 suggests that the tensile strength of cardanol-formaldehyde novolac is higher than that of the resol system. The tensile strengths of the novolacs reach a maximum when it is cured with 4% HMTA. Further addition of HMTA results in a decrease of the tensile strength. At high HMTA composition, the polymer becomes brittle and hence results in lower tensile strength.

3.3.1.2 Oligomerized cardanol-formaldehyde

The poor mechanical properties of cardanol-formaldehyde in comparison with that of phenol-formaldehyde is attributed to steric hindrance and the strains in the linkages introduced by the aliphatic substitution at the aromatic nuclei. The molecular weight build up in the cardanol-formaldehyde system was expected to be not very high. Hence, formaldehyde condensation was carried out on cardanol which is first oligomerized through the double bonds in the side chain with a view to increase the molecular weight. The oligomerization of cardanol was carried out using diethyl sulphate - sulphuric acid catalyst system as described in the experimental section of Chapter 2. Formaldehyde condensation polymer of oligomerized cardanol was synthesized under idential composition as that for cardanol-formaldehyde (resol). However, the reaction temperature had to be raised to 120°C as the product did not give any mouldable material at 70°C. The mechanical properties of oligomerized cardanol-formaldehyde in comparison with that of cardanol-formaldehyde (resol) is given in Table 3.2.

TABLE 3.2 MECHANICAL PROPERTIES OF OLIGOMERIZED CARDANOL-FORMALDEHYDE (RESOL) AND CARDANOL-FORMALDEHYDE (RESOL)

System	UTS kg/cm^2	% Elongation	Hardness	
			Shore A	Shore D
Oligomerized cardanol-formaldehyde (resol)	4.42	57.5	40.4	8
Cardanol-formaldehyde (resol)	26.3	2.9	92	57.5

The tensile strength of oligomerized cardanol-formaldehyde have decreased considerably to a low value of 4 kg/cm^2 and % elongation has increased to around 40% on oligomerization of cardanol through the side chain and then synthesizing formaldehyde condensation polymers. The structure of oligomerized cardanol-formaldehyde (resol) could be represen- as follows (Fig. 3.2).

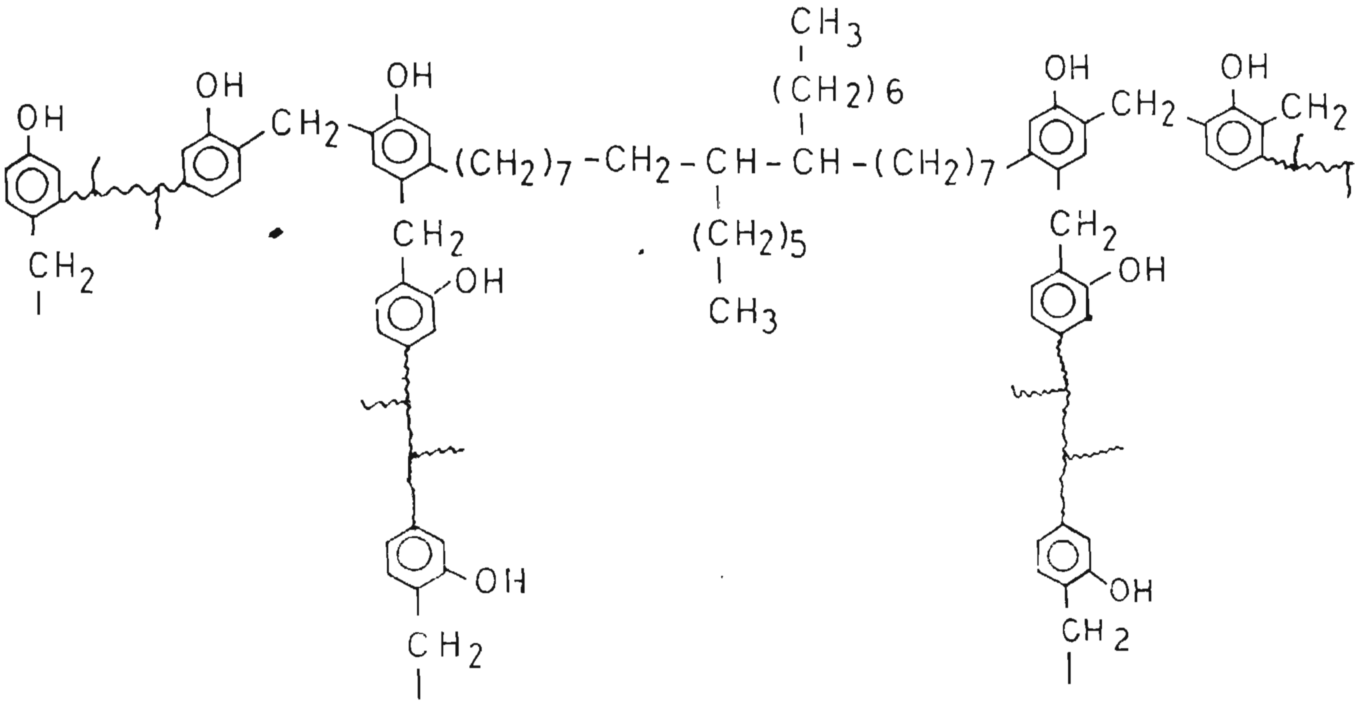


Fig. 3. 2 Oligomerized cardanol-formaldehyde (resol)

Oligomerization causes the formation of linear thermoplastic polymer when the product is condensed with formaldehyde. The joining of molecules through the side chain leads to a branched C_{15}-C_{15} linkage connecting the aromatic nuclei and this has possibly restricted the formaldehyde condensation. Because of the long side chain link up, the sites for formaldehyde concensation will be reduced by steric restrictions and hence the crosslink density will be lower. Oligomerized cardanol-formaldehyde (resol) is rubbery in nature whereas, the cardanol-formaldehyde (resol) system is a plastic.

3.3.1.3 Cardanol-formaldehyde (novolac and resol) - poly (methylmethacrylate) semi-IPNs

The interpenetrating networks of PMMA and cardanol-formaldehyde (novolac and resol) were synthesized by synthesizing cardanol-formaldehyde prepolymer and further polymerizing and crosslinking it after mixing with MMA and its initiator. MMA polymerization progresses along with the polymerization and crosslinking of cardanol-formaldehyde prepolymer. This is expected to give rise to semi-IPNs of cardanol-formaldehyde and PMMA. The details of synthesis are described in the experimental section.

Table 3.3 and 3.4 indicate the mechanical properties at varying compositions of semi-IPNs of PMMA with cardanol-formaldehyde - novolac and resol-respectively. In both the cases of novolac and resol based semi-IPNs, the values indicate that incorporation of considerable amount of PMMA (as high as 50% for novolac and 75% for resol) does not have any marked effect on the tensile strength. The % elongation of these products have reduced marginally. Incorporation of PMMA at higher percentages, however, helps in increasing the tensile strength. The variation in tensile strength with the % of cardanol-formaldehyde resin is given in Fig. 3.3. From the plot, it is observed that in the case of novolac based semi-IPN systems, the tensile strength passes through a maximum at 87.5% PMMA and, then, decreases on further addition of PMMA. The % elongation also indicates a decrease. In the case of semi-IPNs based on resol system, tensile strength decreases when the PMMA content is reduced from 90%. Compared to the reported property improvement effected by semi-IPN formation of two polymeric networks[1], the changes in mechanical properties of cardanol-formaldehyde on interpenetration with PMMA appear to be

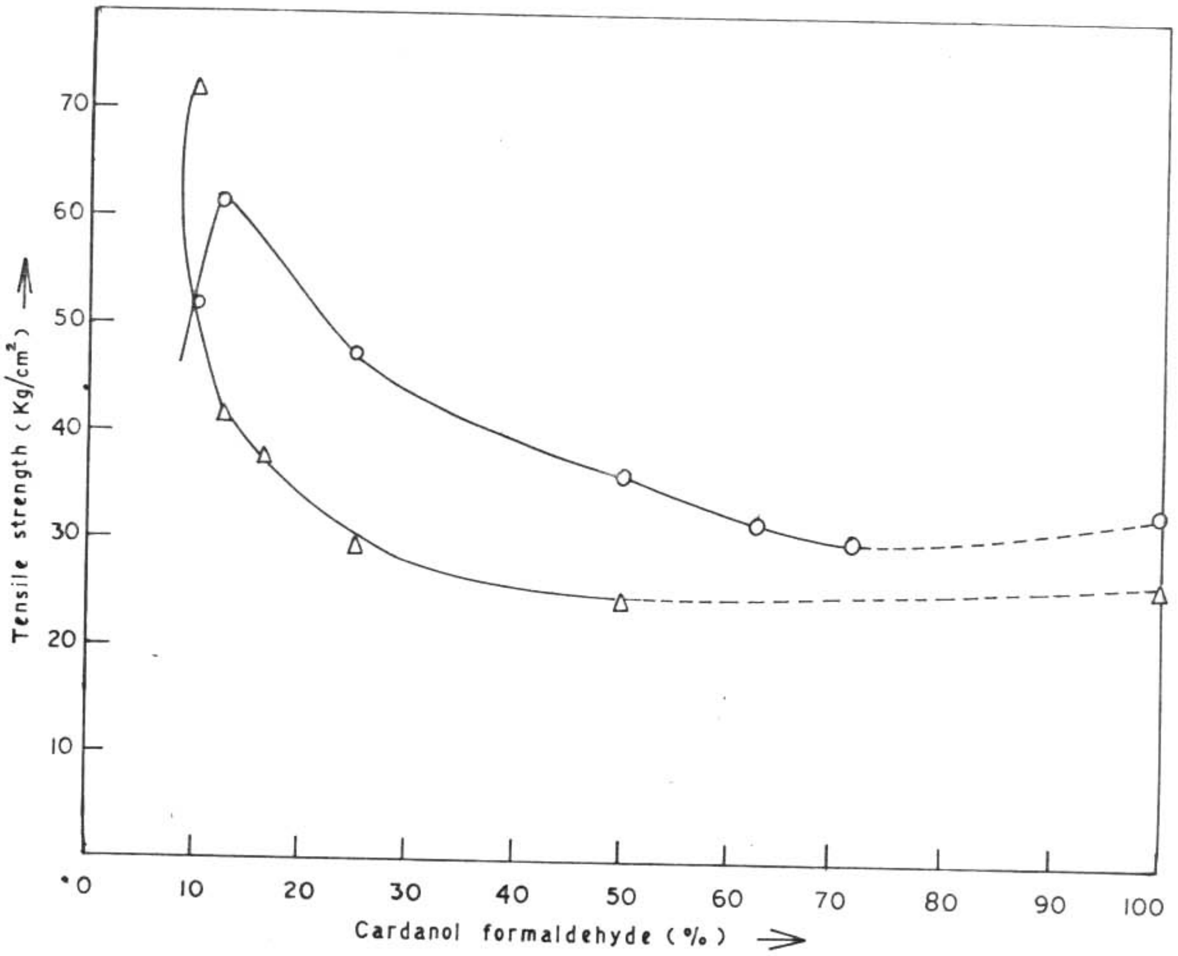


Fig 3.3 Plot of Tensile strength (Kg/cm^2) Vs Cardanol formaldehyde(%) for IPN system

o—o IPN from cardanol formaldehyde (novolac) & PMMA

Δ—Δ IPN from cardanol formaldehyde (resol) & PMMA marginal. Incorporation of PMMA upto 87.5% into novolac system has increased the strength from 33.40 kg/cm^2 to 61.31 kg/cm^2 and the trend of marginal improvement on the tensile strength is observed to reverse on further incorporation in the case of PMMA whereas, semi-IPNs based on resol system, product containing 90% PMMA shows a tensile strength of 71.7 kg/cm^2 and the strength decreases with the decrease in PMMA content. This is in comparison with the tensile strength of more than 500 kg/cm^2 for PMMA[33] homopolymer. Improvement in strength properties of cardanol formaldehyde interpenetrated with PMMA is quite marginal when compared with the reported high and synergistic improvements in mechanical properties brought about by IPN formation. For example, Sperling et al had shown that incorporation of 60% polystyrene into a castor oil polyurethane network has increased the tensile strength from a value of 9.7 kg/cm^2 to 241 kg/cm^2 and synergistic increase in % elongation to a value of 108% from 58%[11,12].

The behaviour in cardanol formaldehyde - PMMA semi-IPNs can be attributed to the variation in the method of synthesis and to the rigidity of the system concerned. Interpenetration of rigid systems are known to give rise to products of drastically poorer mechanical properties. The drastic decrease in mechanical properties of PMMA by incorporation of low percentages of cardanol-formaldehyde and vice versa could thus be attributed to the rigidity in both the homopolymeric systems.

Mixing of two different polymers is not expected to impart any mutual strain. But placing of two polymers in juxta position and restricting their mobilities by crosslinking them independently at different points could lead to strain of the chain segments between crosslinks and subsequent bending and uncoiling of the chain segments[21]. This will be pronounced when both the polymeric networks involved are rigid in nature. A similar observation had been reported earlier in the case of epoxy poly (n-butyl acrylate) SINs[24]. Weakest materials were formed on simultaneous gelation of the two polymers and the subsequent formation of fine phase domain structures whereas when one or the other polymer was allowed to polymerize faster providing nonsimultaneous gelation condition, the phase domain were large and the products stronger.

The basic descrepancy in strength properties can also be attributed to the inability of the PMMA chains to interpenetrate freely with the sterically restricted cardanol-formaldehyde system. And it is noteworthy that most of the IPNs reported so far involve heterogeneous systems usually constituting one rubbery phase and other glassy. This combination of rubbery and glassy polymer networks gives a rather interesting situation where a particular IPN system can range from a filler reinforced elastomeric material (to a leathery material) and to a rubber reinforced (high impact) plastic material depending on which component becomes the continuous phase[14]. The cardanol formaldehyde - PMMA semi-IPNs studied in this case do not fall under the elastomer - plastic IPN system. Both networks in the semi-IPN are plastic materials and this will also result in restricting the property improvements. The plastic ingredients lack the ability to mutually interpenetrate and hence could have resulted in individual domains which are interpenetrated to a very low level. Hence, the expected synergistic behaviour is not reflected in the observed mechanical properties. The property improvement also depends on various factors such as nature of the two chains, method of their synthesis, relative rate of formation of each network and their compatibility.

TABLE 3.3 MECHANICAL PROPERTIES OF CARDANOL FORMALDEHYDE (NOVOLAC) - PMMA SEMI-IPNS

Composition of semi-IPNs		UTS kg/cm^2	% Elongation	Hardness	
novolac resin, %	PMMA %			Shore A	Shore D
10	90	51.8	1.08	90	54
12.5	87.5	61.3	0.5	88	50
25	75	47.3	3.4	94	46
50	50	36.1	2.4	84	43
62.5	37.5	31.8	4.1	84	38
71.4	28.6	30.4	4.1	85	39
100	0	33.4	9.9	92	38

TABLE 3.4 MECHANICAL PROPERTIES OF CARDANOL FORMALDEHYDE (RESOL) - PMMA SEMI-IPNs

Composition of semi-IPNs		UTS kg/cm^2	% Elongation	Hardness	
resol resin %	PMMA %			Shore A	Shore D
10	90	71.7	3.3	83	55
12.5	87.5	41.,3	2.0	Out of scale	66
16.6	83.3	37.0	1.8	"	58
25	75	26.7	1.8	85	56
50	50	24.3	1.4	90	65
100	0	26.3	2.9	92	57.5

3.3.2 Scanning Electron Microscopic Studies

The surface structure of cardanol formaldehyde - PMMA semi-IPNs are studied using scanning electron microscope. Micrographs of the surface test specimens of cardanol-formaldehyde novolac, cardanol-formaldehyde (novolac) - PMMA semi-IPNs for two magnifications are shown in Figures 3.4, 3.5 and 3.6. Distinct changes can be observed from the comparison of the cardanol-formaldehyde (novolac) (100%), 50 cardanol-formaldehyde (novolac) - 50 PMMA and 12.5 cardanol formaldehyde (novolac) - 87.5 PMMA semi-IPNs. Discontinuous cardanol-formaldehyde (novolac) phase is observed in the case of both the IPNs.

Electron micrographs of 71.4 cardanol-formaldehyde (resol) - 28.6 PMMA and 16.7 cardanol-formaldehyde (resol) - 83.3 PMMA semi-IPNs are shown in Figures 3.7 and 3.8. Comparison of these micrographs with those of the novolac semi-IPNs suggest a different structure for resols. 71.4 cardanol-formaldehyde (resol) - 28.6 PMMA has a more or less a layered structure and cardanol-formaldehyde (resol) phase for both the semi-IPN compositions appear to be more continuous in comparison with the novolac phase in the novolac based IPNs.

3.3.3 Glass transition temperature studies of semi IPNs

The glass transition temperatures of the homopolymer and semi-IPNs were deduced from the thermomechanical analysis. The details of the experiments and the results are discussed in Chapter 4.

3.4 Conclusions

1. Mechanical properties of cardanol-formaldehyde polymers are lower compared to phenol-formaldehyde systems.

2. Synthesising cardanol-formaldehyde polymer using oligomerized cardanol gives a rubbery product and the tensile strength is reduced and the % elongation is increased.

3. Both resol and novolac resins based PMMA semi-IPNs show only marginal improvements in tensile strength compared to cardanol-formaldehyde homopolymers.

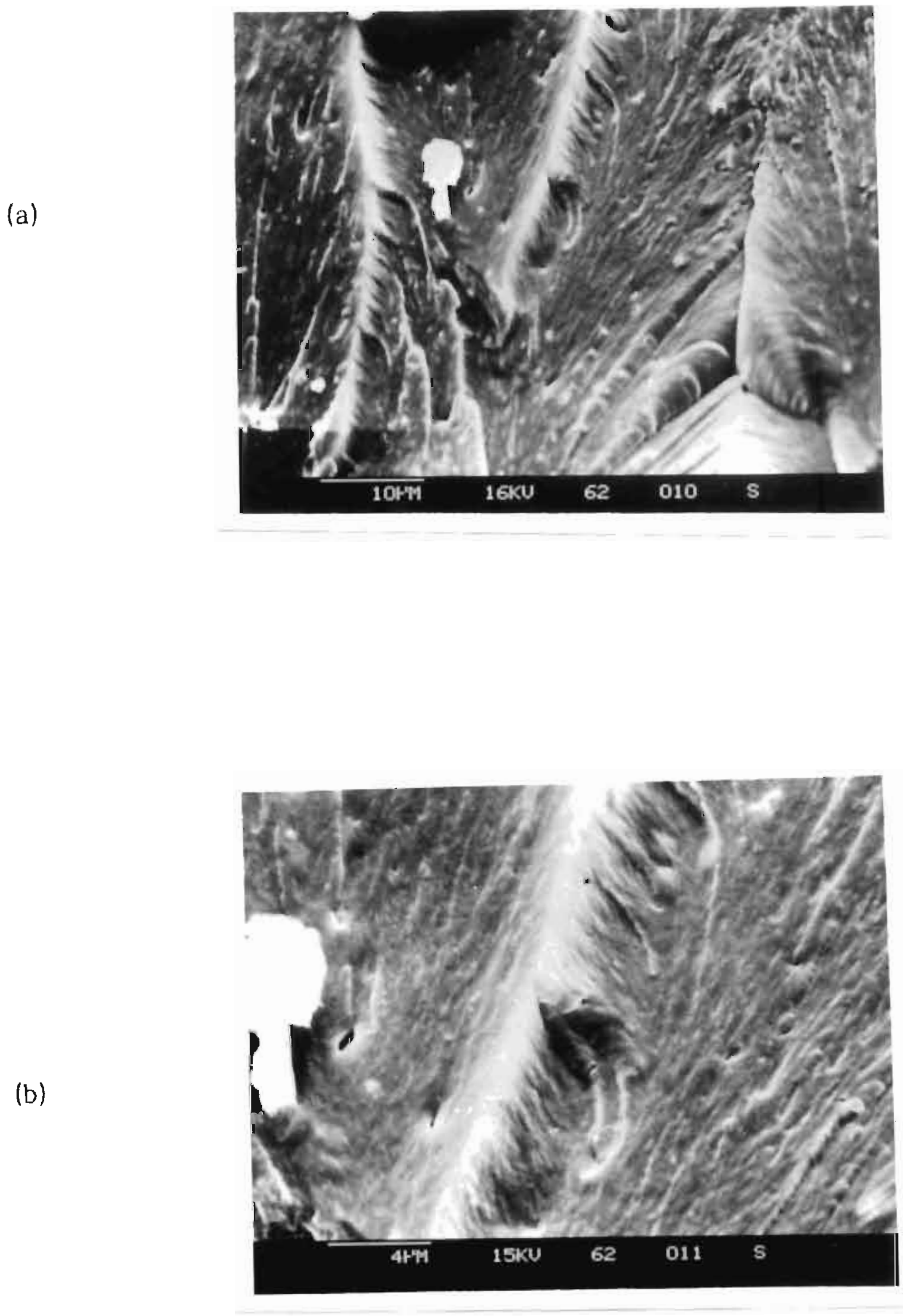


Fig. 3.4 SEM photographs of cardanol-formaldehyde (novolac)-PMMA semi-IPNs containing 0% PMMA at (a) 1700, and (b) 4500 magnifications.

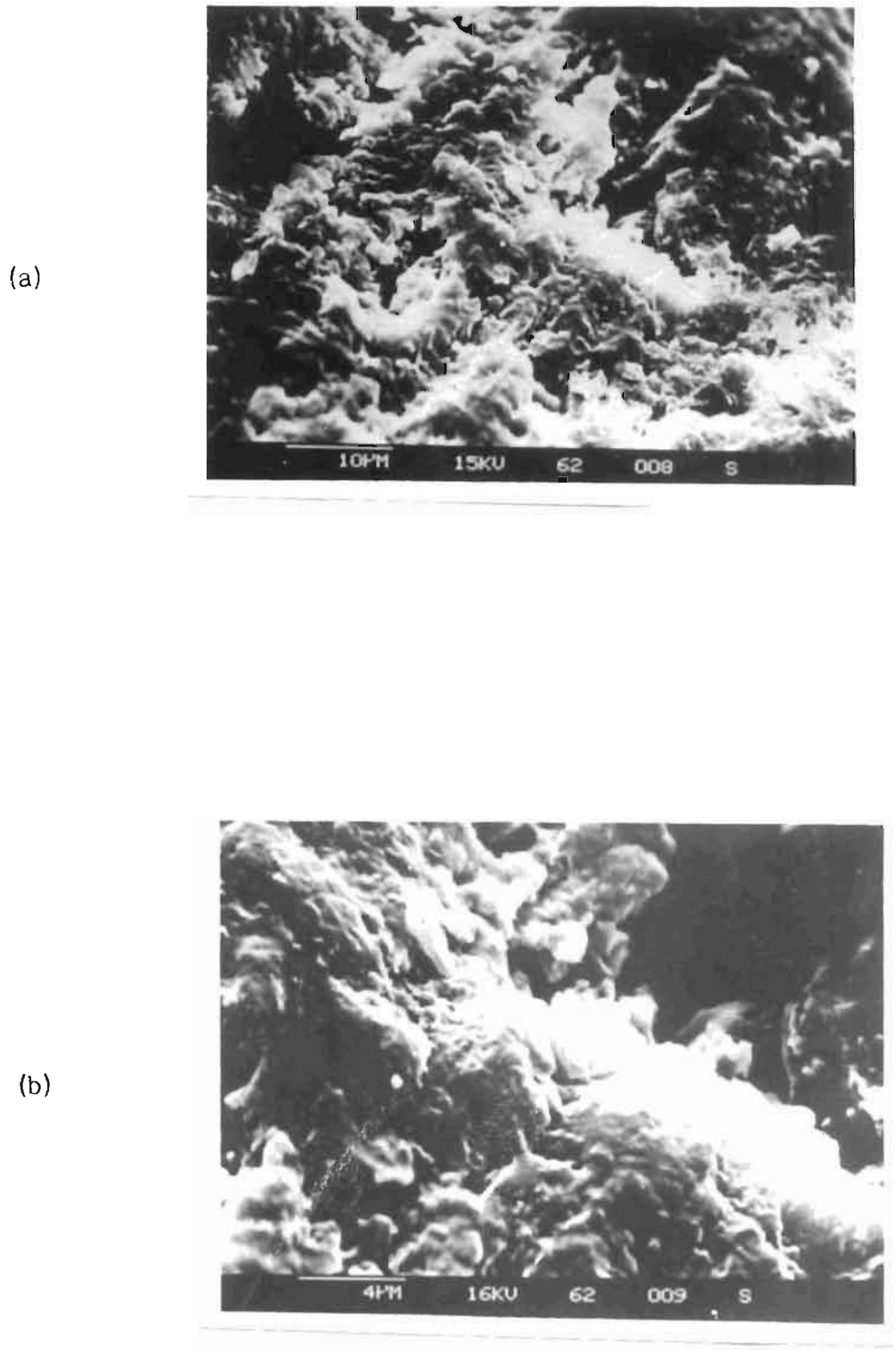


Fig. 3.5 SEM photographs of cardanol-formaldehyde (novolac)-PMMA semi-IPNs containing 50% PMMA at (a) 1700, and (b) 4500 magnifications.

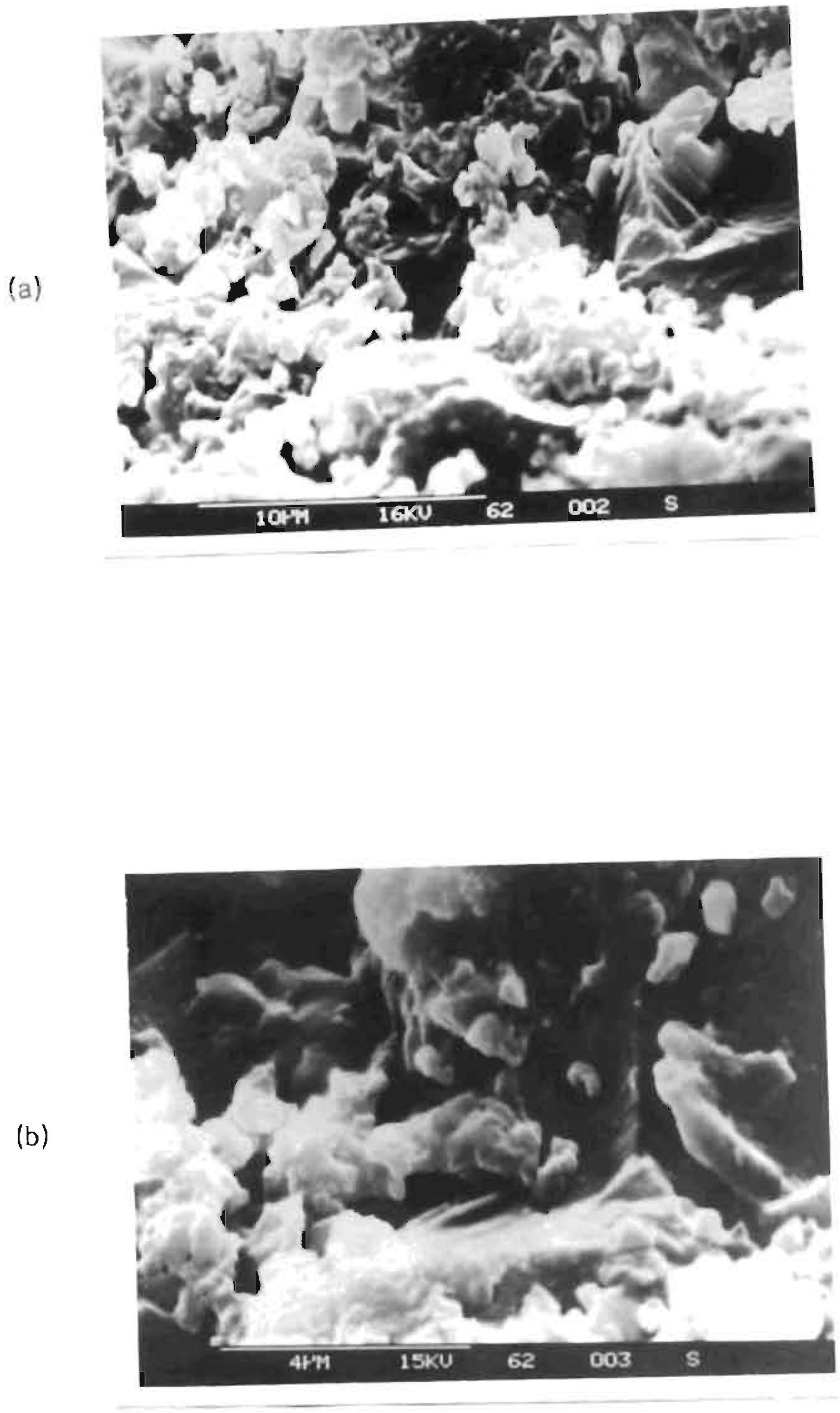


Fig. 3.6 SEM photographs of cardanol-formaldehyde (novolac)-PMMA semi-IPNs containing 87.5% PMMA at (a) 4500, and (b) 1000 magnifications.

Fig. 3.7 SEM photographs of cardanol-formaldehyde (resol)-PMMA semi-IPNs containing 28.5% PMMA at (a) 4500, and (b) 1000 magnifications.

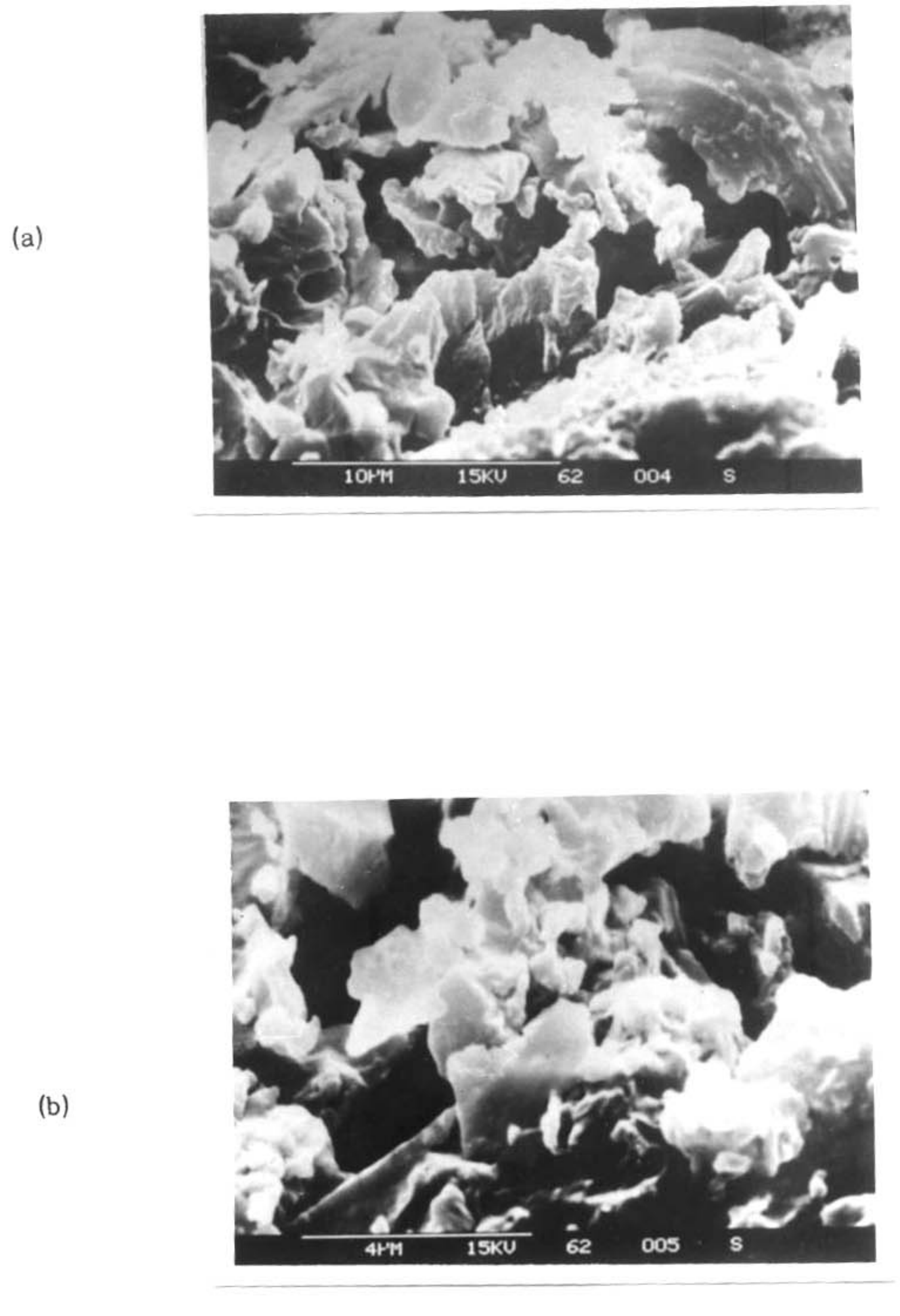


Fig. 3.8 SEM photographs of cardanol-formaldehyde (resol) - PMMA semi-IPNs containing 83.3% PMMA at (a) 4500, and (b) 1000 magnifications.

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CHAPTER 4

THERMAL CHARACTERIZATION OF CARDANOL-FORMALDEHYDE (POLYMERS) AND CARDANOL-FORMALDEHYDE RESIN BASED INTERPENETRATING NETWORKS

CHAPTER 4

THERMAL CHARACTERIZATION OF CARDANOL-FORMALDEHYDE (POLYMERS) AND CARDANOL FORMALDEHYDE RESIN BASED INTERPENETRATING NETWORKS

4.1 Introduction

Thermal analysis is now established as an invaluable and rapid method for the characterization of materials and evaluation of kinetic and thermodynamic parameters over a wide range of temperatures. Thermal analysis had been defined as a group of techniques in which physical property of a substance and or its reaction products is measured as a function of temperature while the substance is subjected to a controlled temperature programme[1,2,3]. The recent ICTA (International Committee for Thermal Analysis) classification of thermal analysis is given in Table 4.1. Almost any analytical technique can be considered as a thermal method, if the measured parameter is determined as a function of temperature. In order to consider a thermal technique as thermoanalytical, three criteria must be satisfied, (1) a physical property has to be measured, (2) the measurement has to be expressed (directly or indirectly) as a function of temperature, (3) the measurement has to be made under a controlled temperature programme[3]. In other words, the physical parameters are a dynamic function of temperatures. Of course, every physico-chemical property is measured at some given temperature; it is only when the measured property changes significantly as a function of temperature so as to yield useful information concerning the chemical system[5]. Thermal analysis has been treated mainly as a chemical analysis tool till the middle of this century[6]. In recent years, it has grown

TABLE 4.1: CLASSIFICATION OF THERMOANALYTICAL TECHNIQUES

Physical property	Derived Technique(s)	Acceptable Abbreviation
Mass	Thermogravimetry	TG
	Isobaric mass change determination	
	Evolved gas determination	EGD
	Evolved gas analysis	EGA
	Emanation thermal analysis	
	Thermoparticulate analysis	
Temperature	Heating curve determination	
	Differential Thermal Analysis	DTA
Enthalpy	Differential Scanning Calorimetry	DSC
Dimensions	Thermodilatometry	
Mechanical characteristics	Thermomechanical analysis	TMA
	Dynamic thermomechanometry	
Acoustic characteristics	Thermosonimetry	
	Thermoacoustimetry	
Optical characteristics	Thermophotometry	
Electrical characteristics	Thermoelectrometry	
Magnetic characteristics	Thermomagnetometry	

into a physico-chemical method and is used for the determination of phase equilibria, enthalpy of transition, specific heat, etc. Now it has been developed as a primary source of information concerning the solid-state thermal decomposition (heterogeneous) kinetics.

The most widely used techniques are Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA). Inorganic materials are those which are most widely studied by thermal analysis techniques, followed by high polymers, metals and metallic alloys and organic substances[3]. It should be noted that, in many cases, the use of only a single thermal analysis technique may not provide sufficient information about a given system. As with many other analytical methods, complementary or supplementary information, as can be furnished by other thermal analysis techniques, may be required. It is fairly common to complement all DTA or DSC data with TGA data[3].

4.1.1 Thermogravimetry (TG)

TG is defined as a technique whereby the mass of a substance, in an environment heated or cooled at controlled rate, is recorded as a function of time and temperature.

The first thermobalance was probably the instrument developed by Honda in 1915[7]. A number of thermobalances with varying capabilities are now commercially available and these have been discussed in various books. Application of thermogravimetry and the factors affecting thermogravimetry were discussed by Wendlandt[3], Blazeck[8], etc. The factors affecting thermogravimetry have been classified as (1) instrumental and (2) sample characteristics; and most important among them are heating rate, sample mass, atmosphere, etc. Instrumental factors include furnace heating rate, chart speed, furnace atmosphere, geometry of sample holder and furnace, sensitivity of recording mechanism and composition of sample container. Sample characteristics include amount of sample, particle size, heat of reaction, sample packing, nature of the sample thermal conductivity, etc.[3]

The essential requirements for the design and construction of an automatic recording thermobalance have been summarised by Lukaszewski and Redfern[9] and others. The main parts of a thermobalance are (1) recording balance, (2) furnace, (3) furnace temperature programmer controller, and (4) recorder.

Thermogravimetry is widely used in almost all the areas of chemistry and allied fields. It is universally applied to a large number of analytical problems in the field of metallurgy, paint and ink sciences, ceramics, minerology, food technology, inorganic and organic chemistry, polymer chemistry, biochemistry and geochemistry. TG is the most widely used thermal technique to study the heterogeneous reaction kinetics[3].

The greatest number of applications of thermogravimetry during the past few years have been in the characterization of polymeric materials which have been useful not only in the applied areas but also in the theoretical aspects of polymer chemistry. Application of TG include comparisons of the relative thermal stability, the effect of additives on the thermal stability, moisture and additive contents, studies of degradation kinetics, direct quantitative analysis of various copolymer systems, oxidation stability[3], etc. In studies of thermal oxidative degradation, TG can reveal the molecular structure and arrangement of repeating units, existence of cross-links between chains, side groups in homopolymer and copolymer chains and so on[10]. Rate constants, reaction orders, frequency factors and activation energies of degradation can also be obtained[11]. Newkirk had described a comparison of the relative thermal stability of a number of different polymers namely PMMA, polystyrene, nylon, polyethylene, etc.[12] Plasticizers are monomeric components that are added to plastics and elastomer formulations to modify the viscoelastic properties of the blend to make it more flexible, deformable and processable. These additives are lower in thermal stability than the polymer and can be separated from the polymers by heating to moderate temperature in a nitrogen atmosphere. Cassel and Gray had developed a TG procedure for the determination of dioctyl phthalate plasticizer in poly (vinyl chloride)[13]. Numerous TG studies had been made on the characterization of copolymer systems. In general, the thermal stability of a copolymer falls between those of the two homopolymers and changes in a regular fashion in the copolymer composition[14]. Thus application studies that include the use of TG to polymeric materials are numerous.

4.1.2 Differential Thermal Analysis (DTA)

DTA is a technique in which the temperature of a sample and a thermally inert reference material are compared, as the sample is heated or cooled at a uniform rate. It is a differential method in which the temperature differential ΔT between the sample and the reference material i.e. $\Delta T = T\ (\text{sample}) - T\ (\text{reference})$, is recorded as a function of temperature. The reference substance should not undergo decomposition or phase transition in the temperature range of interest[15].

The technique of DTA was first developed by Le Chatelier in 1887[16] and the most important development in DTA instrumentation was brought about by Stone for using it in controlled atmosphere of H_2O, CO_2, etc.[17]

The basic components of DTA are (1) furnace, (2) sample holder, (3) temperature sensor, (4) property sensor, (5) recorder, and (6) furnace temperature programmer[18]. A large number of DTA instruments are available and they have been discussed in several monographs and books[19].

DTA is a useful thermal technique which has varied applications. Wittels in 1951 used DTA for microcalorimetry[20]. Norton identified clay minerals using DTA[21]. In 1957, Borchardt and Daniels developed the necessary theory for the application of DTA to the study of reaction kinetics in stirred solutions[22]. DTA is nowadays extensively used for the study of heterogeneous reaction kinetics.

DTA has wide applications in the polymer field also. DTA is used to measure melting points, degree of crystallinity, heats of fusion, etc. Chiu studied a physical mixture of seven commercial polymers[23], and only very small amount is required for the experiment. Murphy et al demonstrated the effect of different catalysts on the curing of Vibrin 135 resin by a DTA method[24]. Schwenker and Beck studied the thermal degradation of polymeric materials used in textile manufacturing in air and nitrogen atmospheres[25]. DTA can detect relatively small changes in the polymer composition or the presence of substituents on the polymer backbone, as well as it is quite valuable for thermal degradations mechanism studies.

4.1.3 Differential Scanning Calorimetry (DSC)

There are two types of DSC instruments which use the same name, (1) differential scanning calorimeters which are heat flow recording instruments ($(dq/dt)_{\Delta T} = 0$) and (2) differential scanning calorimeters which are differential recording instruments ($\Delta T \neq 0$). The former is also known as power compensated DSC[15].

Differential scanning calorimetry is a technique in which the difference in energy inputs into a sample and a reference material is measured as a function of temperature, while the sample and the reference are subjected to a controlled temperature programme[26]. Gray had developed the basic equation relating (dH/dt) to the material properties[27].

DSC measurements are considered to be quantitative and kinetics and mechanisms of solid state thermal decomposition reaction can be studied by DSC[28]. A bibliography of literature in DSC has been compiled by Perkin-Elmer Corporation[29].

The basic components of DSC are the same as that of DTA.

DSC has a large number of applications which includes the study of decomposition reactions, phase diagrams, reaction kinetics, solid-state reactions, dehydration reactions, heats of adsorption, heats of reaction, Curie point determination, thermal stability, oxidation stability, glass transition determination, etc.[3] It can also be used to solve analytical chemistry problems. DSC can be used as a control for comparing similar but not identical materials. As a control technique, DSC may be used to distinguish between raw materials quickly and easily[3].

Thus nearly every chemical field has been touched by this technique, although much of the recent emphasis has been in the area of polymer chemistry. The largest use of DSC has been in some phase of polymer characterization. DSC is routinely used to measure glass transition temperature, melting points, degree of crystallinity, heats of fusion and crystallization, decomposition temperatures, and numerous other parameters[3].

DSC is widely used to study a variety of polymeric substances. Among them are rubber[30], molded resins[31], polymer films[32], engineering thermoplastics[33], etc. DSC is used to predict the potential explosive hazard of materials in an ASTM method[3]. DSC is also used to judge the thermal or oxidative stability of a resin and this method offers the advantage of shorter analysis time for well-stabilized resins[3]. Gray had reviewed the determination of polymer crystallinity by using DSC[34].

4.1.4 Thermomechanical analysis (TMA)

The changes of volume, shape, length and other properties relating to the physical shape of a substance constitute the broad area of thermal analysis known as thermomechanical methods. Three techniques are commonly included that are related by expansion behaviour and viscoelastic effect[35]. They are thermodilatometry (TDA), thermomechanical analysis (TMA) and dynamic thermomechanometry (DMA). The difference among these three techniques lies in their method of measurement. For TMA, a stress is applied to the sample that is nonoscillatory and the deformation under load is measured. Thus TMA involves the measurement of deformation under nonoscillatory load which is recorded as a function of sample temperature while the sample is being heated at a linear rate. Daniels correlated the behaviour of a sample with the 3 techniques[35]. In TMA, the bulk effect of the sample's molecular response to changes in thermal energy is measured. These changes involve crystal structure, lattice vibrations, and physical and chemical states, all of which can result in the change of length of a solid sample. Thus TMA response is a combination of expansion behaviour and viscoelastic effect.

The instrumentation of TMA had been described by Daniel[35], and the changes in the dimensions of a sample are detected by a mechanical, optical or electrical transducer although the transducer is usually a linear variable differential transformer.

TMA is widely used to study the properties of polymers and other materials under various conditions in the temperature range from -200 to +800°C, but almost all applications of TMA have been to polymeric systems[3]. It is used to measure the thermal expansion characteristics of the polymer and hence to determine the glass transition temperature[36].

Miller[37], Barton[36] and others prepared reviews on the application of TMA to polymers. TMA can also be used to determine the thermoplastic melt viscosity of polymers. In the present study TG, DSC, and TMA are used for polymer evaluation.

4.1.5 Kinetic Analysis of Reactions

TG and DSC are the most widely used thermoanalytical techniques to study the kinetics of chemical reactions and to determine the basic kinetic constants, viz., rate constant k, activation energy E, pre-exponential factor A and order parameter n.

The method of thermal analysis can be divided into two: (1) static and (2) dynamic. The static method itself can be classed into isobaric and isothermal. In isobaric changes, the equilibrium property of a substance is measured as a function of temperature and in isothermal method, property changes are measured as a function of time. Dynamic method consists of the measurement of properties under a programmed temperature conditions[15].

Isothermal Kinetic Analysis

Isothermal method is considered to be the most accurate method fo he analysis of reaction kinetics. The simple method of obtaining ki c parameters from experimental data is based on the formal kinetic eq ion

$$\frac{d\alpha}{dt} = k(1-\alpha)^{n} \qquad \ldots\ldots\ldots\ldots\ (1)$$

= rate of the reaction, but rate constant k is related to activation parameters A and E by the relation

$$k = Ae^{-E/RT} \qquad \ldots\ldots\ldots\ldots\ldots (2)$$

wh A is the pre-exponential factor, E is the activation energy, R the gas constant. On substitution of equation (2) in equation (1),

$$\frac{d\alpha}{dt} = Ae^{-E/RT}(1-\alpha)^{n} \qquad \ldots\ldots\ldots\ (3)$$

For he correct value of n, plot of $\frac{d\alpha}{dt}$ vs $(1 - \alpha)^{n}$ will give a straight line with slope = k. (The value of k can be determined at different isothermal temperatures). Taking logarithm of Arrehenius equation (2),

$$\ln k = \ln A - \frac{E}{RT}$$

Thus from the plot of ln k vs 1/T, A and E can be determined.

Non-Isothermal Reaction Analysis

Flynn[38] had given a very good account of the historical development of non-isothermal kinetics. The analytical determination of specific reaction quantities, E and A is based on the experiments performed at programmed temperature conditions. So, the kinetic law and Arrehenius equation are to be considered. The functional relation between activation parameters and fractional conversions in non-isothermal methods had been discussed by Achar et al[39], Horowitz and Metzger[40].

The advantage of determining the kinetic parameters by non-isothermal methods had been listed by Wendlandt[5] and they are, (1) results can be obtained from a single TG experiment. (2) The kinetics can be calculated over an entire temperature range in a continuous manner. (3) Only a single sample is required. (4) When the sample undergoes considerable reaction on being raised to the required temperature, the results obtained by isothermal methods are questionable. But non-isothermal method had certain disadvantages also. (1) The reaction mechanism cannot be usually determined and it gives only an overall kinetic expression and (2) the greater susceptibility to procedural factors[15]. However, non-isothermal method is used more commonly because it required only a single TG experiment to compile the results.

Non-Isothermal kinetic equations for the analysis of TG data

The most widely used thermal technique to study heterogeneous kinetics is TG[8]. Three different approaches have been made for the calculation of kinetic parameters[41]. They are (1) Differential methods, (2) Integral methods, (3) Approximation methods. Using the three approaches, a number of equations have been derived by different authors and they have been given in number of publications[42].

Coats and Redfern derived an equation using the integral methods. These authors[43] evaluated the comparative integral with the aid of the Rainville[44] function and put forward Coats-Redfern equation, the final form of which can be written as follows:

$$\ln\left[g(\alpha)/T^2\right] = \ln\left[\left(\frac{AR}{\phi E}\right)\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

where

T = Temperature

R = Universal gas constant

E = Activation energy

A = Pre-exponential factor

ϕ = Heating rate

$g(\alpha) = -\ln(1-\alpha)$ where $n = 1$

or $g(\alpha) = \dfrac{1-(1-\alpha)^{1-n}}{(1-n)}$ where $n \neq 1$

where

α = fraction decomposed

n = order parameter

These authors have shwon that for the usual values of E and temperature range over which reaction generally occurs, the term ln $(AR/\phi E)(1 - 2RT/E)$ is sensibly constant[42] since $2RT/E \ll 1$. A plot of lon $(g(\alpha)/T^2)$ vs $1/T$ would, therefore, be linear. E and A can be calculated from the slope and intercept of the linear plot. The authors have recommended a trial and error method for determining the form of $g(\alpha)$ i.e. the values of n is determined by trial and error[15]. The equation derived by Coats and Redfern is the most popular and well known integral method. Hence, in this work the kinetic parameters were evaluated by using Coats-Redfern equation.

Thus TG, DSC and DTA can be used for determining the thermal stability, thermal decomposition, kinetic parameters of decomposition, etc. Of the three methods, TG is the most ideal and reliable method because weighing is the most reliable method.

This Chapter is mainly concerned with the study of thermal stability, thermal decomposition, kinetic parameters of decomposition, glass transition, etc. of two polymeric systems : (1) cardanol-formaldehyde polymers (novolac and resol), and (2) cardanol formaldehyde (both novolac and resol) - poly (methylmethacrylate) interpenetrating networks (IPNs). The synthesis of these two systems are described in detail in Chapter 3.

4.2 Experimental

4.2.1 Synthesis

The synthesis of cardanol formaldehyde polymers and cardanol formaldehyde - poly(methylmethacrylate) IPNs are described in detail in the experimental section of Chapter 3.

4.2.2 Methods

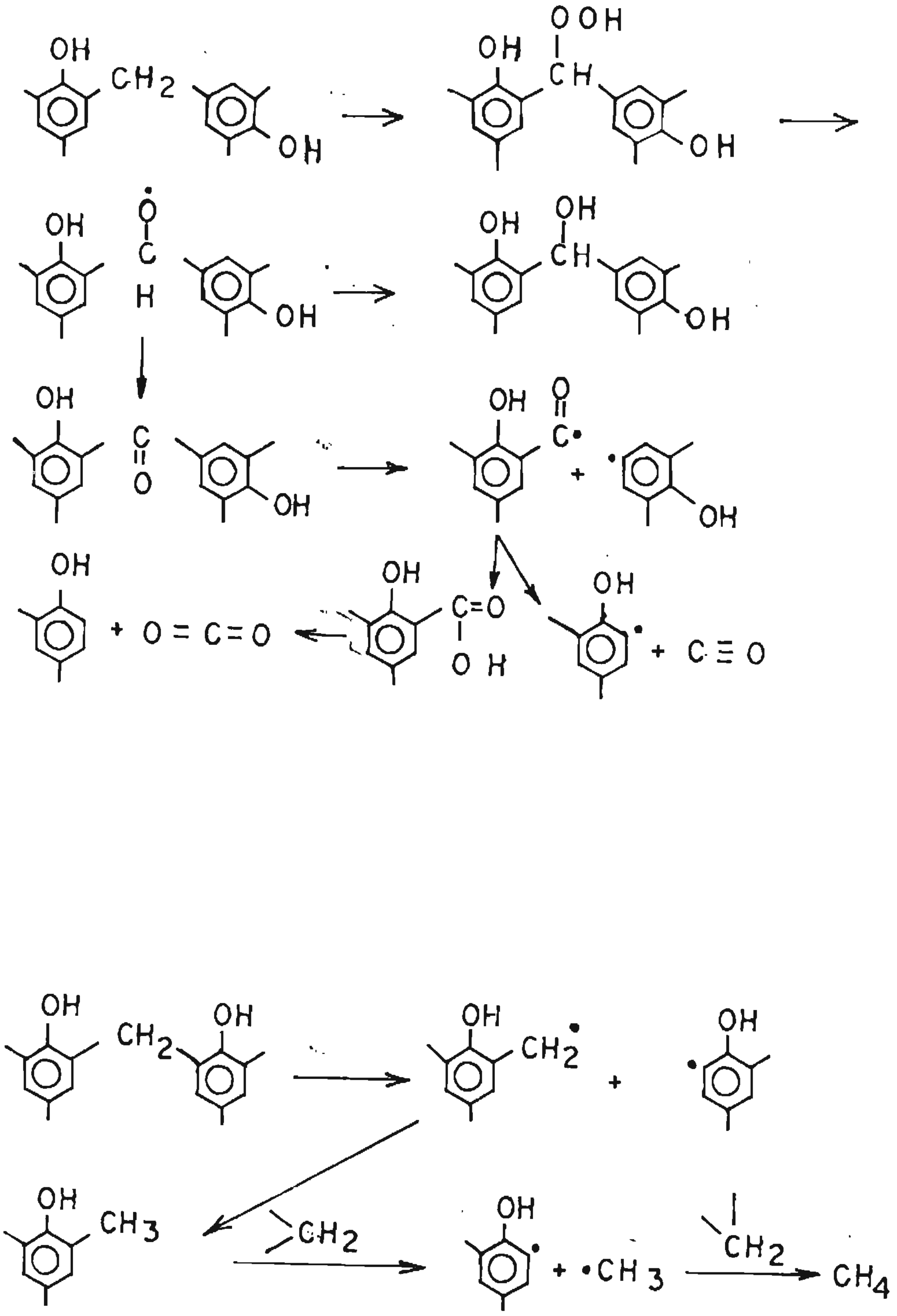
4.2.2.1 Thermal characterization

A Dupont 990 Modular Thermal Analysis system consisting of 951 TGA, 905 DSC and 942 TMA was used for thermal analysis. All TG and DSC were recorded in N_2 atmosphere at a flow rate of 50 cm^3/min, the heating rate was 10^o/min and for TG the sample weight was 10 ± 0.2 mg and for DSC it was 10 ± 0.2 mg. For TMA 3-4 mm cubical sample was used. Experimental conditions were maintained identical for all samples.

4.3 Results and Discussion

4.3.1 TG studies

Phenol-formaldehyde results are temperature resistant plastics and result in high yields of char on thermal degradation. Thermal degradation of phenol-formaldehyde resin takes place in two stage[45,46] (300-600°C and > 600°C). The mechanism of thermo-chemical degradation of phenol-formaldehyde resins was thoroughly investigated by Conley[47] and Gautherot[48]. The reaction is reported to take place through a thermo-oxidative process irrespective of whether the reaction takes place in an oxidative or inert atmosphere. Phenolic resins by themselves have high oxygen content and this is shown to be the reason for the oxidative degradation process. Major components of the products of thermal degradation of phenol formaldehyde are benzene, toluene, phenol, substituted phenols, carbon dioxide, carbon monoxide, phenolic acids and keto phenols. The degradation is schematised as follows[47] (Scheme 4.1).



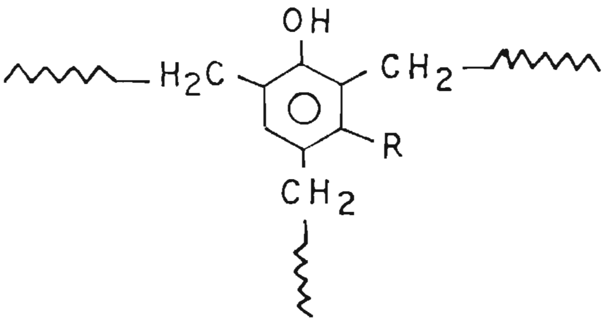
Scheme 4.1

The thermal degradation of phenol-formaldehyde and cardanol-formaldehyde polymers were compared and table 4.1 indicates the reported decomposition temperature for 10% and 50% TG weight loss for cardanol-formaldehyde and phenol-formaldehyde (in air)[49]. Cardanol-formaldehyde has a poorer thermal stability and loses 50% of its weight at 485°C, whereas phenol-formaldehyde requires 830°C for the same weight loss.

TABLE 4.1 THERMAL DEGRADATION DATA OF CARDANOL-FORMALDEHYDE AND PHENOL-FORMALDEHYDE

System	10% DT, °C	50% DT, 0°C
Cardanol-formaldehyde	340	485
Phenol-formaldehyde	430	830

This difference in thermal stability is attributed to the structural features of cardanol-formaldehyde. The structure of cardanol-formaldehyde and phenol-formaldehyde are represented as follows:



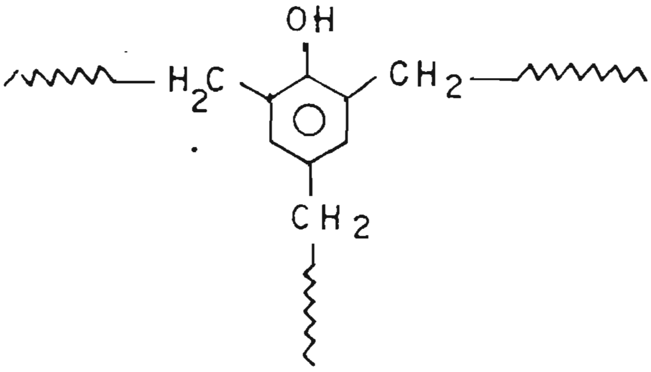
R = $-(CH_2)_6 - CH_2 - (CH_2)_7 - CH_3$

R = $-(CH_2)_6 - CH_2 - CH = CH - (CH_2)_5 - CH_3$ (major component)

R = $-(CH_2)_6 - CH_2 - CH = CH - CH_2 - CH = CH - (CH_2)_2 - CH_3$

R = $-(CH_2)_6 - CH_2 - CH = CH - CH_2 - CH = CH - CH_2 - CH = CH_2$

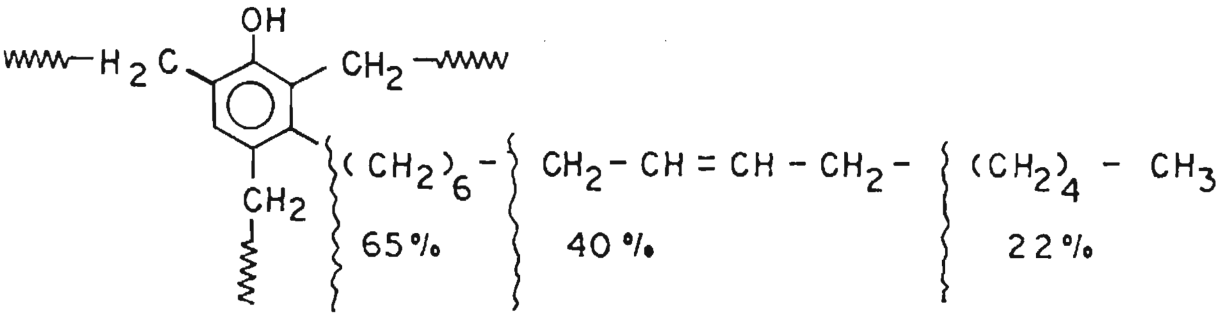
Cardanol-formaldehyde



Phenol-formaldehyde

The long side chain (containing between zero, one, two or three double bonds) does not form part of the network. Structure and degradation of the side chain is expected at a relatively low temperature due to the facile β - cleavage at the double bonds.

The major component of cardanol is the monoene with the double bond at 8 position and β - cleavage at the sixth carbon atom or tenth carbon atom would lead to a weight loss of approximately 40% and 22% respectively. A loss of the whole side chain would result in a weight loss of around 65% (Scheme 4.2).



Scheme 4.2

Figure 4.1 gives TGs of phenol-formaldehyde (resol), phenol-formaldehyde (novolac, 5% HMTA), cardanol-formaldehyde (resol) and cardanol-formaldehyde (novolac, 5% HMTA) prepared as described in the experimental of Chapter 3. The Table 4.2 gives % weight loss at different temperatures for each of the samples. As is the case with reported

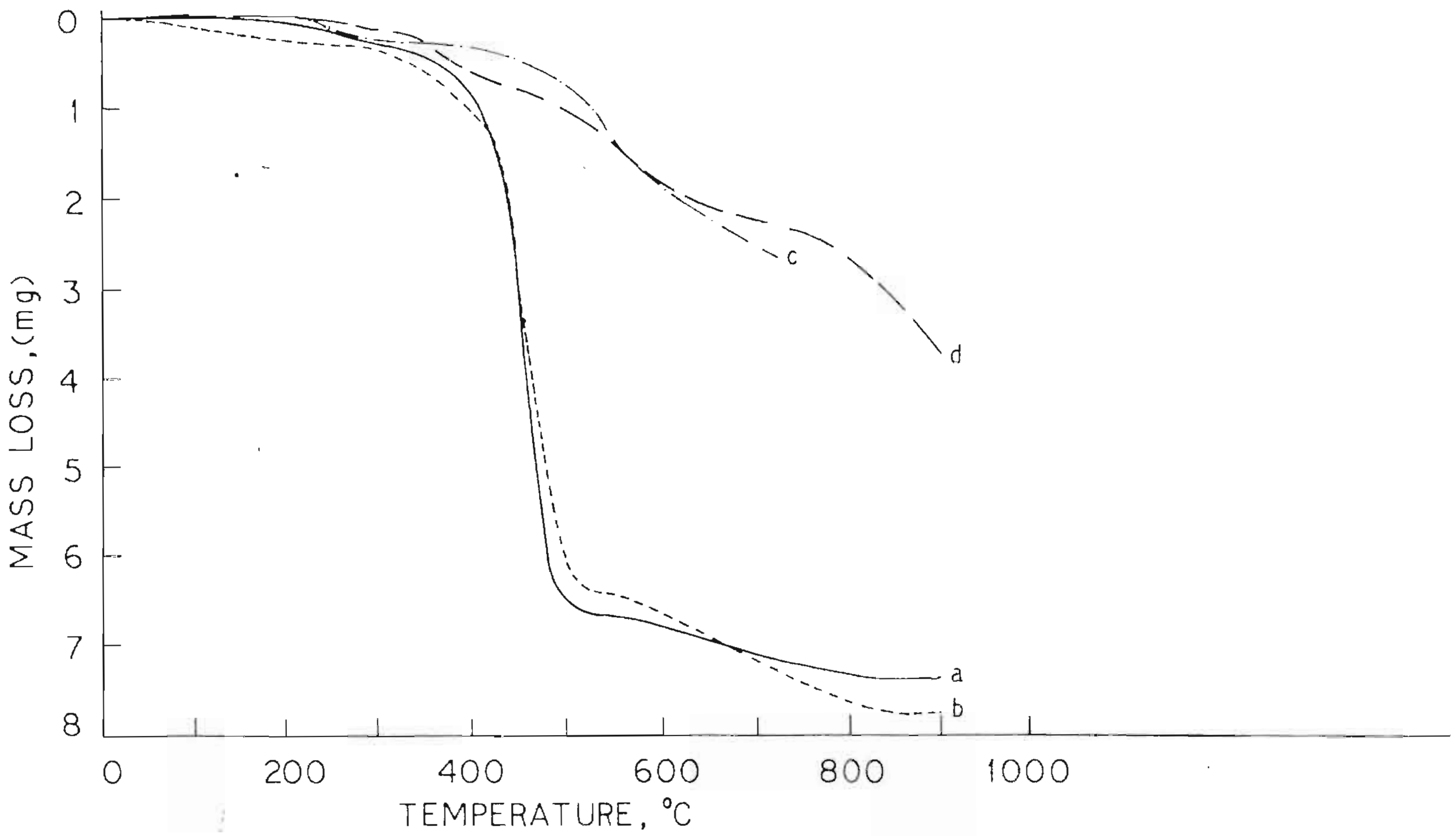


FIG.4.1. THERMOGRAMS OF

a. CARDANOL – FORMALDEHYDE (RESOL)
b. CARDANOL – FORMALDEHYDE (NOVOLAC)
c. PHENOL – FORMALDEHYDE (RESOL)
d. PHENOL – FORMALDEHYDE (NOVOLAC)

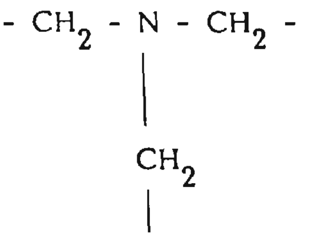
TABLE 4.2 % WEIGHT LOSS DATA FOR CARDANOL-FORMALDEHYDE AND PHENOL-FORMALDEHYDE POLYMERS

Temp. °C	Cardanol-formaldehyde (resol)	Cardanol-formaldehyde (novolac)	Phenol-formaldehyde (resol)	Phenol-formaldehyde (novolac)
1	2	3	4	5
250	0.6	0	1.4	0
260	1.25	1.9	2.4	0.5
270	1.25	1.9	2.5	1.12
280	1.5	2.1	2.6	1.25
290	2.4	2.2	2.7	1.4
300	2.5	3.5	3.1	1.5
310	2.6	2.7	3.6	1.9
320	2.8	3.1	3.8	2.3
330	3.5	3.8	3.8	2.5
340	3.8	4.0	3.8	2.6
350	4.0	5.0	3.8	3.5
360	5.0	6.3	3.9	4.8
370	5.2	7.1	4.0	5.2
380	6.3	8.8	4.1	6.5
390	7.5	10	4.3	7.5
400	8.8	11.3	4.6	7.6

1	2	3	4	5
410	11.7	12.1	5.0	8.5
420	15.0	13.0	5.1	8.75
430	15.8	17.5	5.3	9.0
440	26.3	23.8	6.3	9.9
450	38.8	36.3	6.5	10.0
460	51.3	46.3	7.4	10.6
470	63.8	55.0	7.8	11.3
480	73.8	62.5	8.8	11.5
490	78.8	68.8	8.9	12.5
500	80.0	73.8	10.0	13.0

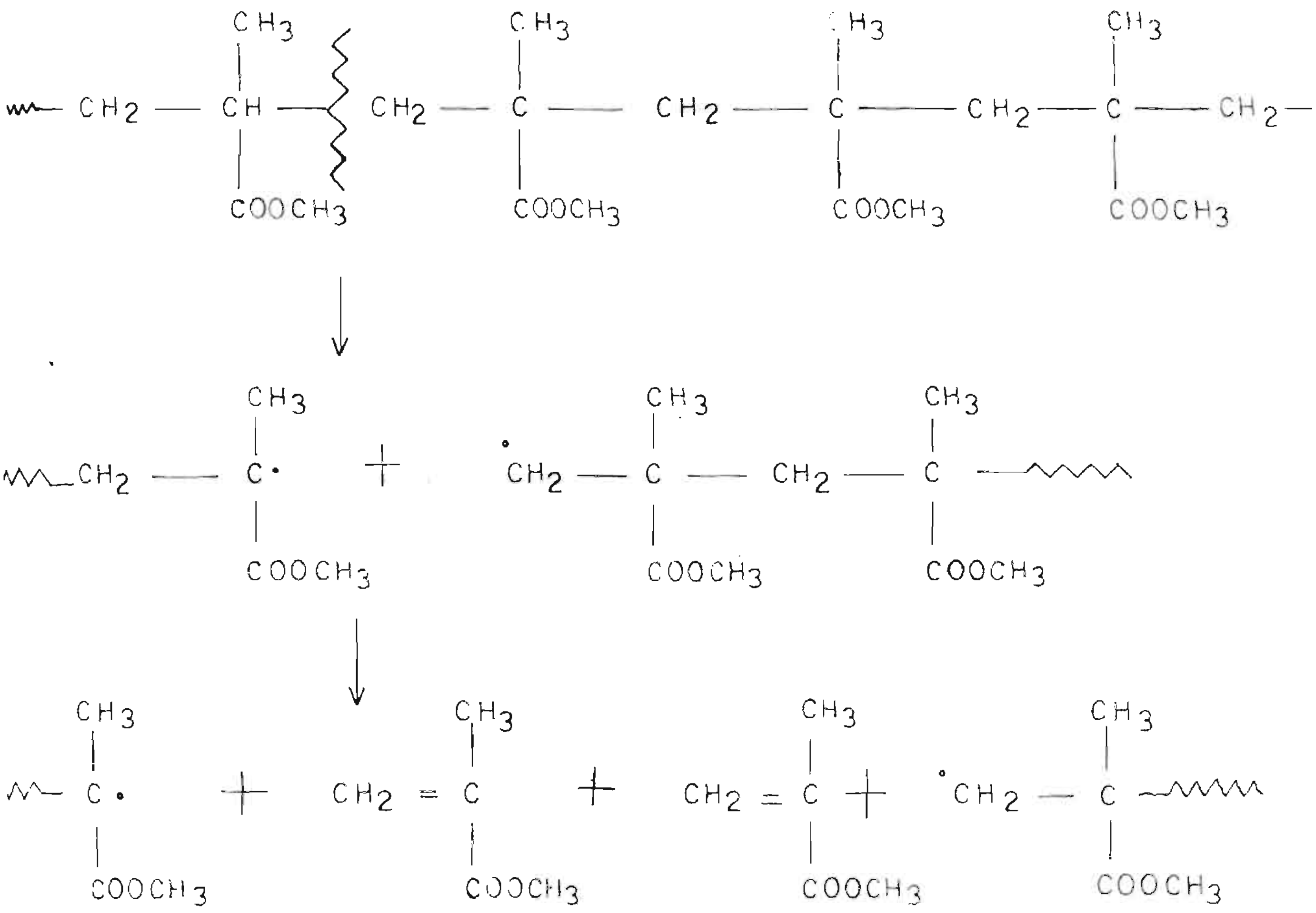
samples, cardanol-formaldehyde products decompose at a much faster rate. Phenol-formaldehyde had a weight loss of about 10-13% in comparison with 74-80% weight loss for cardanol-formaldehyde. The increased weight loss approximately accounts for the loss of C_{15}-side chain. Comparison between the degradation patterns of cardanol-formaldehyde resol and novolac suggests an almost identical pattern upto around 50% weight loss (460°C). Above this temperature resol decomposes at a faster rate than novolac. This decreased rate in thermal decomposition above 460°C for novolac in comparison with resol could be due to the increased crosslinking brought about by HMTA.

The tertiary amine $(- CH_2 - N - CH_2 -)$ crosslink points in novolac could also be expected to play a role in scavenging the radicals formed during the decomposition, thereby increasing the thermal stability.



$$(- CH_2 - \underset{\underset{|}{\underset{CH_2}{|}}}{N} - CH_2 -)$$

Fig. 4.2 gives the TGs of cardanol-formaldehyde (resol) - PMMA semi-IPNs containing various proportions of PMMA content. The weight loss at various temperature for each of the product is tabulated in Table 4.3. Thermal degradation of PMMA homopolymer is extensively investigated[50]. The PMMA is known to degrade to around 25%, 50% and 90% weight loss at 300°C, 350°C and 400°C respectively via a stepwise unzipping process. The polymer chain breaks at random vulnerable points and the depolymerization occurs through a chain mechanism. The unzipping of PMMA by thermal degradation could be represented as follows (Scheme 4.3).



Scheme 4.3

Table 4.3 indicates only a low % of weight loss of the order less than 15% even at 350°C for the products under study. This is considerably low considering the fact that some of the samples contain high % of PMMA content varying from 37.5 to 90%. This suggests the influence of cardanol-formaldehyde (resol) on the mechanism of PMMA degradation. The likely mechanism for this improvement in thermal degradation could be the interaction of cardanol-formaldehyde phenolic units with the PMMA free radicals generated by PMMA decomposition, thereby slowing down or preventing the chain depolymerization of PMMA and phenols acting as a free radical trap. Substituted phenols are known to interact efficiently with free radicals. Similar stabilization of polymer networks for

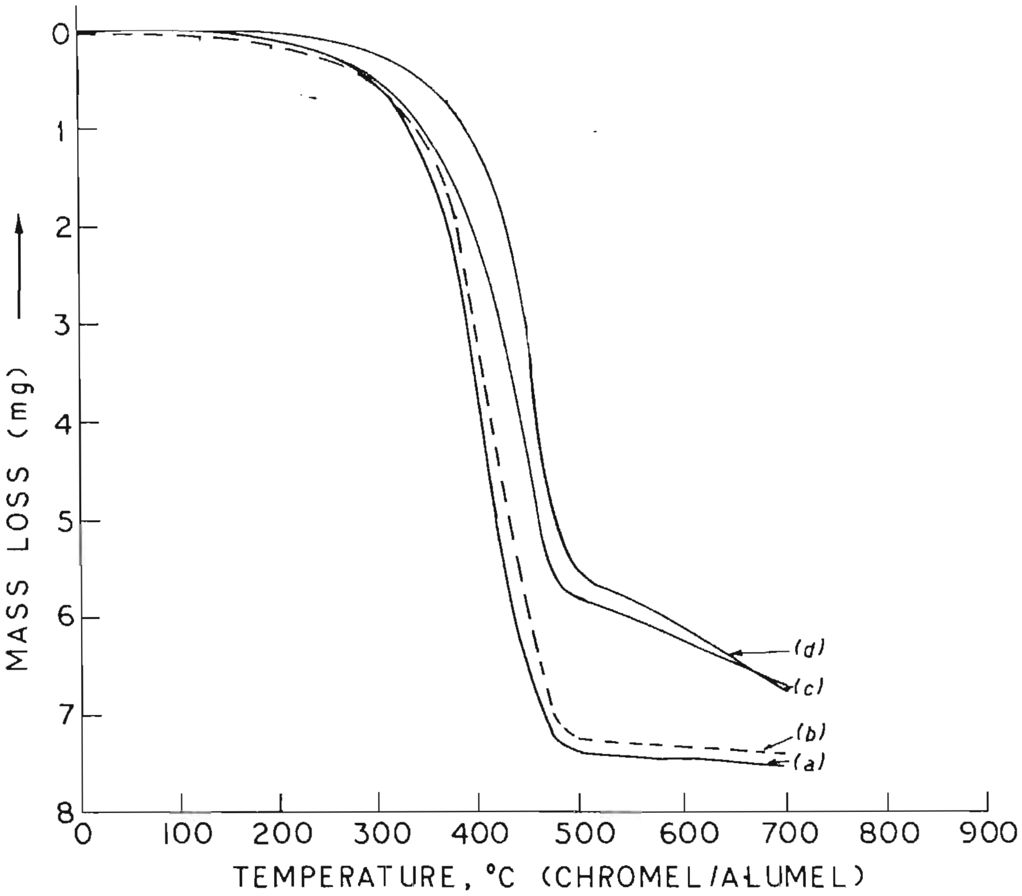


Fig. 4.2 Thermograms of cardanol-formaldehyde (resol)-PMMA semi-IPNs containing

(a) 90% PMMA
(b) 83.3% PMMA
(c) 75% PMMA
(d) 40% PMMA

TABLE 4.3 % WEIGHT LOSS DATA FOR CARDANOL-FORMALDEHYDE (RESOL) - PMMA SEMI-IPNs

Temp. °C	100% PMMA	90% PMMA	83.3% PMMA	75% PMMA	44% PMMA	0% PMMA
1	2	3	4	5	6	7
250	7.5	2.0	2.0	1.8	0	0.6
260	8.8	2.5	2.5	2.5	0.13	1.25
270	12.5	3.1	3.1	2.6	0.25	1.25
280	15.0	3.75	3.8	3.8	0.8	1.5
290	18.8	5.0	4.0	3.9	1.12	2.4
300	23.8	5.25	5.25	5.0	1.25	2.5
310	28.8	6.5	6.5	6.3	2.5	2.6
320	32.5	8.75	8.4	6.9	2.6	2.8
330	38.5	10.0	10.0	8.8	3.8	3.5
340	43.8	12.5	11.3	10.0	4.4	3.8
350	48.8	15.0	13.8	11.3	5.1	4.0
360	55.0	17.5	16.3	13.4	6.3	5.0
370	63.8	21.3	20.0	15.0	7.5	5.2
380	73.8	26.3	25.0	17.5	8.8	6.3
390	82.5	33.8	32.5	21.3	11.9	7.5
400	90.0	43.8	40.0	25.0	13.8	8.8
410	93.8	53.8	48.8	30.0	17.5	11.7

1	2	3	4	5	6	7
420	96.3	62.5	56.3	35.0	21.3	15.0
430	97.5	70.0	63.8	40.0	26.3	15.8
440	97.5	81.3	70.0	46.3	32.5	26.3
450	97.5	81.3	76.3	54.0	40.0	38.8
460	97.5	85.0	82.5	61.3	50.0	57.3
470	97.5	87.5	87.5	66.3	57.5	63.8
480	97.5	90.0	89.4	68.8	63.8	73.8
490	97.5	91.0	90.0	100.0	66.3	78.5
500	97.5	100.0	96.8	100.0	68.1	80.0

thermal degradation by incorporation into IPN network have, in fact, been reported in the case of polyurethane/PMMA-IPNs where PMMA has acted as a radical scavenger[51], stabilising the polyurethane degradation.

The explanation offered by Belyakov et al in the case of thermal stabilisation of polyurethane brought about by PMMA interpenetration is slightly in variance with the one offered here. Belyakov suggested that PMMA degrades first via a stepwise unzipping process and this more easily degradable component of the IPN absorbing free radicals, stabilising and protecting less easily degradable polyurethane component. In the present case the more easily degradable PMMA degradation is suggested to be stabilised by the phenol groups of cardanol-formaldehyde polymer by interacting with the radicals generated. However, in both cases the stabilisation is by scavenging the free radicals generated during thermal degradation. Kim et al[52] have also reported thermal stabilisation effects due to interpenetration in polyurethane/polystyrene systems. Placement of two different polymers in juxta position could thus bring about thermal stabilisation effects in addition to changes in mechanical properties.

Comparison of the thermal degradation pattern of the cardanol-formaldehyde (resol) - PMMA semi-IPNs with cardanol-formaldehyde (resol) homopolymer also indicates a char content of around 12% for the homopolymer in comparison with almost no char content for the semi-IPNs at 500°C.

Figure 4.3 gives TGs of cardanol-formaldehyde (novolac) - PMMA-semi IPNs and Table 4.4 gives the % weight loss data. The data indicates

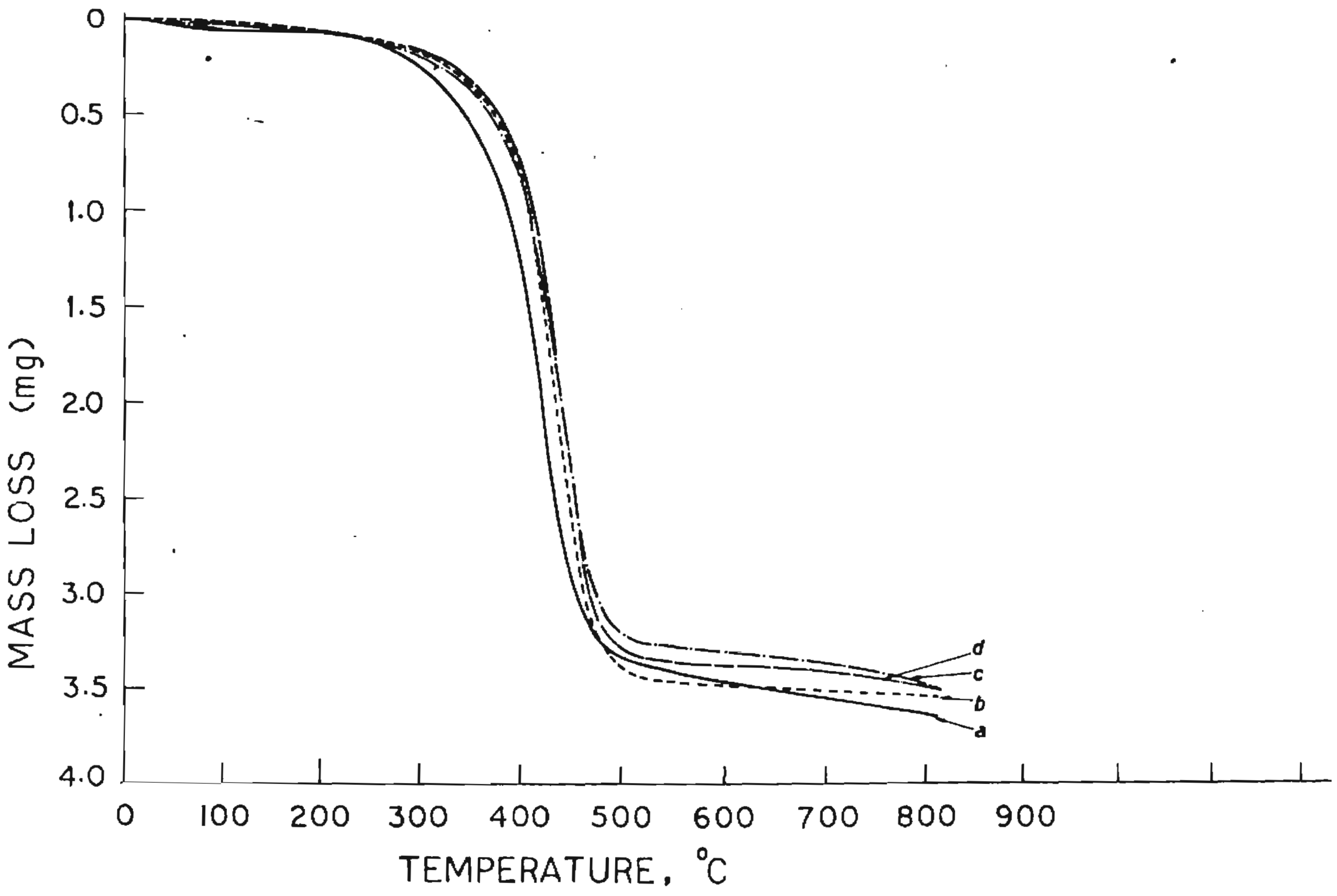


Fig. 4.3. Thermograms of cadanol formaldehyde (novolac)–PMMA semi-IPNs containing

a) 87.5 % PMMA. b) 83.3 % PMMA.

c) 75.0 % PMMA. d) 50.0 % PMMA.

TABLE 4.4 % WEIGHT LOSS DATA FOR CARDANOL-FORMALDEHYDE (NOVOLAC) - PMMA SEMI-IPNs

Temp. °C	100% PMMA	87.5% PMMA	83.3% PMMA	75% PMMA	50 % PMMA	0% PMMA
1	2	3	4	5	6	7
250	7.5	0.6	0.12	0.12	0	0
260	8.8	1.25	0.25	1.125	0.12	1.9
270	12.5	1.8	0.88	1.25	0.25	1.9
280	15.0	2.5	1.25	1.37	1.0	2.1
290	18.8	3.2	1.3	1.5	1.25	2.2
300	23.8	3.8	2.5	2.5	1.37	2.5
310	28.8	5.0	2.5	2.6	2.5	2.7
320	32.5	6.3	3.75	3.75	3.1	3.1
330	38.8	7.5	4.3	4.4	3.75	3.8
340	43.8	10.0	5.0	5.0	5.0	4.0
350	48.8	11.3	6.3	6.3	5.25	5.0
360	55.0	13.0	7.5	8.8	7.5	6.3
370	63.8	16.3	8.8	10.0	8.75	7.1
380	73.8	20.0	11.3	12.5	11.0	8.8
390	82.5	23.0	13.0	15.0	13.0	10.0
400	90.0	30.0	17.5	18.8	16.3	11.3
410	93.8	38.9	25.0	23.8	22.5	12.1

1	2	3	4	5	6	7
420	96.0	47.0	32.5	30.0	28.8	13.0
430	97.5	57.0	42.5	38.8	37.5	17.5
440	98.0	65.0	52.5	47.5	46.3	23.0
450	98.0	70.0	62.5	56.3	56.3	36.3
460	98.0	75.0	71.0	65.0	66.3	46.3
470	98.0	77.5	76.3	76.0	73.8	55.0
480	98.0	80.0	78.0	73.0	76.0	62.0
490	98.0	80.5	81.3	76.0	78.9	68.8
500	81.0	82.5	82.8	77.3	80.0	73.8

greater stabilisation of PMMA decomposition in comparison with that in the resol system. For a 75% PMMA semi-IPN, approximately 50% weight loss was observed in the case of resol semi-IPNs whereas only 37% weight loss is indicated in the case of novolac semi-IPNs. Comparison of the cardanol-formaldehyde (resol and novolac) homopolymer has already been discussed earlier wherein the decomposition pattern was found to be almost identical upto 450 to 460°C. The increased thermal stability of PMMA in the case of novolac semi-IPNs could be attributed to the presence of tertiary amino crosslink points in addition to the phenolic groups both of which could act as a scavenger for the radicals of thermal degradation of PMMA.

The % weight loss at 300°, 350°, 400° and 450°C are plotted Vs % PMMA content for resol and novolac semi-IPNs in figures 4.4 and 4.5 respectively. The plots show a linear trend for the different semi-IPNs, whereas the homopolymer (0 and 100% PMMA) give rise to distinctly discontinuous points in the graph. This result could also be indicative of mechanistic involvement of cardanol-formaldehyde in the thermal degradation of PMMA and vice versa.

Figures 4.6, 4.7 and 4.8 give the Coats-Redfern[43] plots for cardanol-formaldehyde polymer, cardanol-formaldehyde (resol)/PMMA and cardanol-formaldehyde (novolac)/PMMA semi-IPNs respectively. Good fits are obtained for the reaction order paramters, $n = 1$. Two distinct stages of decomposition are indicated in both cases, first stage between 200 and 400°C and the second stage between 400 and 500°C. Activation energies for these two stages of decomposition for the different samples are

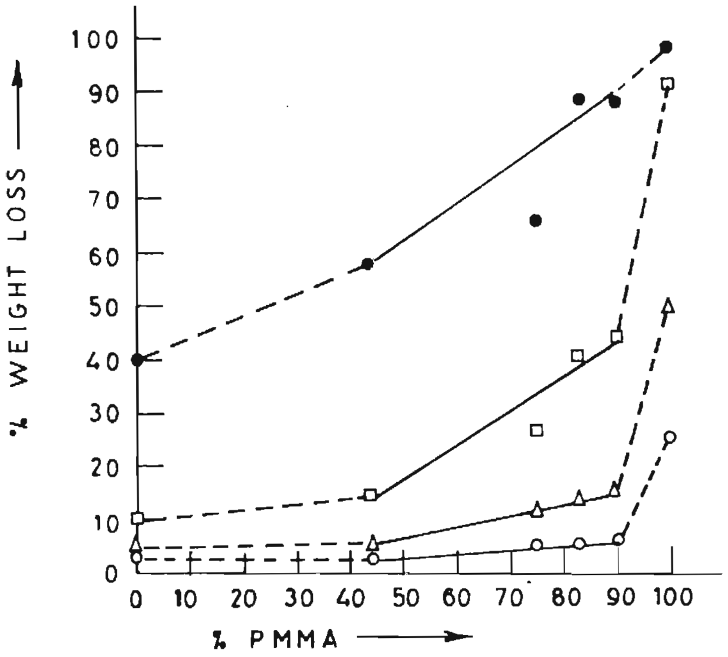


Fig. 4.4 Plot of weight loss (TGA) Vs PMMA content for cardanol formaldehyde (resol)- PMMA semi-IPNS at

○ 300° C
△ 350° C
□ 400° C
● 450° C

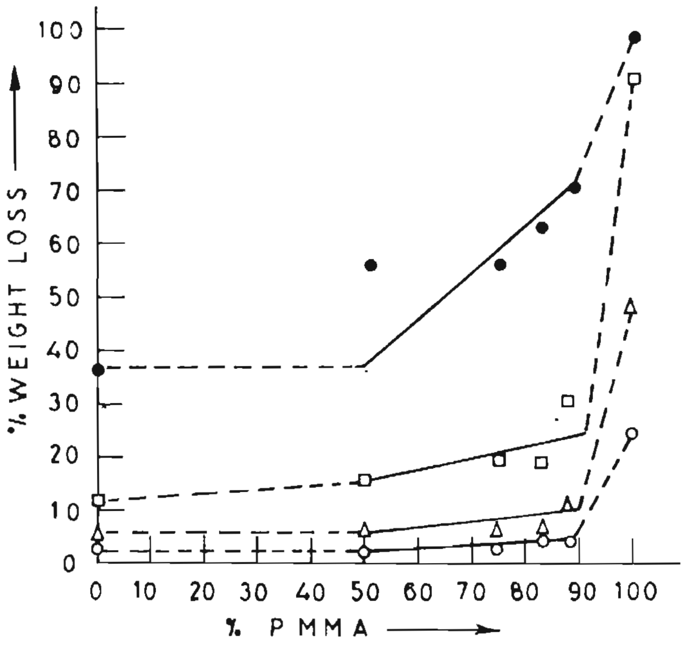


Fig. 4·5 Plot of % weight loss (TGA) Vs % PMMA content for cardanol-Formaldehyde (novolac)-PMMA semi-IPNs at

○ 300° C
△ 350° C
□ 400° C
● 450° C

deduced from the slopes of the Coats-Redfern plot (Table 4.5). Activation energies for the first stage of decomposition for the cardanol-formaldehyde (resol) - PMMA semi-IPNs range between 40 and 55 K Joules/mole whereas the corresponding values for semi-IPNs based on novolac system range between 44 and 65 K Joules/mole. This higher activation energy for the novolac system is also in accordance with the increased thermal stability of novolac based semi-IPNs deduced from the % weight loss calculation. The second stage of decomposition which is between 400 and 500°C has an activation energy ranging between 90 and 110 K Joules/mole for semi-IPNs whereas for the cardanol-formaldehyde homopolymers the value is higher (138 K Joules/mole).

Comparison of the activation energies of the two stages indicate large difference in activation energies between the first and second stages. The activation energy for the first stage of decomposition has a value around 40 to 50 K Joules/mole, the magnitude of which is low for a possible free radical type of decomposition. The cardanol side chain decomposition preferably taking place during the first stage of decomposition could, infact, follow an ionic mechanism by attack of the double bonds by acid protons (available from the phenolic groups) and further undergoing β - cleavage of the carbonium ions formed.

The second stage of decomposition having an activation energy around 140 K Joules/mole, might, in all probability, follow a radical decomposition mechanism.

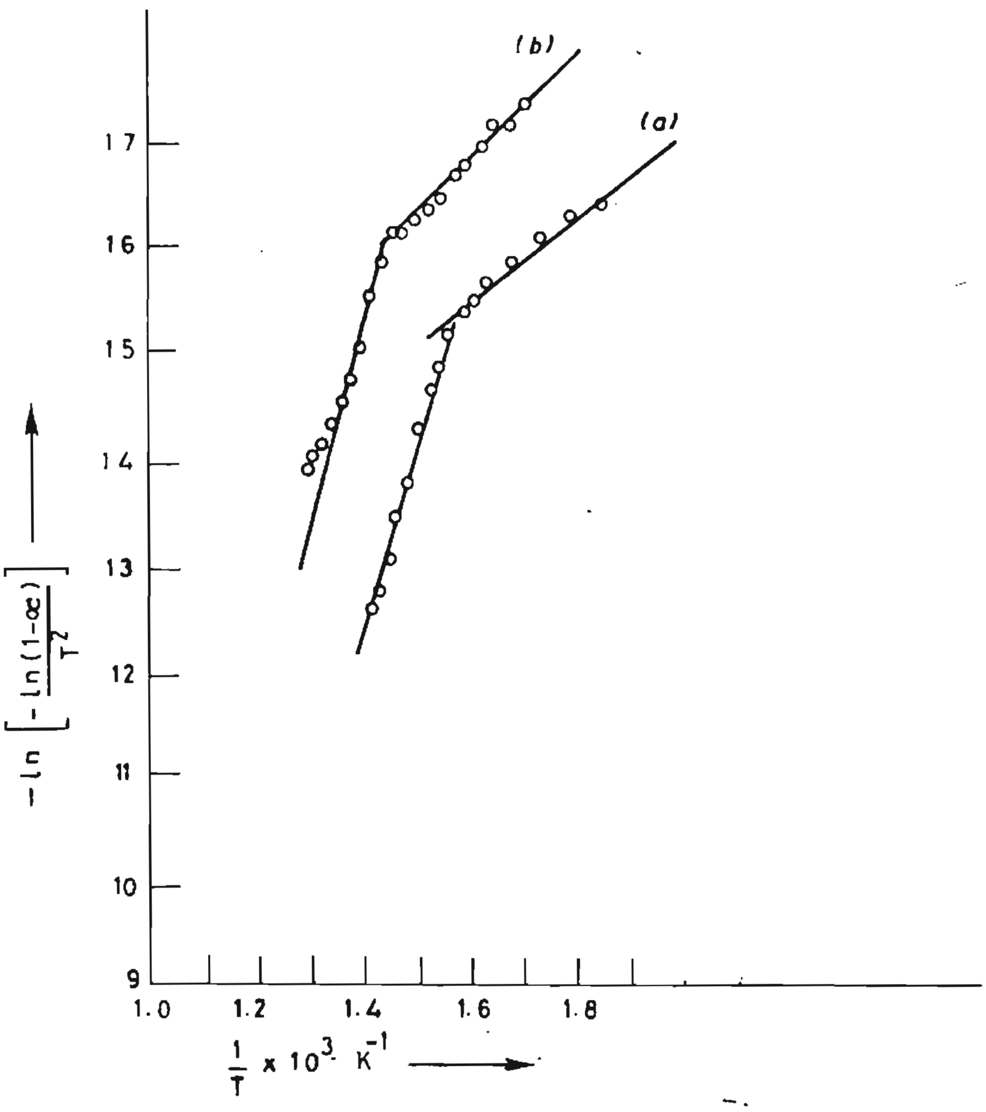


Fig. 4·6 Coats - Redfern plot for
(a) Cardanol - formaldehyde (resol)
(b) Cardanol - formaldehyde (novolac)

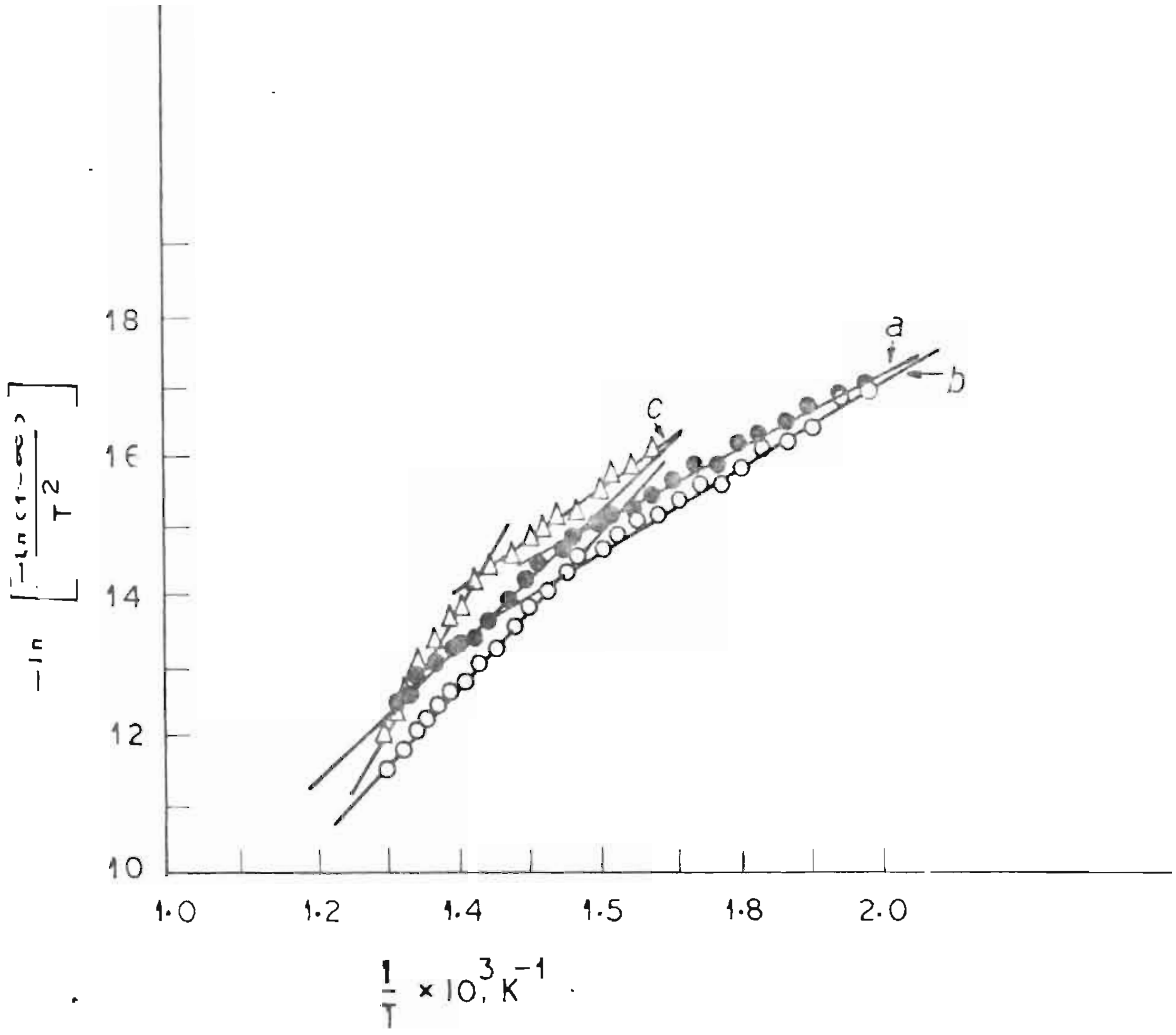


Fig. 4.7. Coats-Red fern plot for Cardanol formaldehyde (resol)-PMMA semi-IPNs containing,

a. 90·0 % PMMA.

b. 83·3 % PMMA.

c. 44·0 % PMMA.

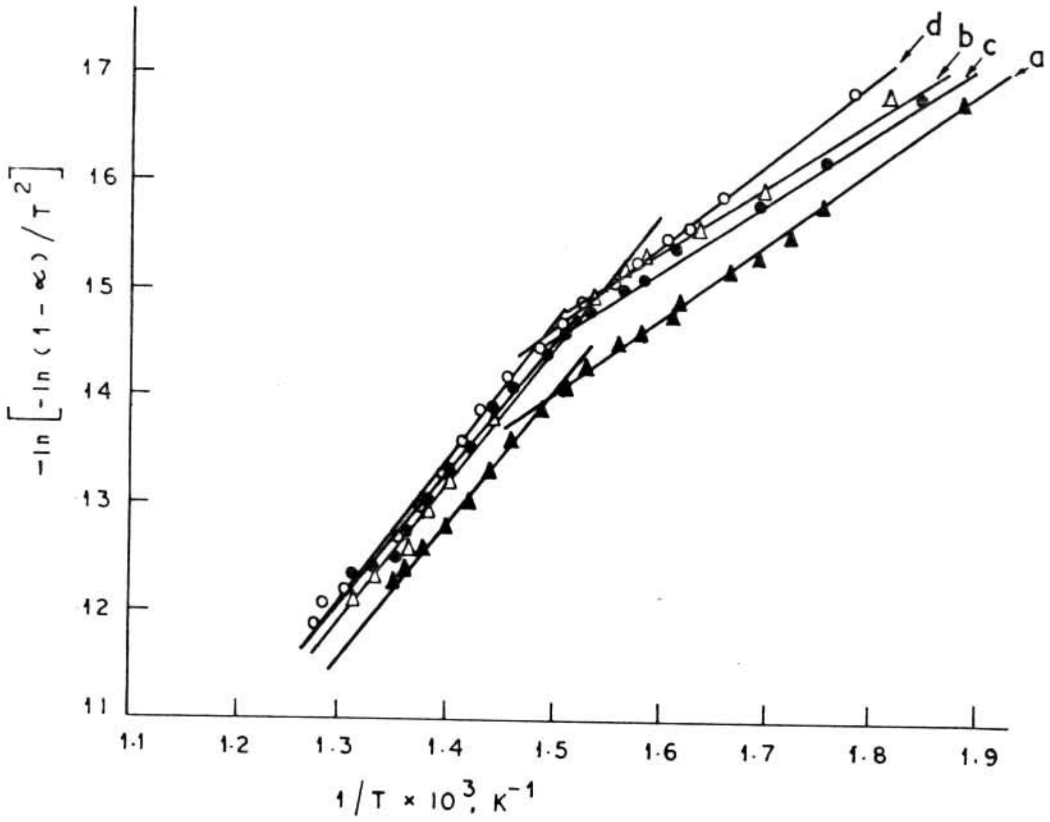


Fig. 4.8. Coats Redfern plot for cardanol formaldehyde (novolac)-PMMA semi-IPNs containing

a. 87.5 % PMMA.
b. 83.3 % PMMA.
c. 75.0 % PMMA.
d. 50.0 % PMMA.

TABLE 4.5 ACTIVATION ENERGY (E) FOR THE THERMAL DECOMPOSITION OF CARDANOL-FORMALDEHYDE — PMMA SEMI-IPNs.

Semi IPN composition		E (KJ/mole) for first stage (200-400^{o}C)	E(KJ/mole) for second stage (400-500^{o}C)
% Cardanol-formaldehyde	% PMMA		
Resol			
10	90	48.55	88.30
16.7	83.3	44.90	90.14
25	75	43.05	92.09
62.5	37.5	55.16	111.81
100	0	32.38	138.0
Novolac			
12.5	87.5	55.70	92.29
16.7	83.3	55.95	101.43
25	75	59.03	106.43
50	50	65.90	107.75
100	0	44.41	138.0

4.3.2 TMA studies and glass transition temperature (T_g) of the semi-IPNs

Studies on glass transition are known to provide quantitative information about the composition of the phase of IPNs. Simultaneous IPN-networks of polyurethane and polyacrylate are reported to show only one Tg intermediate in temperature to the Tg's of the component networks[53]. Frisch and coworkers attributed this to the thermodynamic compatibility of the two systems. This observation, which is in accordance with the copolymer equations for Tg, apply directly to compatible IPNs.

$$Tg = w_1 Tg_1 + w_2 Tg_2$$

where Tg_1 and Tg_2 represent glass transition temperature of polymer I and polymer II, and w_1 and w_2 are their weight fractions. An identical system of IPN studied by Klempner et al[54], where there was a difference in synthetic routes, showed two glass transitions indicating a heterophase. The Tgs were shifted inwards indicating some molecular mixing of the two polymers.

Thermomechanical analysis (TMA) is used to evaluate glass transition temperatures of the cardanol-formaldehyde - PMMA semi-IPNs. Fig. 4.9 and 4.10 show the TMA plots for cardanol formaldehyde (resol)-PMMA semi-IPNs and cardanol-formaldehyde (novolac) - PMMA semi-IPNs respectively. The Tgs deduced from the TMA plots are tabulated in Table 4.6 and 4.7. Two Tgs are shown for all the semi-IPN samples studied. The lower Tg (Tg_1) corresponds to the PMMA phase and the higher one (Tg_2) corresponds to the cardanol-formaldehyde phase. The increase in Tg_1 with increasing PMMA content for the cardanol-formaldehyde (novolac) - PMMA system indicates improved interaction between the phases on increasing PMMA content. However, the increasing Tg for the cardanol-formaldehyde (novolac) phase (increasing from 128 to 144°C) is an unusual phenomena. The reported trend on Tgs suggests the glass transition temperatures to lie between the individual Tgs of homopolymers. Cardanol-formaldehyde (novolac) homopolymer has a Tg only 128°C, which increases to 144 for 12.5 cardanol-formaldehyde (novolac) - 87.5 PMMA semi-IPN, suggest restrictions in the segmental motion of the cardanol-formaldehyde (novolac) chains brought about by mixing with another rigid polymer system like PMMA.

A similar trend is observed for the cardanol-formaldehyde (resol) PMMA semi-IPNs as far as the Tg_2 is concerned. There appears to be not much change in the Tg of the PMMA phase in this case.

4.4 Conclusions

1. Cardanol-formaldehyde polymers have poorer thermal stability when compared with phenol-formaldehyde.
2. The poorer thermal stability of cardanol-formaldehyde is attributed to the facile decomposition of the C_{15}-side chain.
3. Interpenetration of cardanol-formaldehyde with PMMA influence the thermal decomposition of PMMA. PMMA decomposition is slowed down by the presence of adjunct cardanol formaldehyde chains.

4. The scavenging of radicals generated during PMMA decomposition by phenol and tertiary amino group of cardanol formaldehyde network is attributed to be the possible mechanism for the thermal stabilization of PMMA.

5. The activation energies for thermal degradation for the two systems of cardanol formaldehyde - PMMA semi-IPNs are in the range of 40 K J/mole and 110 K J/mole (for the first and second stages of thermal decomposition respectively).

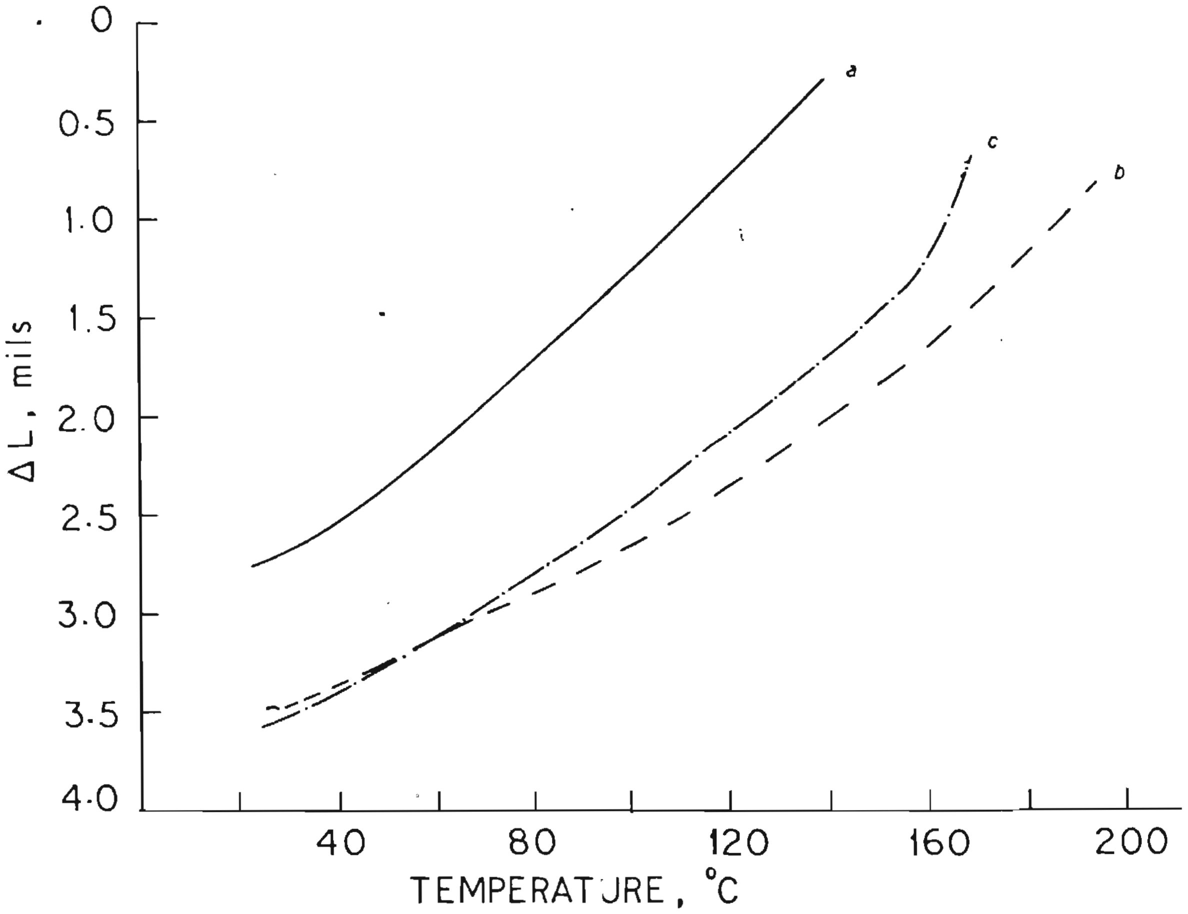


FIG. 4.9. TMA CURVES OF CARDANOL FORMALDEHYDE (RESOL)-PMMA-SEMI-IPNs CONTAINING

a. 0% PMMA b. 50% PMMA.

c. 75% PMMA.

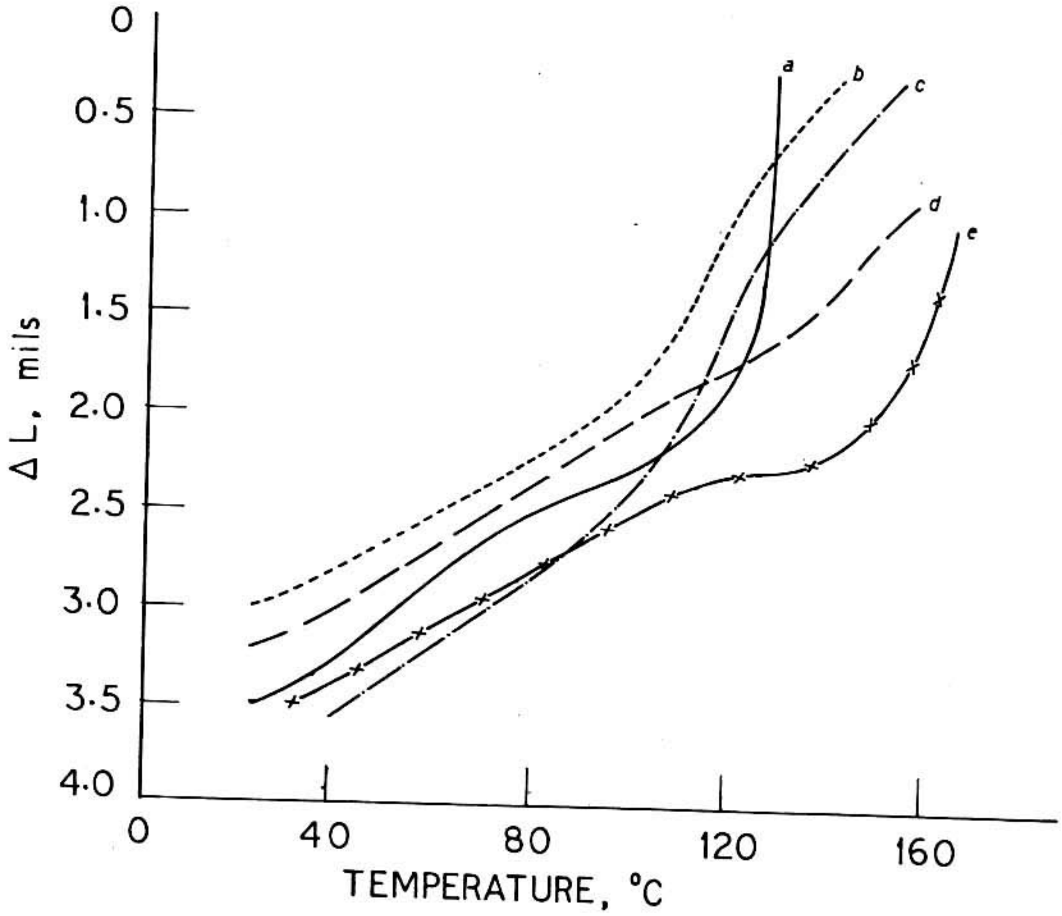


FIG. 4.10. TMA CURVES OF CARDANOL FORMALDEHYDE (NOVOLAC)-PMMA SEMI-IPN S CONTAINING

a. 0% PMMA b. 50 % PMMA

c. 75% PMMA d. 83.3% PMMA

e. 87.5% PMMA

TABLE 4.7 GLASS TRANSITION TEMPERATURE OF CARDANOL FORMALDEHYDE (NOVOLAC) - PMMA SEMI-IPNs

Semi IPN composition		Tg_1 (^oC)	Tg_2 (^oC)
novolac, resin %	PMMA %		
0	100	105	-
12.5	87.5	110	144
16.7	83.3	110	136
25	75	108	132
50	50	106	128
100	0	-	128

TABLE 4.6 GLASS TRANSITION TEMPERATURE OF CARDANOL FORMALDEHYDE (RESOL) - PMMA SEMI-IPNs

Semi IPN composition		Tg_1 (°C)	Tg_2 (°C)
resol, resin %	PMMA, %		
0	100	105	-
25	75	106	152
50	50	106	156
100	0	-	126

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CHAPTER 5

STUDIES ON POLYMERIZATION OF THE PHENOLIC COMPONENTS OF COCONUT SHELL TAR

CHAPTER 5

STUDIES ON POLYMERIZATION OF THE PHENOLIC COMPONENTS OF COCONUT SHELL TAR

5.1 Introduction

Coconut shell tar (CST) is a byproduct obtained during the distillation process of coconut shells and except for some antimicrobial uses, it was considered as a waste so far[1]. The distillation products of coconut shells are indicated in Figure 5.1 Preliminary chemical studies show that it contains about 30% phenolic substances[2,3]. Besides phenolics, CST contains crotonaldehyde, furfural, acetic acid (22%), caproic acid, p-hydroxy benzoic acid, and p-cresol[4]. The main objective of this work is to enrich the phenol content of CST and to study the polymerization behaviour of phenol enriched CST.

5.2 Experimental

5.2.1 Materials

Coconut shell tar (CST): CST was obtained from M/s. Carbo Chemicals Industries Ltd., Calicut, India, and the same was used without further purification. All other reagents used were of the AR grade and used without further purification.

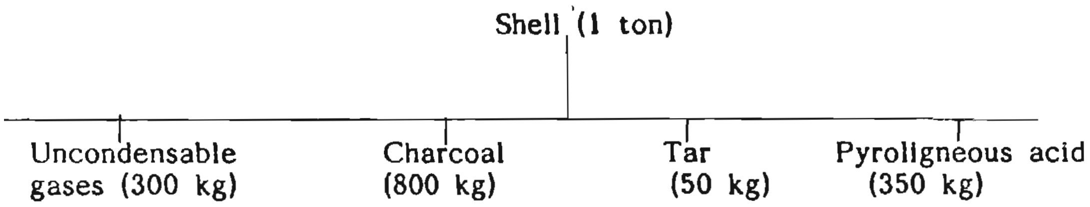
5.2.2 Methods

5.2.2.1 Synthesis

5.2.2.1.1 Enrichment of phenolic components of CST:

CST was distilled at atmospheric pressure and fraction coming out at 100°C, 103-105°C and at 118-120°C were collected. The first fraction was water (22%), the second fraction was crotonaldehyde (3%)

Fig. 5.1: COCONUT SHELL DISTILLATION PRODUCTS



and the third fraction was acetic acid (22%). The fractions were identified using standard analytical methods. The residue was refluxed with 3% sodium hydroxide for 2 hrs and neutralized with glacial acetic acid. The product was dissolved in acetone and filtered to remove free carbon. The filtrate, after the removal of acetone, was used for polymerization.

5.2.2.1.2 Synthesis of CST-formaldehyde (novolac)[5]:

A 500 ml resin kettle was fitted with a reflux condenser, stirrer and a thermometer. To the reaction vessel were added 33.8 g (0.16 mole) CST, 10.38 ml (0.128 mole) of 37% aqueous formaldehyde and 1 g (0.0078 mole) of oxalic acid. The reaction mixture was stirred and heated in a water bath at 100°C for 5 hrs. Vacuum was then applied to remove the water of condensation. The yield of the resin was found to be 97%.

5.2.2.1.3 Synthesis of phenol-formaldehyde (novolac)[5]:

130 g (1.38 mole) phenol was mixed with 92.4 g (1.14 mole) of 37% aqueous formaldehyde and 1 g (0.0078 mole) of oxalic acid dihydrate. The mixture was stirred and heated in a water bath at 100°C for 5 hrs. Vacuum is then applied to remove water of condensation and the resin was dried.

5.2.2.2 Physical and chemical characterization

5.2.2.2.1 Viscosity

The method of measuring intrinsic viscosity is described in detail in the experimental section of Chapter 2.

5.2.2.2.2 Acid value[6]

A resin sample is dissolved in 100 ml of ethanol, and titrated with 0.1 N aqueous sodium hydroxide using phenolphthalein as indicator until a pink colour persists. The acid value (in mg KOH per g) is calculated using the formula.

Acid number = $56.1\ v\ n\ /m$

where v = the volume (ml) of sodium hydroxide titrant consumed in titrating the resin sample.

n = normality of the titrant

m = weight of the resin sample, g

5.2.2.2.3 Total phenol content[7]

This method is based on the reaction of phenol to form tribromophenol in the presence of excess bromine.

A bromide-bromate solution is prepared by dissolving 10.20 g of potassium bromide and 2.80 g of potassium bromate in water and solution is diluted to 1 litre and mixed thoroughly. An accurately weighed sample containing .02 to 0.03 millimoles of phenol is introduced into a 125 ml iodine flask and if the sample is water soluble, it is dissolved in 5 ml water. If it is not soluble in water, then a 2% sodium hydroxide solution is to be used. 5 ml of the bromide-bromate solution is added by a pipette, followed by the addition of 5 ml of water and the flask is wrapped with aluminium foil. The flask is then swirled and 2 ml of 1 : 1 hydrochloric acid is introduced quickly. The flask is stoppered and vigorously shaken and is allowed to stand for 15 minutes in the dark. Then the aluminium foil is removed, 10 ml of 20% potassium iodide is added to the iodine flask and also 3 ml of water. The stopper is replaced and the flask is shaked vigorously for 3 seconds. 2-3 ml water is further added to this and is titrated against 0.1 N sodium thiosulphate solution with starch as the indicator.

$$\text{Phenol \% by wt} = \frac{(B-A)\ N \times M_w \times 100}{100 \times W \times n}$$

A = vol. of sodium thiosulphate used for sample titration in ml

B = volume of sodium thiosulphate used for blank titration in ml

N = Normality of sodium thiosulphate

M_w = gram molecular weight of phenol

W = sample weight, g

n = Number of bromine atoms substituted in 1 phenol molecule

5.2.2.2.4 Free carbon

A definite weight of the resin is dissolved in acetone and filtered using a previously weighed sintered crucible (G_3). The residue is washed with acetone till washings are colourless. The crucible is dried in the oven to remove acetone, cooled and weighed to constant weight.

$$\text{\% of free carbon} = \frac{(W - M) \times 100}{n}$$

W = Weight of crucible + residue

M = Weight of empty crucible

n = Weight of the resin

5.2.2.3 Mechanical properties

5.2.2.3.1 Preparation of specimen for lap shear test

CST-Formaldehyde (novolac)

2 g (0.009 mole) of the novolac resin obtained from CST was mixed with 0.016 g hexamine (0.001 mole). The mixture was dissolved in acetone and the resin was placed between two plywood pieces and hot pressed at 130°C for 1.5 hours using a hand press at a pressure of 69 to 138 kg/cm^2. A series of samples were prepared by varying the solid content and open tack time.

Phenol-formaldehyde (novolac)

Phenol-formaldehyde polymer was also worked out as in the case of cardanol-formaldehyde (novolac) system.

5.2.2.3.2 Mechanical testing

Shear strength[7]

Shear strength was measured using an Instron Universal Testing Machine (Instron Model 1195) at a cross-head speed of 20 mm/min. The specimens are placed in the grips so that outer 25 mm of each end are in contact with the jaws and long axis of the test specimen coincides with the direction of applied pull through the centre line of the grip assembly. The loading is applied and continued till failure. The load at failure is the shear strength expressed in kg/cm^2 of shear area.

5.2.2.4 Electron Microscopic studies

Scanning Electron Microscope (SEM)

SEM photographs were taken using a JEOL 35 C Microscope.

5.3 Results and Discussion

Tabel 5.1 shows the results of the preliminary examination of CST, phenol enriched CST and the CST-formaldehyde resin. The phenol enrichment of CST is carried out by distilling off the crotonaldehyde, acetic acid and water components as is described in the experimental. The product analysis after phenol enrichment thus indicates reduction in acid value (63.59 to 15.503 mg KOH/g) and loss of other ingredients like crotonaldehyde and water is reflected in the improvement in the phenol content (from 35% to 45%). The phenol enriched CST still contains a solid free carbon content of about 6.5% and this is removed by dissolving the product in acetone and filtering off the free carbon. The phenol content of the carbon free, phenol enriched-CST is estimated to be 51.5%. The flow diagram for the process of phenol enrichment of CST is given in Figure 5.2.

The phenol enriched CST, having a phenol content of 51.5%, is heated with formaldehyde and oxalic acid to obtain phenol enriched CST-formaldehyde resin. In an identical treatment pure phenol was also converted into phenol formaldehyde for comparison purposes. The intrinsic viscosity of CST-formaldehyde resin in acetone at 30°C was determined to be 0.025 dl/g whereas the corresponding value for phenol-formaldehyde was 0.035 dl/g. Figures 5.3(a) and 5.3(b) show the SEM surfaces of the uncured CST-formaldehyde and phenol formaldehyde resins, respectively. The SEM surfaces appear to be similar in nature. The CST-formaldehyde and phenol-formaldehyde resins were cured by heating with hexamine at 130°C. When the CST-formaldehyde resin was placed between two wood pieces and hot pressed, good adhesion was indicated. The shear strength of the resin was measured using an Instron Testing Machine. The comparative evaluation of the adhesive property of cured CST-formaldehyde and ured phenol formaldehyde resin are given in Table 5.2. Fig. 5.4. shows a plot of shear strength against open tack time for CST-formaldehyde resin with 13.8% and 27.7% solid contents. At a solid content of 13.8%, the maximum shear strength obtained was 9.46 kg/cm^2 at an open tack time of 45 seconds and the corresponding values at 27.7% solid content were 7.13kg/cm^2 and 60 seconds.

The shear strength values indicate the phenol-formaldehyde resin to have almost double the values in comparison with that of CST-formaldehyde resin. Figures 5.5(a) and 5.5(b) give the SEM photographs of the

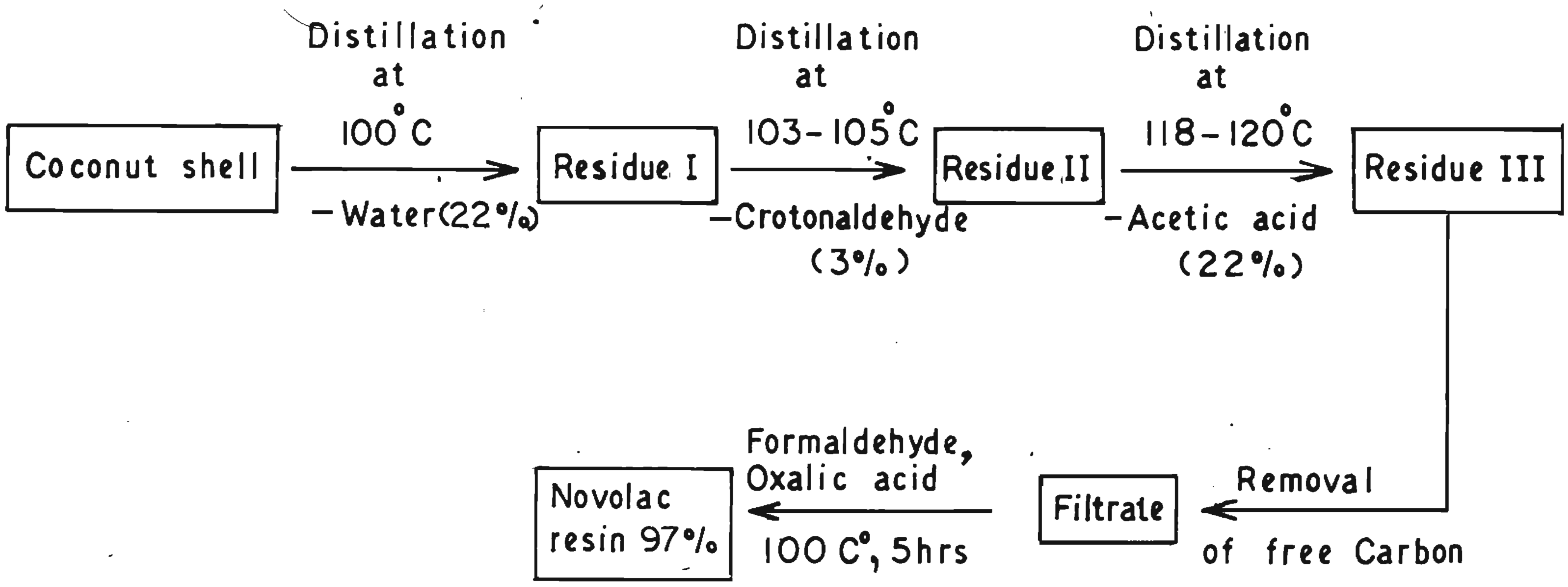


Fig 5.2 Flow sheet for the enrichment of the phenolic component of Coconut shell Tar

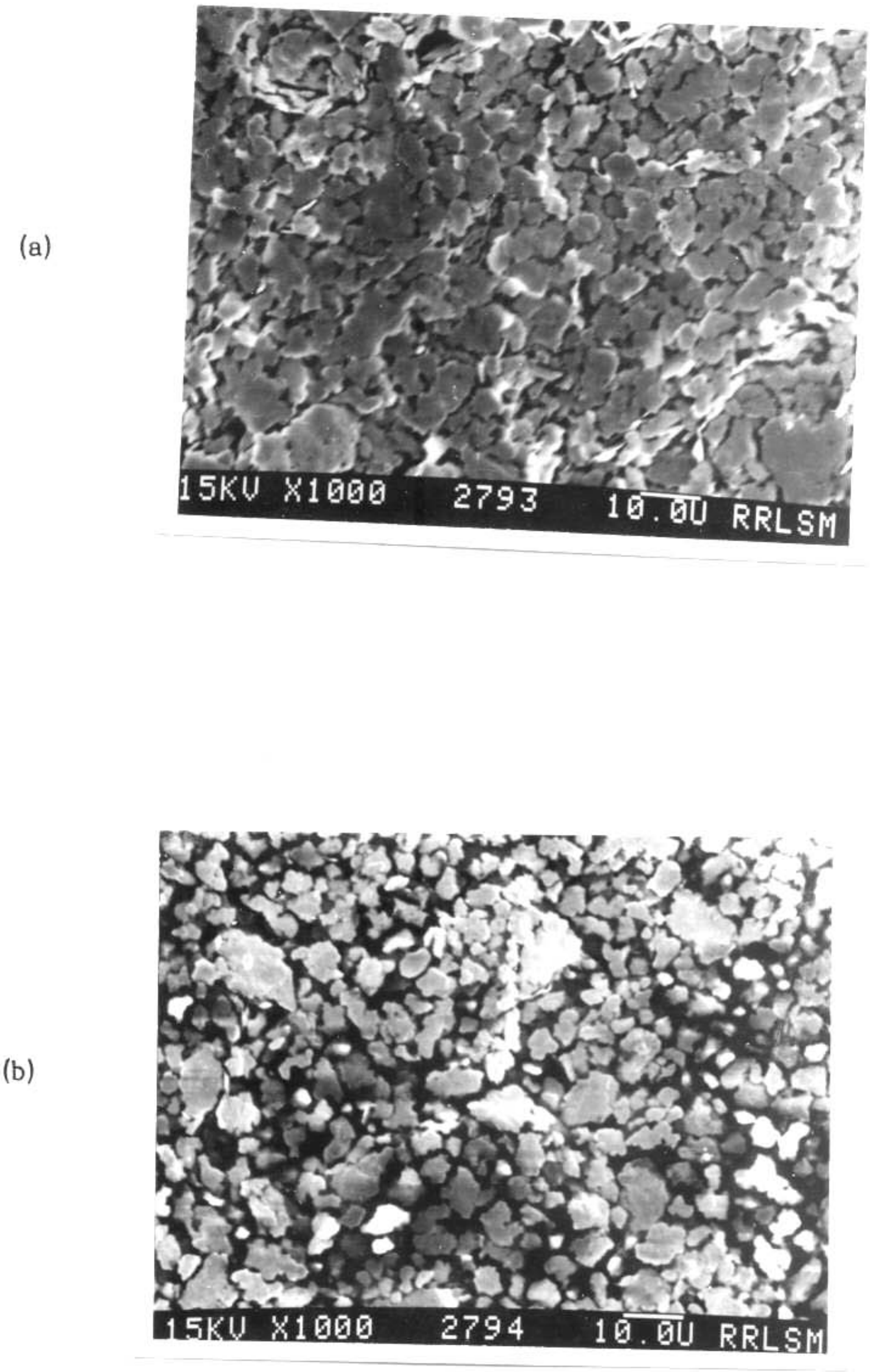


Fig. 5.3 SEM photographs of the uncured polymer obtained from
(a) CST-formaldehyde resins, and
(b) phenol-formaldehyde resins

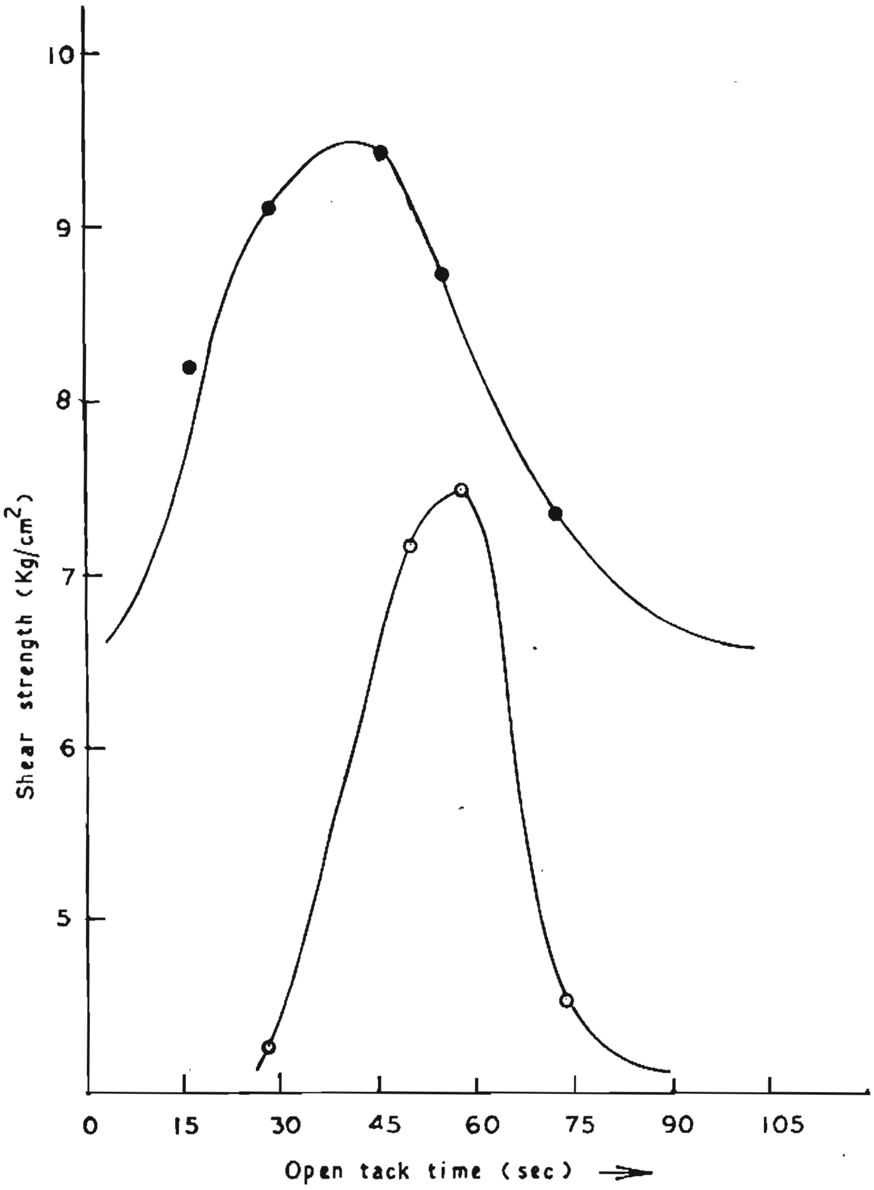


Fig 5.4 Plot of shear strength against open tack time.

●—● Solid content 13·8%

○—○ Solid content 27·7 %

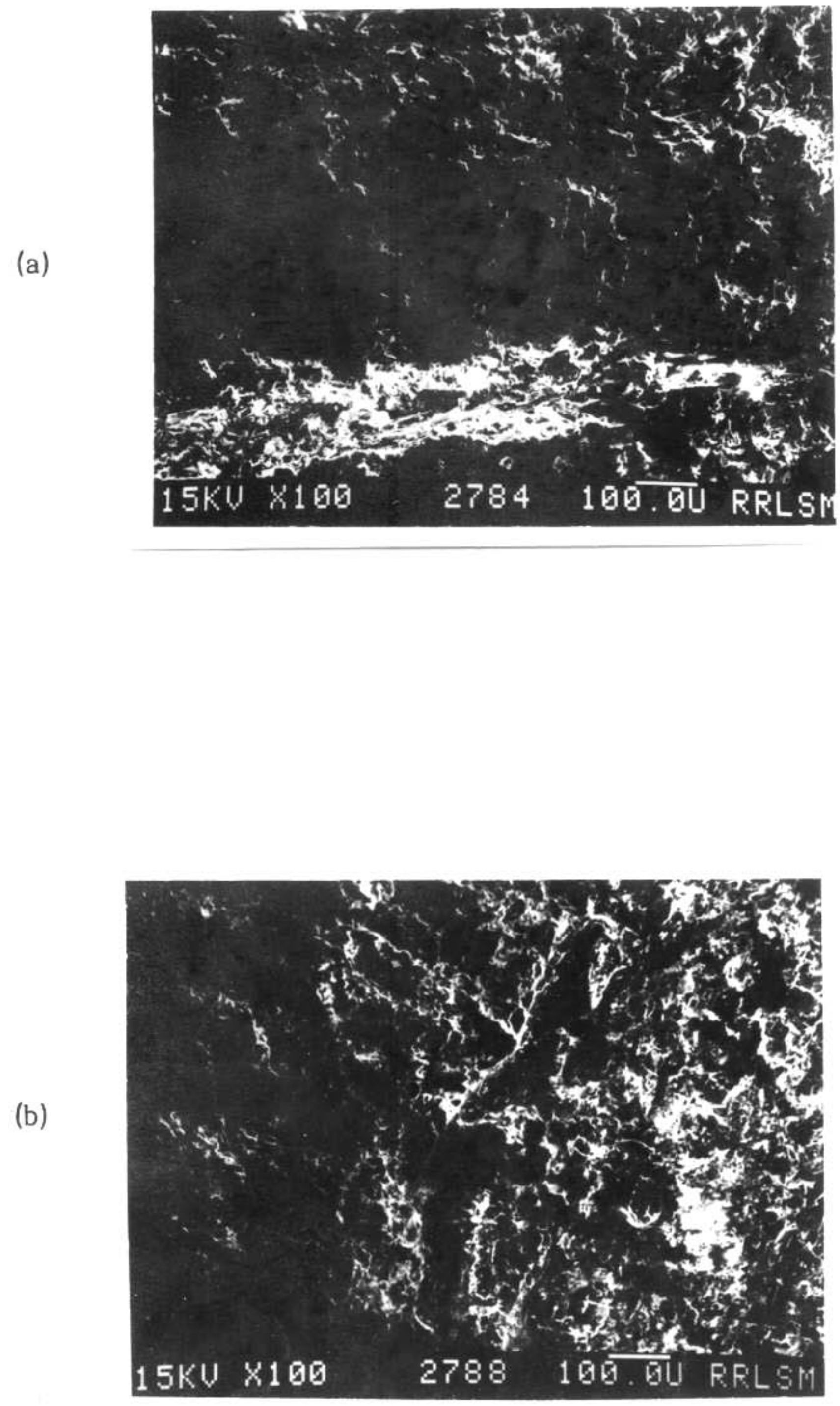


Fig. 5.5 SEM photographs of the fractured surface obtained after the lap shear test of (a) CST-formaldehyde resin, and (b) phenol-formaldehyde resin.

TABLE 5.1: PHYSICAL AND ANALYTICAL DATA

	CST	Phenol-enriched CST	CST-formaldehyde resin
Acid value, mg KOH/g	63.59	15.503	20.62
Total phenol content, %	35	45	-
Free carbon, %	1.57	6.5	-
Density g/cc	1.178	-	1.2995

TABLE 5.2: COMPARISON OF THE SHEAR STRENGTH VALUES OF CST RESIN AND PHENOL-FORMALDEHYDE RESIN

System	Solid content (%)	Open tack time (sec)	Shear strength (kg/cm^2)
CST-formaldehyde resin	13.8	45	9.46
	27.7	60	7.13
Phenol-formaldehyde resin	13.8	60	23·25
	27.7	60	16.74

fractured surfaces of CST and phenolic resin respectively (lap shear test samples). The photographs suggest that both the samples got fractured in a similar pattern though there is a large difference in strength properties.

It is apparent from these results that the strength of CST resin is only just half of that of phenol-formaldehyde resin. But it had been indicated early that CST contains a large number of components and only the major non-polymerizable components like water and acetic acid are removed. The system still contains other ingredients in small amounts which may give rise to bond weakening effects or which may form weak boundary layers weakening the adhesive bond. In addition the molecular weight build up during the formaldehyde condensation could also be lower in the case of CST due to the presence of impurities.

5.4 Conclusions

1. Though the shear strength of CST resin was about half of that of phenol-formaldehyde, the polymer could be of use for adhesive applications where the strength requirements are of that order.
2. CST being much cheaper compared to phenol, its adhesive material with improvement would provide useful end product.
3. The work also indicates the possibility of using CST as a phenolic source.

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SUMMARY

The theme of this thesis is to find out and evaluate renewable resources for polymers. The polymerization characteristics of two such monomers namely, cashewnut shell liquid (CNSL) and coconut shell tar (CST) are studied and the properties of the polymeric products are described.

A review in the available biomonomers for polymerization along with literature survey in CNSL and CST constitutes the first Chapter.

The second Chapter describes oligomerization of cardanol - the major component of CNSL - using various acidic catalyst systems like diethyl sulphate - sulphuric acid, diethyl sulphate - phosphoric acid and boron trifluoride - etherate. The products are characterized using IR and NMR spectroscopy and gel permeation chromatography. The kinetics of some of the oligomerized systems is also studied using GPC analysis. NMR studies of oligomerization revealed the possibility of the aromatic nuclei also to involve to some extent in the oligomerization reactions in addition to the oligomerization through the double bonds in the side chain of cardanol.

Semi interpenetrating networks of cardanol-formaldehyde (novolac and resol) with poly(methylmethacrylate) (PMMA) are synthesized. The synthesis and mechanical properties of the semi-IPNs are described in Chapter 3. The semi-IPNs do not show any dramatic improvement in the mechanical properties of cardanol formaldehyde. Semi-IPNs based novolac

systems show marginal increase in tensile strength only after the addition of more than 50% PMMA.

Thermal analysis (TG, TMA) of cardanol-formaldehyde (novolac and resol) and cardanol-formaldehyde - PMMA semi-IPNs are described in Chapter 3 and are evaluated in Chapter 4. TG analysis indicate that cardanol-formaldehyde system is less thermally stable in comparison with phenol-formaldehyde system and this decreased thermal stability is attributed to the presence of the C_{15} - side chain in the aromatic nuclei. Thermal stability studies of semi-IPNs suggest that cardanol-formaldehyde resins impart thermal stability to PMMA. A possible mechanism for this enhanced thermal stability of PMMA is that the phenolic group of cardanol-formaldehyde scavenge the radicals generated by PMMA degradation. Kinetics of thermal degradation of these semi-IPNs are also given. Glass transition temperature of these semi-IPNs are determined from the TMA curves.

Chapter 5 deals with the enrichment of phenolic components of coconut shell tar. The shear strength properties of phenol enriched coconut shell tar - formaldehyde are compared with that of phenol-formaldehyde.

Polymeric Resin from Renewable Resources: Studies on Polymerization of the Phenolic Component of Coconut Shell Tar

Today there is much discussion on the utilization of renewable resources for polymer applications. This is partly due to the recognition that the supply of petroleum and coal is limited and that the cost of petrochemicals is on the increase. Thus, biomass which consists mostly of polymers and monomers of natural origin offers itself as a suitable renewable resource. A good number of reviews and research papers have already come up indicating their importance.[1-5]

Materials based on the coconut tree form a major renewable resource of the tropical regions of the world.[6] Of these materials, the coconut shells are available to the tune of about 4.2 million tons per year.[6] The shells on destructive distillation give (see Fig. 1) coconut shell char, which is used as a filler in plastics and for the development of activated carbon. Coconut shell tar (CST) is a byproduct obtained during the distillation process and was considered as a waste so far. The CST is a tarry oil, dark brown in color with a characteristic unpleasant empyreumatic odor. Except for some identification of the components, not much work has been done on it. It is reported to contain many monomers, the major one being phenolic in nature.[7] This paper deals with the enrichment and polymerization of the phenolic components of CST.

EXPERIMENTAL

Materials and Methods

CST was obtained from M/s. Carbo Chemicals Industries Ltd., Calicut, and the same was used without further purification. Phenol (GR) and formaldehyde (AR) were obtained from Glaxo Laboratories. Acetone (GR), oxalic acid (GR), sodium hydroxide (GR), and hexamethylene tetramine were obtained from Sarabhai M. Chemicals.

Isolation and Separation of Phenolic Components of CST

CST (100 mL) was distilled at atmospheric pressure, and fractions coming out at 100°C, at 103–105°C, and at 118–120°C were collected. The first fraction was water (22%), the second fraction was crotonaldehyde (3%), and the third fraction was acetic acid (11%). The residue was refluxed with 3% sodium hydroxide for 2 h and neutralized with glacial acetic acid. It was dissolved in acetone and filtered to remove free carbon. The filtrate, after the removal of acetone, was used for polymerization.

Polymerization

A two-stage Novolak resin (P:F mol ratio = 1:0.8) was prepared from CST. A 500-mL resin kettle was fitted with a reflux condenser, stirrer, and thermometer. To the reaction vessel

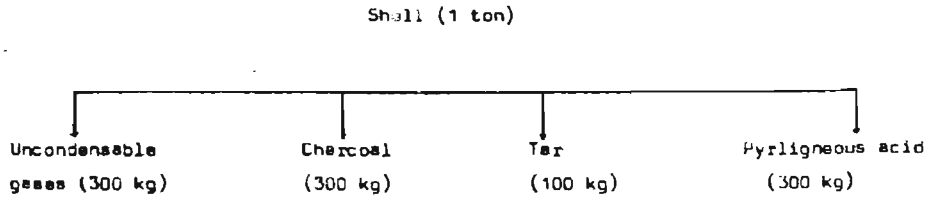

Fig. 1. Coconut shell distillation products.

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was added 33.8 g (0.16 mol) of CST, 10.38 mL of 37% aqueous (0.128 mol) formaldehyde, and 1 g of oxalic acid. The reaction mixture was stirred and heated in a water bath at 100°C for 5 h. Vacuum was then applied to remove water of condensation. The yield was found to be 97%. The resin thus obtained was soluble in acetone and alkali. It was cured by mixing with hexamine (0.8%) and then hot pressing at the pressure of 1000–2000 lbf/in.^{2} at 130°C for 1.5 h. Viscosity measurements of the polymer were carried out using a ubbelohde viscometer at 30°C.

Mechanical Testing—Lap Shear Test

Lap Shear test of the Novolak resin was carried out according to ASTM standard D 1002.* A solution of the resin and hexamine in acetone was applied between two plywood pieces each of length 3.5 in. and thickness 0.06 in. (area of overlap was 1 in.^{2}) cured at 130°C (curing time 1.5 h) and shear strength was measured using an Instron Testing Machine at a crosshead speed of 20 mm/min.

Scanning electron micrographs were taken using a Jeol 35 C Microscope.

RESULTS AND DISCUSSION

Results of the preliminary examination of CST, the phenol enriched CST and the Novolak resin is given in Table I. The total phenol content after distillation was raised from 36% to 45% and after the removal of free carbon to 51.5%. Figure 2 gives the data on the process of enriching the phenol in CST. The intrinsic viscosity of the Novolak obtained was 0.025 dL/g whereas the corresponding value for phenol formaldehyde resin prepared under the same condition was 0.035 dL/g. Figures 3(a) and (b) show the SEM of the surface of the uncured resin of CST and phenol, respectively, and appear to be similar in nature.

The Novolak obtained from CST on curing with hexamine at 130°C gave a hard product. When the resin was placed between two wood pieces and pressed, good adhesion was indicated. Pending the development of the final formulation, only open tack time and lap shear were measured in this case. Shear strength obtained through lap shear experiment (according to ASTM D 1002) using the Instron Testing Machine gave a comparatively good idea about the strength property of the CST resin. The shear strength of CST resin was measured at solid contents of 13.8% and 27.7% with varying open tack time (Fig. 4). At 13.8%, CST resin showed a maximum opentack time of 45 s and shear strength of 94.55 N/cm^2. At 27.7% corresponding values were 60 s and 71.30 N/cm^2. These results are compared with that of a P–F resin under similar condition (Table II).

The SEM photographs of the fractured surface of CST and phenol resin (lap shear test samples) indicate that both the samples have gotten fractured in a similar pattern, though the shear strength of the latter is about double that of the former [Figs. 5(a) and (b)].

It is apparent from these results that the strength of the CST resin is only just half of that of P–F resin. It has been indicated early that CST contains a large number of components and only the nonpolymerizable and major components like water and acetic acid are removed. The system therefore contains other ingredients in small amount, which may give rise to bond weakening effects or which may form weak boundary layers weakening the adhesive bond.

TABLE I
Chemical and Physical Analytical Data

	CST	Phenol-enriched CST	CST Novolak resin
Acid value	63.59	15.503	20.62
Total phenol content (%)	35	45	—
Free carbon (%)	1.57	6.5	—
Density (g/cc)	1.178	—	1.2995
Intrinsic viscosity (dL/g)	—	—	0.025

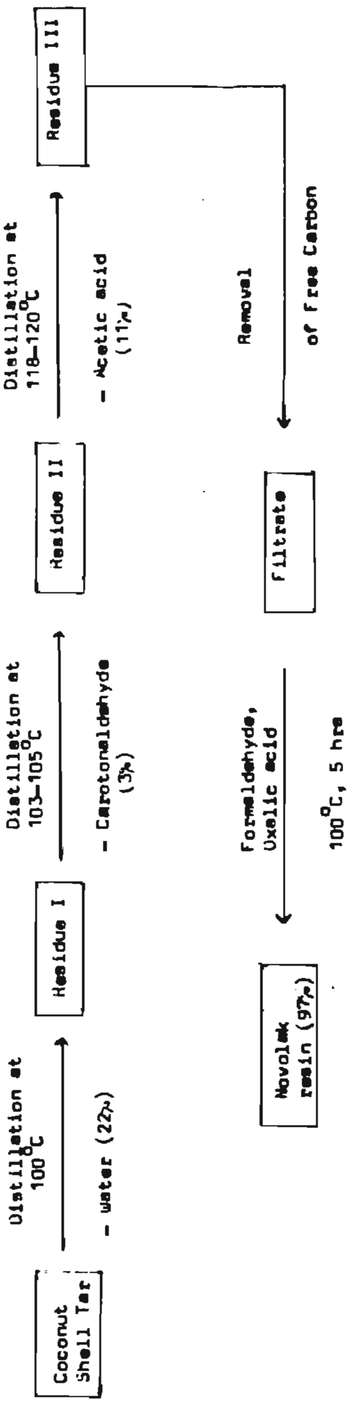
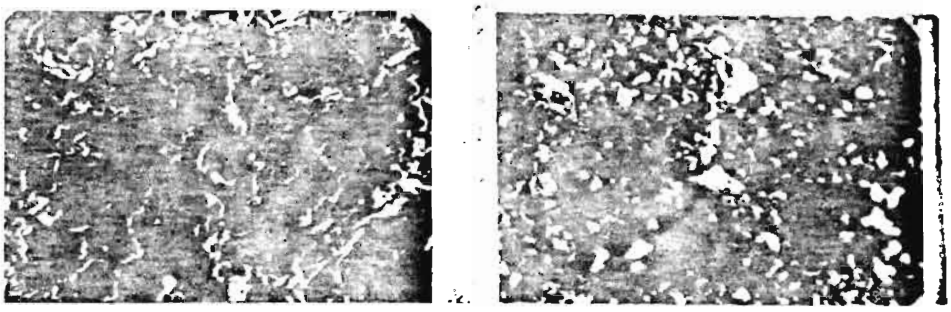


Fig. 2. Flow sheet for the enrichment of the phenolic component of coconut shell tar.



(a) (b)

Fig. 3. SEM Photographs of the surface of the uncured polymer obtained from (a) CST and (b) phenol-formaldehyde.

The system therefore needs further purification of phenol content of CST to remove the bond weakening substances. The present work, however, indicates the possibility of utilization of CST and similar materials as a source of phenol.

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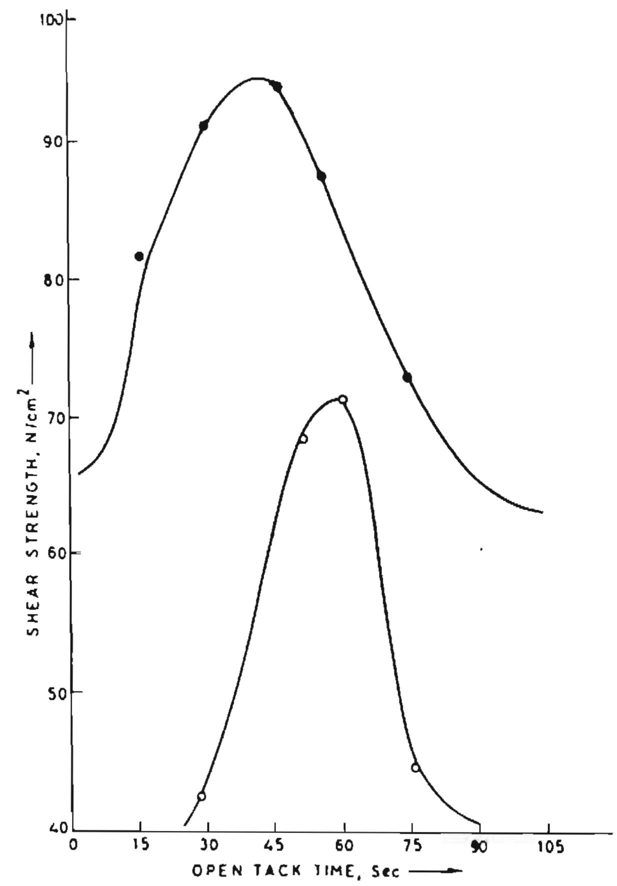

Fig. 4. Plot of shear strength against open tack time: (●) solid content 13.8%; (○) solid content 27.7%.

TABLE II
Comparison of the Shear Strength Values of Coconut Shell Tar Resin with That of Phenol Formaldehyde Resin

	Solid content (%)	Open tack time (s)	Shear strength (N/cm²)
CST resin	13.8	45	94.55
	27.7	60	71.30
PF resin	13.8	60	232.50
	27.7	60	167.40

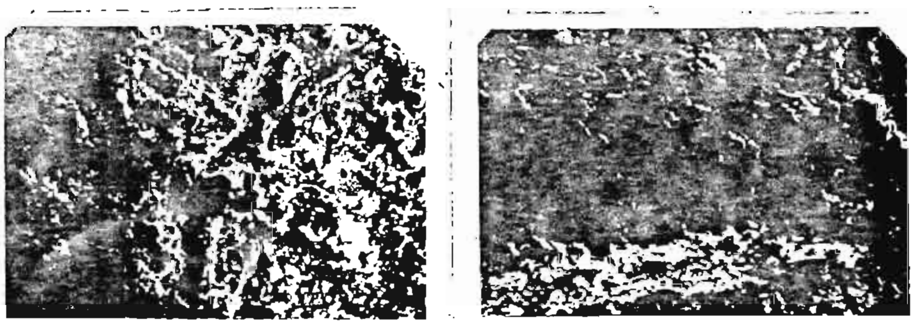
(a) (b)

Fig. 5. SEM Photographs of the fractured surface obtained after the lap shear test of (a) CST resin and (b) phenol–formaldehyde resin.

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Feature Article

Naturally Occurring Organic Bio-Monomers as Possible Future Sources for Polymers

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Abstract

There exists a number of naturally occurring organic biomonomers which would be of potential use as possible future sources of monomers for polymer production. Some of these monomers have already been polymerized and used as resins, adhesives, paints, etc. The potential of a good number of them has not yet been explored. This review gives a brief overview of such biomonomers that could be polymerized through well established polymerization techniques and their properties and uses established.

Keywords

Renewable resources, biomonomers, polymerizability, alternate feedstock

Introduction

After the 1973 oil embargo, there has been much thinking on the future availability of petrochemicals at comparatively reasonable price. Since more than 90 % of polymers depend on petrochemicals for their resources, the cost advantage of polymeric materials over the conventional materials such as metals and ceramics has been of late much eroded by the increase in the price of oil and gas (1). Though there is now a downward trend in the price of oil, it may not necessarily affect the price of petrochemicals and related products. Oil and gas as a feed stock are not renewable and one day sooner or later it will dry out. This has prompted research activities all over the world to find alternative feed stocks for polymers. One of such main alternative resources is the renewable resources or biomass. Ranging from algae to wood, its availability is limited only by the photosynthetic efficiency of plant (2).

Biomass is generally constituted of polymers, oligomers, monomers and other nonpolymerizable simple organic compounds including metallic salts and complexes. Polymers are, of course, the major components. However, there are a variety of monomeric components that exist free or in combined form in plant materials. For example, when plant tissues are extracted with non-polar solvents, the polymeric constituents such as lignin, carbohydrate polymers, proteins and nucleic acids are separated (1). The soluble portion contains, for example lipids, oils, fatty acids, waxes, triglycerides, terpenes, prostaglandins, steroids etc. There is ample literature on the nature, structure and properties of the polymeric constituents. But the literature on the monomeric constituents of biomass materials is scattered and no organized body of data exist. This paper, therefore, aims to collect and codify the available data on monomeric constituents of biomass. This is however, not exhaustive but an attempt has been made here to point out the significance of the unexploited areas. Some of the monomers have, in fact, (for example, furfural, diterpene etc.) been well utilized. Monomers that are obtained by cleavage, depolymerization and degradation are not considered here.

Naturally Occurring Monomers: Classification

In general, naturally occurring organic polymers are classified into the following groups: Hydrocarbon polymers (Natural rubber, guttapercha etc.), carbohydrate (Starch, Cellulose etc.), polyphenolic compounds (lignin and other polyphenols), proteins and nucleic acids (3). Monomers associated with the above polymers can be found free in nature, though it cannot be taken as a general rule (for e.g., though natural rubber is polyisoprene, the plant does not produce isoprene, the monomer as such). However, a preliminary survey indicated the availability of innumerable

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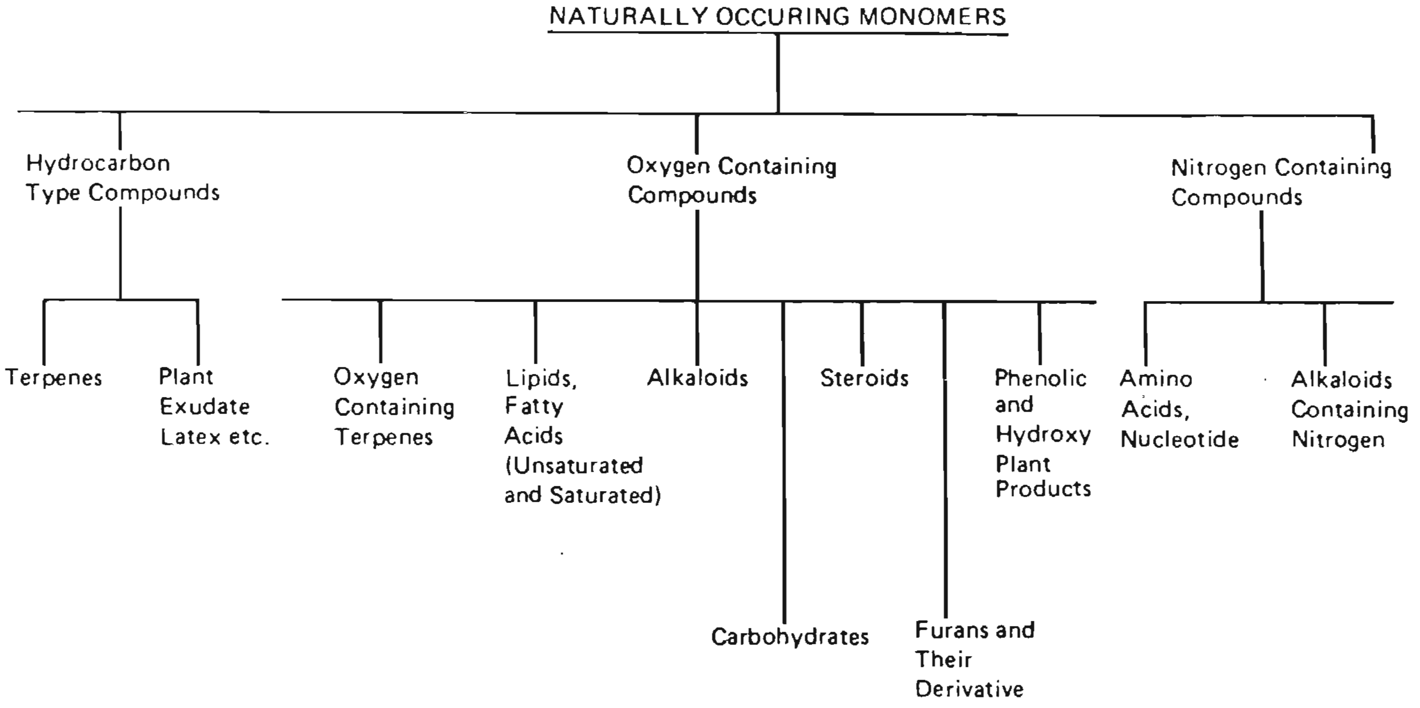

FIGURE 1

number of monomers from various sources such as alkaloids, terpenes, lipids, fatty acids, amino acids etc. For the sake of clarity the naturally occurring monomers have been classified as shown in Figure 1. However, all these compounds cannot be considered monomers and only those that have more potential in terms of polymerization are discussed. The following discussion is organized into subgroups and only those that are considered more potential in terms of polymerization are discussed. Compounds whose functionality is more than one is considered a potential monomer but actual polymerization may depend on many factors. For example, steric hindrance may inhibit a potential monomer from polymerization.

Methods of Polymerization and Applications

It should be noted that some of the naturally occurring monomers have already found applications in the polymer field. The monomer can either be modified to other suitable monomers or can be polymerized directly into a useful polymer. An example of the latter is furfural which acts as a precursor to hexamethylene diamine and adipic acid, the latter two utilized to form nylon-6,6 (1). Furfural or its derivatives are known to be utilized for the production of phenolic resins (4).

Another example of modification is the dry distillation of castor oil to get sebacic acid, a monomer for the production of nylon (5). Another example is that of terpene resins polymerized from terpene such as α-pinene. Terpene resins have found use as pressure sensitive adhesive, coating etc. (6). Natural oils such as linseed oil, tung oil etc., have formed the basis for paints (drying involves an oxidative polymerization at the double bonds leading to a crosslinked network) (7). The alkyd resins can also be considered in this case, although they are partly synthetic (8).

Since the methods of polymerization and characterization of polymers are now well established (9, 10), a detailed discussion on it is out of place here. The application of a particular polymerization technique generally depend upon the structure of the monomer. For example a monomer having two or more functional groups such as -hydroxyl, -carboxyl, -amino etc., can undergo what is generally known as condensation polymerization (11). When unsaturated bonds are available, chain reactions can be initiated by appropriate catalysts called initiators (12). Table 1 provides the list of naturally occurring monomers which have already been polymerized and used commercially. Table 2 provides probable methods of polymerization of naturally occurring monomers which have not been attempted for polymerization. Possible applications from the point of view of the structure of the monomers are also envisaged. A brief discussion of the commercially used polymers made from biomonomers is also discussed as given below:

1. Fatty acids polymers;
2. Terpene resins;
3. Furfural polymers.

1. Fatty Acids Polymers

Dicarboxylic acids: The industrially important polyesters and alkyd resins are primarily based on phthalic anhydride (coating resins) and terephthalic acids (fibers). These are modified in certain cases with an aliphatic dicarboxylic acid say, adipic acid, to improve flexibility.

Dicarboxylic acids react with polyols and polyamines to give polymeric materials useful in the manufacture of plastics and resins. The polyesters are prepared by the reaction between dicarboxylic acids like adipic acid with various glycols like ethylene glycol, diethylene glycol etc. The resulting elastomers exhibit high tensile strength, excellent aging

TABLE 1. POLYMERIZATION METHODS USED IN POLYMERIZING NATURALLY OCCURRING MONOMERS

Monomer	Source	Sample Polymerization Techniques
1	2	3
Myrcene (15)	Turpentine oil	Polymerized using silica gel, synthetic magnesium or aluminum silicate (16, 17).
Ocimene (15)	Essential oil of Ocimum basilicum	Polymerized using silica gel, fuller's earth, or artificial silicate of metals of group 2 or 3 of the periodic table (16).
Nerol (18)	Neroli and bergamot oil	Polymerized with ethylene oxide to form water soluble perfumes (19).
Limonene (15)	Lemon, orange and bergamot oil	Polymerized with triisobutyl aluminum-monochloride to get low molecular weight polymers (20).
1:8 Terpin (21)	Essential oil of Myro carpus sylvestris	Polymerized by condensation with bis (cyclohexyl oxy) dichlorosilane and gave water repellent coating (22).
Eugenol (21)	Constituent of volatile oil of Myrtaceae and Lauraceae	When treated with $SnCl_4$ polymers with molecular weight of the order of 2000 are formed (23).
Car-3-ene (15)	Turpentine oil, Swedish pine needle oil.	Polymerized by mixing with anhydrous $AlCl_3$, when mixture of dimer, higher polymers and tetramer are formed (24).
α-Pinene (15)	Coniferae, oil of Turpentine	Polymerized using $AlCl_3$-dibutyl tin chloride catalysts (25).
β-Pinene (21)	Coniferae, oil of Turpentine	Polymers are prepared by initiation with high energy radiation, free radical catalyst & cationic catalysts (25).
Camphene (18)	Oil of orange and lemon	Polymerized in gasoline solvents in presence of hydrogen fluoride below 30°C (26).
Citronellol (18)	Rose and Lemon oil	Condensed with ethylene oxide to give water soluble perfumes (19).
Abietic acid (15)	Oleoresin of P. paulstris	Esters are prepared by refluxing poly-glycerol-diglycerol with resin and zinc dust and are used in varnishes (27).
Squalene (15)	Vegetable oil, olive oil and rice bran oil	Polymerized using acid clay catalyst at 200°C for 30 min. to give 56-58% polymer (28).
Citral (18)	Lemon grass oil, Mandarin oil	It is polymerized using catalysts and initiators (29).
Linalool (18)	Sweet orange, Mysore oil	It is condensed with ethylene oxide to give water soluble perfumes (19).
Crotonic acid (30)	Croton oil	It is co-polymerized with vinyl acetate using peroxide catalyst system (31).
Oleic acid (30)	Olive oil and almond oil	It is polymerized by heating a mixture of oleic acid, water, sodium hydroxide and acid activated mortmorillonite clay at 240°C kept under steam pressure of 135 lb/sq. inch (32).
Linoleic acid (30)	Fatty acid of grape seed, Tobacco seed and sun flower seed oil	It is polymerized in presence of Iron pentacarbonyl catalyst or $SnCl_4$. The polymeric fraction mainly contained dimer and a small fraction of high molecular weight polymer (33).
Linolenic acid (30)	Linseed oil, hempseed oil and perilla oil	This acid in the form of its methyl ester can be polymerized by heating at 300°C in presence of hydrogen for 6 to 10 hours and molecular weight doubled (34).
Eleostearic acid (35)	Bagilum-bang nut oil	This acid is polymerized to form elastic gel by heating (30).

TABLE 1. (CONT'D)

Monomer	Source	Sample Polymerization Techniques
1	2	3
Ricinoleic acid (36)	Castor oil, argot oil	It is used as surface active agent by condensing castor oil with ethylene oxide (36).
Succinic acid (37)	Oil, Fungi, turpentine	It is polymerized in combination with a dicarboxylic acid (38).
Glutaric acid (39)	Green sugar, beet juice	This will react with xylitol to give polyesters (40).
Adipic acid (41)	Sugar beet	It undergoes polymerization to give artificial resin, plastics and urethane. It is used in the manufacture of nylon-6,6 (38).
Sebacic acid (42)	Castor oil	It is polymerized to synthetic resin of alkyd/polyester type and also polyester rubbers and synthetic fiber of polyamide type (38).
Cinnamic acid (43)	Natural balsam, cocoa leaves, cinnamol oil	It is polymerized using uv radiation or thermal co-polymerization with styrene (44).
Tartaric acid (45)	Shizardra, Chimnsis, Tamarindus	It polymerizes in the form of its ester to give thermoplastic resins (46).
Fumaric acid (47)	Tagestes erecta	It is copolymerized with styrene, vinyl toluene, etc. to give rubbers, coatings, etc. (48).
Isamic acid (30)	Ongokea oil	It polymerizes when heating above 250°C. It is used as a drying oil (49).
Sabinic acid (30)	Juniperus sabina	It gives 11% lactone, 69% dimeric lactone, and 20% trimeric lactone when it is lactonized by boiling in benzene with $PhSO_3H$ (50).
P-aminophenyl alanine (51)	Vigina vexillata	A co-polymer of P-aminophenyl alanine and L-leucine is reported (52).
Glutamine (53)	Sugar beet, lemon	A polyamino acid can be obtained by the polycondensation of aromatic amino carboxylic acid in a solvent mixture of P_2O_5 and lower dialkyl phosphates in presence of alkaline compounds (54).
Furfuraldehyde (55)	Enteromorpha, Corncobs	It forms thermosetting resins with phenols and also used in the manufacture of coated abrasive (4).
Furfuryl alcohol (56)	Oil of cloves	This compound, water and sulphuric acid when heated to 60°C give a liquid resin of uniform molecular size (57).
β-Furoic acid (50)	Eronymus atropurpureus	It is polymerized by heating with 98% sulphuric acid and a cation exchange resin was obtained (58).
Teracacidin (56)	Tannin, exudates from woody plants	When it is heated with mineral acid, a polymeric material is formed (50).
Ascaridole (59)	Chenopodium oil	1,2- and 1,4-addition occurs with the formation of polymeric peroxides of dienes (60).
Vanillin (61)	Vanilla	It is polymerized by treating with $HS(CH_2)_6SH$ and $HS(CH_2)_{10}SH$ and reaction is catalyzed by hydrochloric acid (62).
Anacardic acid (63)	Anacardium occidentale	Methyl and ethyl esters of anacardic acid act as excellent plasticizers for chloroprene rubber and also improve the aging and elongation characteristics of cured rubber (63).
Cardol (64)	Anacardium occidentale	Derivatives of cardol are used as anti-oxidants and also monomers (65).

TABLE 1. (CONT'D)

Monomer	Source	Sample Polymerization Techniques
1	2	3
Urushiol (65)	Rhus vernicifera	High adhesion, acid and alkali resistant epoxy resin paints based on urushiol. Salts of thiophosphate esters of urushiol have been found used in lubricants and adhesives (65).
Cardanol (66)	Anacardium occidentale	Cardanol give vinyl resin which give films with excellent adhesion, flexibility, resistance to oils, grease, water and chemicals. It can be polymerized by both addition and condensation techniques and polymers have a variety of uses as surface coatings, adhesives, sealants and also has applications in brake linings, polymer composites etc. (67, 68).

TABLE 2. POSSIBLE POLYMERIZATION ROUTES FOR NATURALLY OCCURRING MONOMERS WHICH HAVE NOT YET BEEN POLYMERIZED

Monomers	Source	Polymerization Technique
1	2	3
Acronylin	Acronychia laurifolia BL	There is possibility of double bond being opened up for polymerization though there will be stearic hindrance.
Alanosine	S. alanosinieus	Self-polymerization is possible. It can also be used as a crosslinking agent due to its multifunctionality.
Anisoxide	Star anise oil	Addition polymerization could be effected but strong stearic hindrance will be there.
Betonicine	Betonica officinalis L	Condensation polymerization is a possibility.
α-Bisabolone	Chrysanthemum flosulosum L	Chain reaction polymerization is possible.
(3-Carboxy-4-Hydroxy phenyl) Glycine	Dyer's weed	Self polymerization is possible. It can be used as a crosslinking agent.
Carnavaline	Cassia carnaval speg.	Condensation polymerization with di-acids, acid chlorides, isocyanates etc. is a possibility.
Carlina oxide	Carline aeaulis L.	Addition polymerization is possible.
Chelidonic acid	Asparagus, Celandine anemone	Polyester type polymer can be prepared.
Chrysin	Pinus species	Condensation polymerization with diacids, acid chlorides, isocyanates, etc.
1,4 Cineole	Piper Cubea	Ring opening with cationic initiators like BF_3, $AlCl_3$, etc. may polymerize the compound.
Convolvulinolic acid	Convolvulacea	It can undergo self condensation to form polyesters.
Coronaric acid	Chrysanthemum coronarium	Epoxide polymers could be prepared.
Daidzein	Pueria thunbergia, Berth	Condensation polymerization with diacids, acid chlorides, isocyanates, etc. is possible.
Embelin	Embelia ribes brum	Condensation polymerization through –OH group is possible.

TABLE 2. (CONT'D)

Monomers 1	Source 2	Polymerization Technique 3
Eremophilone	Eremophila mitcheli	Chain polymerization is possible.
Eugenin	Eugenia caryophyllata	Condensation polymerization with aldehydes is possible.
Euparin	E. Cannabinum	Chain reaction polymerization is possible.
Farnesol	Flower oil of rose, Ambretta seed oil	Addition polymerization can be carried out or double bond could be epoxified and epoxy-fatty acid polymers could be prepared. The system could also be considered as IPN polymer.
Funtumine	Funtamia latifolia, Stapf	This could be suitably modified to produce diamine functional groups and it can either be used as curing agents or in the development of polyamides.
Gorlic acid	Seeds of onsoba, gorlid seed	Chain reaction polymerization is possible.
Holarrihidine	Holarrhena antidysenterica	This could be used as a monomer for polyamide system and can be used as curing agents.
Hordenine	Anhalonium species.	Aldehydes condensation is a possibility.
Jacobine	S. Jacobaca L.	Condensation polymerization will be affected through $-COOH$ group and polyesters with epoxide could be prepared.
5,6-Dehydro-kawain	Aniba firmule, kawa root	It could be polymerized by chain reaction polymerization.
Kojic acid	Aspergilli	Condensation polymerization can be carried out.
Meconic acid	Papaveracea	Polyester type polymer can be prepared.
Mimosine	Leucena glauca	Self polymerization is possible. It can also be used as a crosslinking agent due to its multifunctionality.
Morin	Calico yellow	It can be used as a crosslinking agent due to its poly-functionality and also could be considered for the development of heat resistant polymers.
Mycophenolic acid	Pencillium brevi, compactum	Addition polymerization is possible and will form oligomers.
Myrtenol	Myrtus cumunis	Ring opening polymerization is possible.
3-Methyl napthalene 1,8-diol	Diopyrosmollis	Condensation polymerization with aldehydes is possible.
Neroli diol	Neroli oil	Addition polymerization can be carried out or double bond could be epoxified and epoxy-fatty acid polymers could be prepared. The system could also be considered for IPN polymer.
O-orsellinic acid	Chaetomium-cochliodes	It can be used as a crosslinking agent.
Oryzoxymycin	S. Venezulae	Condensation polymerization through $-OH$ and $-NH_2$ group with appropriate bifunctional reagents is a possibility and probability of development of high temperature systems are envisaged.
Perillaldehyde	Perilla manlcinesis	Chain reaction polymerization can be initiated at the double bond in the side chain by normal techniques.

TABLE 2. (CONT'D)

Monomers	Source	Polymerization Technique
1	2	3
Perillene	Perilla citriodora, Makino	Chain reaction polymerization is possible though there will be stearic hindrance.
Podocarpic acid	Resin of podocarpus cupressinium	Condensation polymerization with suitable bi-functional monomers is possible. Polymers with structural rigidity can be obtained from this and can be used for high temperature applications.
Pontica epoxide	Artemisia including A. Pontica L	Further epoxidation is possible and epoxide polymer can be prepared.
Prosopine	Prosopis afficana, Taub	Condensation polymerization is possible. It can be used as a crosslinking agent.
Quercetin	Aesculus	Condensation polymerization with diacids, acid-chlorides, isocyanates etc. is possible.
5-Nondecyl. resorcinol	Wheat bran	Condensation polymerization with aldehyde systems can be carried out. Side chain will impart interval plasticization.
5-Tridecyl resorcinol	Grevillea robusta A.	Same as above.
Sabinol	Oil of Juniper	There is a possibility that ring opening polymerization can be carried out. The presence of —OH group will give hydrophilic character to the polymer.
Selinene	Celery seed oil	Chain polymerization is possible.
Selareol	Salvia Sclarea L.	Chain reaction polymerization is possible through the double bond in the side chain. Condensation polymerization also can be initiated through the —OH group.
Siamin	Casia Sianea	Condensation polymerization with aldehyde is possible.
Solacongenstidine	Solanium Congestiflorum	The presence of —OH group will allow ready modification of monomer and incorporation into polymer structure.
Stigma sterol	Calaber bean, soyabean oil	The double bond in the side chain can be opened up and polymerized. Possibility of development of rigid polymers due to condensed ring systems.
Stizolobic acid	Stizolobium hassjoo	Self polymerization is possible. It can also be used as a crosslinking agent due to its multi-functionality.
Trans- epoxy succinic acid	Aspergillus-Fumigatus	Epoxide polymers could be prepared.
Tariric acid	Tariric seed or bitter bush oil	Chain reaction polymerization is a possibility.
Vaccenic acid	Vegetable fats	Chain reaction polymerization is a possibility.
Vernolic acid	Vernonia-anthelmintica wild	Epoxide polymers could be prepared.
Verticine	Fritillaria verticillata, wild	It can be used as crosslinking agent and can also be polymerized through —OH group.
Zingiberene	Oil of ginger	Chain reaction polymerization is a possibility. High molecular weight polymers are difficult due to stearic hindrance.

characteristics and outstanding abrasion resistance (13).

Unsaturated acids: On exposure to air, these polyunsaturated fatty acids undergo complex oxidation and polymerization reactions to give crosslinks that harden the material. Polymerization of unsaturated acids result in the formation of dimers and trimers. Conjugated linoleate esters form co-oligomers with styrene with cationic catalysts. The resulting dibasic acids or esters can be condensed with ethylene amine oligomers to make reactive polyamides, useful for producing frothed epoxy compositions and as a catalyst for crosslinking rigid urethane foams (14).

2. Terpene Resins

The polymerization of terpenes can be initiated by high energy radiation, Zeigler-type catalyst, free radical and cationic catalysts. For example, α- and β-pinene are polymerized readily with cationic catalyst. Terpene monomers are copolymerized with each other to form resinous materials.

Terpene resins are thermoplastic hydrocarbon which exhibit a high degree of tackiness. Terpene resins are used in the manufacture of pressure sensitive tapes. They are also used for sizing paper and textile materials. Terpene-Phenol resins are effective heat stabilizers for high density polyethylene.

3. Furfural Polymers

The most important polymers of furfural and its common important derivatives furfuryl alcohol are based on its ability to react with phenol to form thermosetting resins in the presence of alkaline catalysts. These resins are widely used in molding compounds and also in the manufacture of coated abrasives. Furfural also reacts with ketones to form polymeric materials which are used to form resin aggregate mixture.

Furfuryl alcohol reacts with formaldehyde, urea and phenol to form soluble polymers varying from low viscosity liquids to brittle fusible solids. Because of their excellent [illegible]tence furfuryl alcohol-formaldehyde resins are used in the construction requiring chemical resistance (4).

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