

CHEMICAL MODIFICATION OF NATURAL MONOMERS AND POLYMERS

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FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN CHEMISTRY**

**BY
GEORGE JOHN**

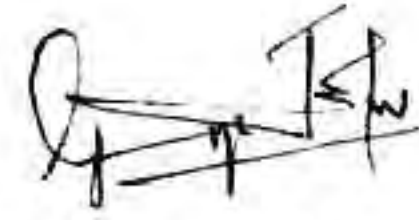
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NOVEMBER 1992

To My Parents & Teachers

DECLARATION

I, **George John**, do hereby declare that this thesis entitled **"Chemical Modification of Natural Monomers and Polymers"** is a bonafide record of research work done by me and that no part of this thesis has been submitted earlier for the award of any other Degree, Diploma, Title or Recognition.



George John

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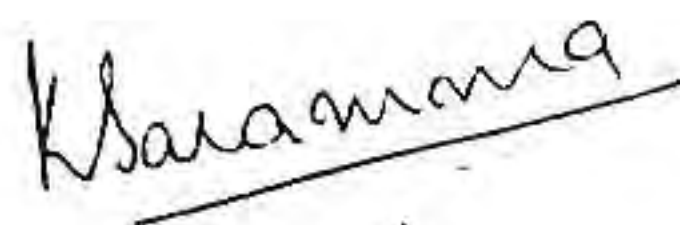
This is to certify that the thesis entitled "**Chemical Modification of Natural Monomers and Polymers**" is an authentic record of the research work carried out by **Mr. George John, M.Sc.** under our supervision in partial fulfilment of the requirements for the degree of **Doctor of Philosophy** of the University of Kerala and further that no part thereof has been presented before for any other degree.



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PREFACE

Despite the availability of a large number of well known synthetic polymers with a wide range of structures and properties, there is still a strong demand for high performance polymers. Recent developments in polymer science and technology have made available information necessary for tailormaking polymers with any desired property for any application and it can equally be applied to renewable resources to bring out modifications in their structures and properties. This has given rise to a resurgence of research and development activities all over the world to develop speciality polymers from natural monomers and polymers.

The present investigation is mainly concerned with the chemical modification of a natural monomer, cardanol and a natural polymer, cellulose. Part A discusses study on the modification of cardanol through hydroxyl group to produce free radically polymerisable monomers and their polymerisation characteristics, and in Part B, the grafting of cardanol onto cellulose, and the photo-induced grafting of MMA onto S-benzoyl cellulose xanthate are envisaged. Spectroscopic, microscopic, and thermo analytical techniques were used in the present study to investigate the system.

This study forms a part of large programme being conducted at the Regional Research Laboratory (CSIR), Trivandrum, to explore the potential of cardanol as a monomer source for development of high performance polymers. So significant structural modifications to bring out property improvement in cardanol based polymer were developed.

The results of the present investigation have been published or are under publication as described below:

1. Self-crosslinkable monomer from cardanol: Crosslinked beads of poly(cardanyl acrylate) by suspension polymerisation, **Makromol. Chem. Rapid. Commun.**, **13** (1992) 255.
2. Synthesis and characterisation of a self-crosslinkable polymer from cardanol: Autoxidation of poly(cardanyl acrylate) to cross-linked transparent film, **J. Polym. Sci. Part A: Polym. Chem.**, (in press).
3. Grafting of bio-monomers 1: cationic graft copolymerisation of cardanol using borontrifluoridediethyletherate onto cellulose, **Polym. Bull.**, **22** (1989) 89.
4. Studies on the nature of the unusually high bulk viscosity of flame retardant prepolymer from cardanol, **Indian J. Chem.**, **29 A** (1990) 897.
5. Photo-induced graft copolymerisation of methyl methacrylate onto cellulose containing benzoyl xanthate chromophore, **Polym. Bull.** (communicated).
6. Characterisation of the autoxidative crosslinking of poly(cardanyl acrylate) by thermal studies (manuscript under preparation).
7. Kinetics of cure reaction and thermal decomposition of poly(cardanyl acrylate) (manuscript under preparation).

8. Chemical modification of cellulose by cationic grafting of vinyl bio-monomers: Structure and properties, 33rd IUPAC International Symposium on Macromolecules, Montreal, Canada, 1990, Abstract Number 430.

Note: For convenience, the references are listed at the end of each chapter; so this arrangement may bring about some repetition in references.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 SIGNIFICANCE OF RENEWABLE RESOURCE MATERIALS AS A POLYMER SOURCE

Nature has an abundant supply of organic materials as chemicals, polymers and other non-polymerisable simple organic compounds including metallic salts and complexes [1,2]. Polymers, of course, are the major components and have been serving human civilizations from time immemorial [3]. Early man used a variety of naturally existing polymers to meet his material needs. Animal proteins, carbohydrates, wood, wool, starch - all of polymer origin were used by him for his survival. Both mechanical [4] (eg. stone, axes, wood carvings, animal skins etc.) and chemical (eg. embalming of corpses) modifications were practiced by early man and this later led to great discoveries such as the tanning of leather, the vulcanization of rubber, the mercerization of cotton and the loading of silk [5]. These discoveries paved the way for the industrial utilization of natural polymers and even today form the basis of continued support and maintenance of these industries against stiff competition from synthetics [6].

Polymer industries and polymeric materials based on natural polymers have been steadily growing till the advent of petrochemicals. The emergence of petrochemicals as a dependable and cost effective feed stock for polymers and their easy availability in pure form brushed aside the natural polymer industry and the world witnessed

over the past few decades a spectacular growth in polymer industry and polymer science and technology [6]. A host of new polymers with unprecedented qualities emerged and some newer materials are replacing even conventional materials such as metals and ceramics in high performance applications [6,7]. The most significant contribution of modern polymer science and technology is the generation of information necessary to tailormake a polymer to meet a specific requirement [8,9]. Although these developments have made man to reach new heights of material sophistications unheard before, there also emerged concomitant problems such as environmental concern on pollution [10], tensions in the gulf countries over oil, the fear of a possible future depletion of oil and the increasing trends in the prices of petroleum products. These and other factors described below naturally give credence to the move to a bio-based materials policy [11-13].

The dependence of chemical industry on petroleum resources could be reduced by the full utilisation of the renewable natural resources wherever it is possible. Ranging from algae to wood, its availability is limited only by the photosynthetic efficiency of the plant [14]. It is renewable and is also adaptable through genetic manipulations [15]. Its availability is flexible through crop switching. 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, hydrocarbon etc. could be synthesised [12,13]. There are a variety of monomeric components that exist in free or in combined form that could be obtained by extraction, cleavage or depolymerisation from biomass [1,2]. When plant tissues

are extracted with solvents, the polymer constituents such as lignin, carbohydrate polymers, proteins and nucleic acids are separated [15]. Bifunctional fatty acids, furan, furfuraldehyde, phenolic compounds and a variety of other monomers could thus be obtained from naturally occurring sources and polymerisation of many of these monomers have been reported [15,16]. The fact that, the structure and properties of polymers can be manipulated to meet a specific need and the availability of such information to effect such a transformation suggest that speciality properties could be built into the existing natural polymers through appropriate chemical modifications to ensure performance in par with synthetics [17]. The abundant availability and structural variety of agricultural and forest products as renewable resources thus lend support to bio-based materials development [11-17]. The relevance of an integrated effort to utilise the natural monomers and polymers for the synthesis of new monomers and polymeric materials or substitution of existing polymeric materials is thus apparent now as never before [11,18-20].

A stock taking on the state-of-the-art knowledge is thus needed. This chapter therefore, deals with a discussion on (1) naturally existing monomers, (2) naturally existing polymers, and (3) their chemical modification. Criteria for selection of a biomonomer and a natural polymer for the present study is then discussed.

1.2 LITERATURE SURVEY OF NATURALLY OCCURRING MONOMERS

1.2.1 Classification

In general, naturally occurring organic monomers are found to be associated with the naturally occurring polymers 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. [1,2]. For the sake of clarity the naturally occurring monomers have been classified as shown in Fig. 1.1. The following discussion is organised into subgroups based on this classification and only those that are considered more potential in terms of polymerisation are discussed. Compounds whose functionality is two or more is considered as a potential monomer but actual polymerisation may depend on many factors. For eg. steric hinderance may inhibit a potential monomer for polymerisation.

1.2.2 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 [21]. This class also includes naturally occurring alcohols, aldehydes, ketones and other derivatives having same carbon skeleton as parent terpene hydrocarbon called terpenoids. Some of the terpenes are detailed elsewhere [22-25].

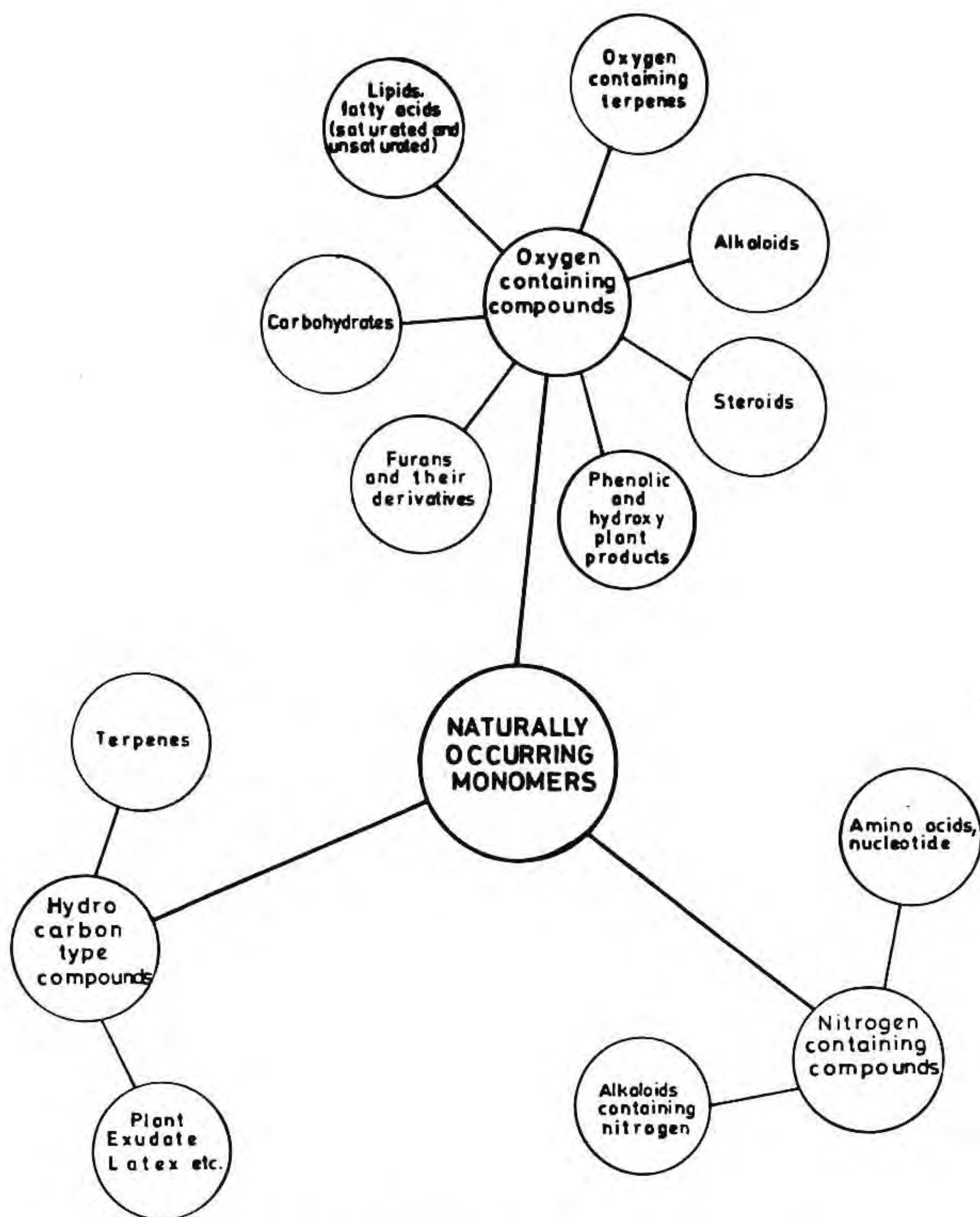


Fig. 1.1 Classification of naturally occurring monomers

1.2.3 Fatty acid monomers

The fatty acids most frequently occurring as components of natural fats and oils can be classified into several groups. One is saturated fatty acid and other group is characterised by the presence of one or more double bonds [26-29].

1.2.4 Alkaloid monomers

They constitute one of the largest groups of natural products. They occur throughout the animal and plant kingdom and display a diversity of structure unmatched by any other group of naturally occurring compounds and exhibit an extraordinary array of pharmacologic activities. A few alkaloids can be considered as monomers [30-33].

1.2.5 Monomers based on phenolic and hydroxy compounds

They form another major category of the natural products. Phenolic compounds and their quinone are of wide spread occurrence in nature [34]. They are abundant in plants and fruits as chromones, glucosides, coumarin derivatives, essential oils, lignin etc. [35-38].

1.2.6 Amino acid monomers

They are a broad class of organic compounds that contains both amine and carboxylic acid functional groups. Here only polymerisable 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 detailed elsewhere [39-41].

1.2.7 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. [42-45].

1.2.8 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 occurring and synthetic substances [46-48].

1.2.9 Monomers based on carbohydrates or sugars

These 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 [49,50].

1.3 LITERATURE SURVEY ON NATURALLY OCCURRING POLYMERS

The literature on natural polymers is quite vast and a few well cited reviews and books are given here for reference [1,2,15-17,51]. The most outstanding aspect of natural polymers is their wide variety which provides innumerable opportunities for structural modification and utilisation. Even among synthetic polymers, a surprising number of them are made from natural polymers. For example sebacic acid derived from castor oil form the '10' component of nylon 6, 10 and alkyd paints are based on triglyceride oils [15]. The point is that

even today natural products are in wide use [17]. While petrochemicals, enjoyed the prime position, renewable resource based polymers have continued to be grown, harvested and used and currently exciting advances are being made in all areas of the field.

As the present work is more concerned with cellulose, detailed discussion on cellulose will be presented and other important natural polymers are introduced.

1.3.1 Hydrocarbon polymers

Natural rubber (NR) is a strategic material of vital importance [52]. NR occurs as particles dispersed in an aqueous serum commonly known as latex which is produced by the *Hevea brasiliensis*. NR is mainly cis-1,4-polyisoprene admixed with small amounts of proteins, lipids, inorganic salts and numerous other compounds [1,2]. Eventhough there are a variety of synthetic rubbers to meet the present requirements, natural rubber is always preferred where it is necessary in service to have a rubber product with high resilience, low hysteresis, low heat build up and excellent tack [53,54]. Chemical modification of natural rubber are possible by many ways such as, vulcanization, grafting, epoxidation reaction etc. Chemical modification of NR can be used to produce new materials, which can compete both technically and economically with certain oil based synthetic elastomers [53,54].

1.3.2 Carbohydrates

Carbohydrates are the most abundant (weightwise) class of

organic compounds, constituting three fourth of the dry weight of the plant world [55]. Among these, cellulose, starch and chitin are more important. Cotton is a good source of cellulose yet the amount of cellulose varies from 85 to 95% depending on the variety of cotton plants. A detailed discussion on cellulose and its importance are given in Section 1.7.

Starch is the reserve carbohydrate of the plant kingdom, where it generally deposited in the form of minute granules or cells ranging from 1 up to 100 μm or more in diameter. These granules are mainly deposited in the seeds, tubers or roots of plants [56]. Chemically, starch is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through $\alpha\text{-D-(1} \rightarrow 4\text{)}$ glucosidic bonds form a branched structure. The abundance of hydroxyl groups imparts hydrophilic properties to the polymer, giving it an affinity for moisture and dispersibility in water. Apart from being used as a food material, modified starches have found many industrial applications as well [56].

Chitin is an important structural polysaccharide which often replaces cellulose in the cell-walls of lower plants. It is found not only in most fungi and in some algae, but also in the animal kingdom in the cuticles of arthropods and molluscs [57]. Crustacean shells are very interesting composites of chitin, polypeptides or proteins, and an inorganic filler, calcium carbonate. Chitin, like cellulose, is inert and insoluble in water. chemically, chitin is a polymer of $\beta\text{-(1} \rightarrow 4\text{)}$ -linked N-acetyl-D-glucosamine residues, and then is similar

to cellulose, but an acetamido group replaces the hydroxyl group on C-2 of the glucose ring. Chitin can be modified by reactions on the hydroxyl groups either by derivatisation or by grafting. The amino acid grafted chitin copolymers find applications as biomaterials [58].

1.3.3 Phenolic and hyxroxy plant products

Lignin

Lignin is a biochemically inert polymer which functions as the structural support material in plants [1,59]. During synthesis of plant cell-walls, polysaccharides such as cellulose and hemicelluloses are laid down first, and then lignin fills the space between the polysaccharides, fibers, cementing together. Lignin is widely found in nature and exists abundantly next to cellulose in higher plants. Technically most of it is obtained as a by-product of pulping processes and is used as fuel. Lignin is believed to be formed by oxidative polymerisation of phenyl propane units to large crosslinked molecules containing carbon-carbon and ether linkages between the monomers [60]. Currently, most of the research work has been concerning the degradation of lignin to mononuclear phenols and their use in the synthesis of high performance polymers [61].

1.3.4 Proteins and nucleic acids

Proteins and nucleic acids are vital to all life processes without which no life can exist, grow and reproduce. While proteins provide structural (eg, muscle [62]) and functional (eg, transport and storage, enzymes, hormones, antibodies etc.) support, nucleic acids are the

hereditary carriers of information for all biological reproduction and growth [1,65]. Both are macromolecules having many orders of hierarchically structured configurations and conformations. In simple forms, proteins are polypeptides formed from condensation of α -amino acids, the arrangement of which is obtained by the information stored in the Deoxyribonucleic acid (DNA). (There are two types of nucleic acids, DNA and RNA (Ribonucleic acids)). Nucleic acids are polynucleotides, with each nucleotide consisting of a heterocyclic base, a sugar (ribose for RNA and deoxyribose for DNA) and a phosphate group.

Whereas cost and availability restrict the use of nucleic acid as materials, proteins were used from time immemorial for the production of various useful materials (fibres, wool, silk, leather and feather are examples). The modification and application of proteins are well studied and reviewed by many authors [63,64,66].

1.4 CHEMICAL MODIFICATION OF NATURAL MONOMERS AND POLYMERS

The chemical modification of polymers [67] as a serious subject of polymer chemistry probably began in 1781 with the isomerisation of natural rubber in the presence of acids [68], although there are prior evidences of chemical modifications practiced without knowing the chemistry behind it. An example is the case of tanning of leather [69]. An important step in the chemical modification of polymers was the development of Staudinger [70] in 1930s of the concept of 'polymer analogous reactions' which consisted in the 'transformation of a polymer into a derivative of equivalent molecular weight'. He obtained evidence for this concept by hydrogenating rubber and polystyrene with almost

no chain degradation. It turns out that reactions with polymers are powerful tools to modify their properties.

The modification of polymers is interdisciplinary in nature cutting across traditional boundaries of chemistry, biochemistry, medicine, physics, biology and material science and engineering [71]. Today, modifications can be roughly grouped into two categories, (a) physical modification including entanglement and entrapment and radiation induced changes, and (b) chemical modifications where chemical reactions on the polymer are emphasized. Academic interest is centered around: (a) The fundamental study of the chemical reactivity of macromolecular chains, and (b) the synthesis of new homopolymers and copolymers, and the functionalisation of linear or crosslinked polymers.

1.4.1 The main objectives for the chemical modification of natural monomers and polymers [72]

Chemical modification is the only way to obtain materials derived from natural macromolecular compounds (cellulose, starch) or polymers with no available monomer (poly(vinyl alcohol)). Even when the monomer is available, chemical modification can be the only way to obtain its polymer, thus, attempts at direct preparation of poly(epi-iodohydrin) were unsuccessful but partial success was achieved by

nucleophilic displacement of the chlorine atom of poly(epichlorohydrin) by sodium iodide in the presence of a small amount of methyl tributyl ammonium in butanol [73].

1.4.2 Main reasons for carrying out modifications include:

- i. Changing the physical properties to improve the biocompatibility, fire retardancy, adhesion, or ability to blend with other polymers etc. Sometimes changes may be required only on the outer surface in order to alter properties such as solvent repellency or friction.
- ii. Preparing polymer-supported reagents. It is advantageous to use reagents in polymeric form. Spent and unreacted reagents are easier to separate from the desired products, and reagent recovery and recycling are facilitated, this is important for expensive reagents and catalysts. A wide range of such substances have been prepared [74,75], and some are commercially available.
- iii. Controlled release drugs and pesticides. This can be achieved by attaching the pharmacologically active unit to a polymer [76].
- iv. Mechanistic studies. There are some reactions where the linking of the reacting groups to polymers facilitates the mechanistic interpretation [77].

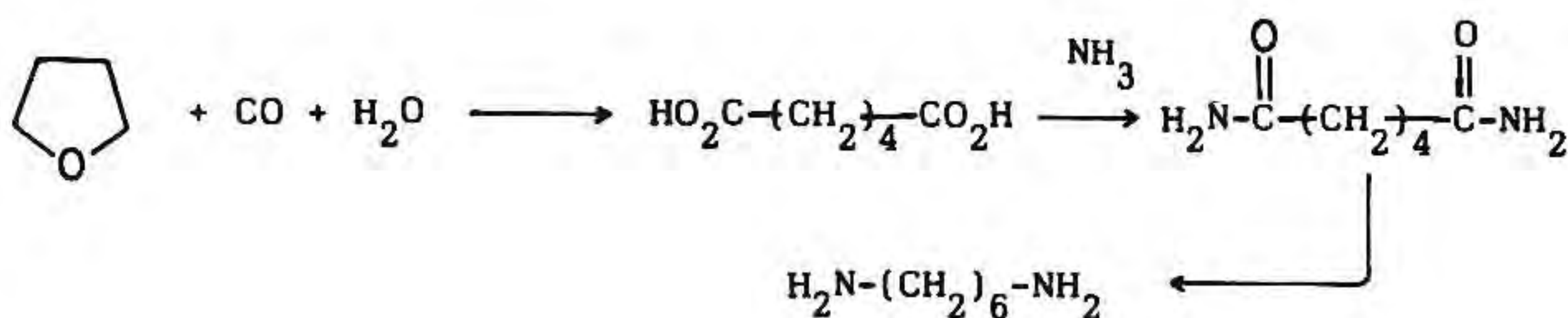
1.4.3 Chemical reaction of monomers and polymers: General aspects

The term modification normally implies the inter-conversion or replacement of functional groups or atoms (including hydrogen) already present, although it may also be an isomerisation of stereoisomeric configuration, such as cis-trans isomers or tacticity. The changes may be directly on the main-chain (backbone) or on pendant groups

linked to the main chain, or specifically at the ends of the chain. Many natural monomers and polymers contain pendant group such as hydroxyls, carboxylic acid, or ester functions or aryl groups attached to the main chain. Numerous methods are available for producing chemical changes in these macromolecules [78] the entire pendant group may be replaced (when the process is a modification of the backbone) but frequently the changes involve addition to or substitution within the pendant unit.

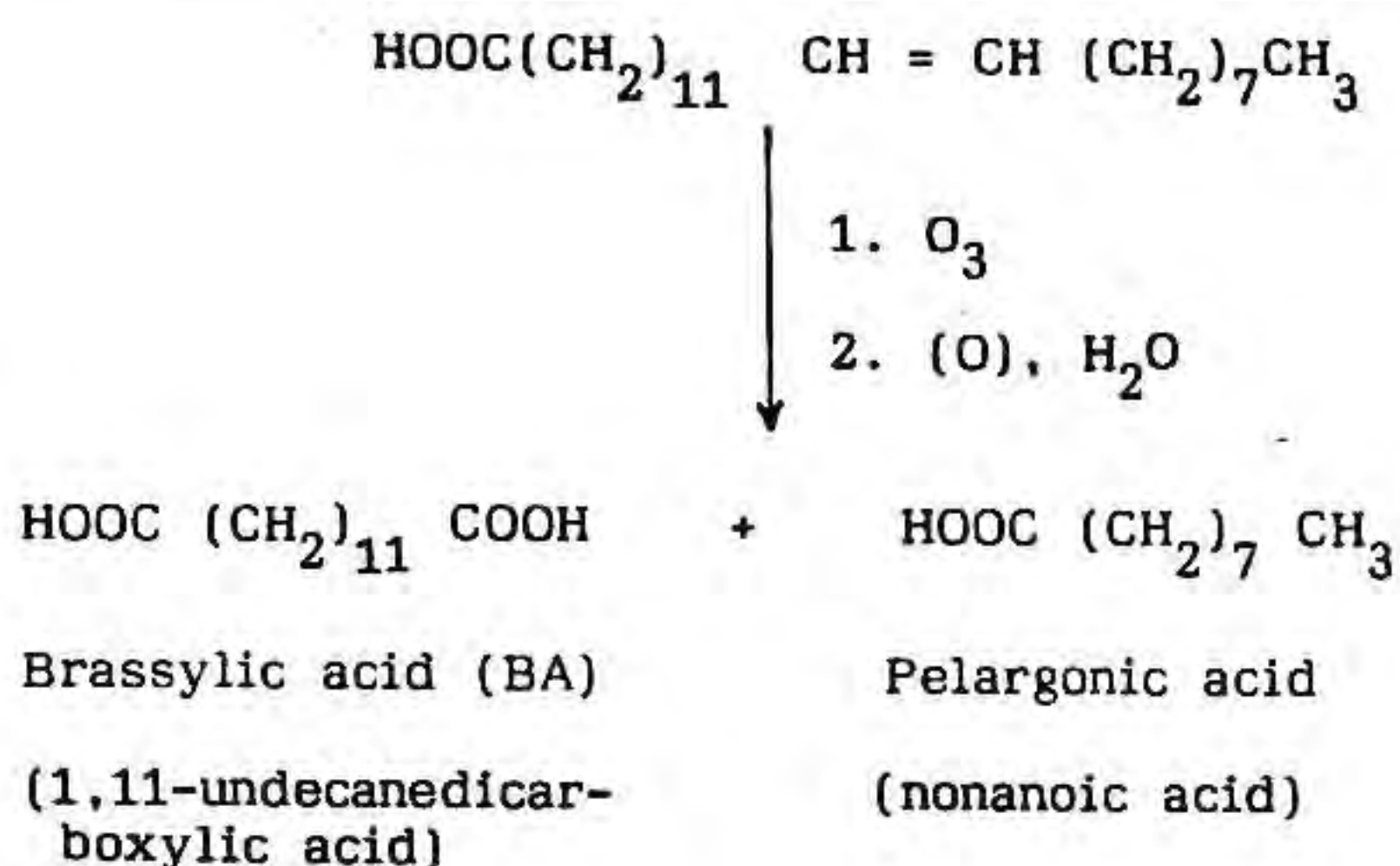
There are a good amount of data on the transformations on the natural polymers, but the literature concerning chemical modifications and polymerisation of biomonomers is rather limited [15-17]. A perusal of the literature on bio-monomers indicate that some of the naturally occurring monomers have already found applications in the polymer field [18]. The monomer can either be modified to other suitable monomers or can be polymerised directly into a useful polymer. An example for this type of application is the production of monomers from renewable resources, such as adipic acid [15], brassylic acid [17] etc. and their utilization in the production of speciality polymers. Few of the examples are listed here.

- i. Furfural, obtained by the steam-acid digestion of corn cobs, bagase, rice husks and oat hulls, acts as the precursor to hexamethylene diamine and adipic acid, the latter two utilised to form nylon-66 [79].



ii. Coatings based on Brassylic acid (An Erucic acid derivative)[17]

Erucic acid $\text{HOOC}(\text{CH}_2)_{11}\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$ can be obtained from rapeseed and crambe abyssinica oils and is potentially a major source of industrial chemicals. Ozonolysis of erucic acid followed by oxidative cleavage of the ozonide to form brassylic acid (BA) and pelargonic acid [79]

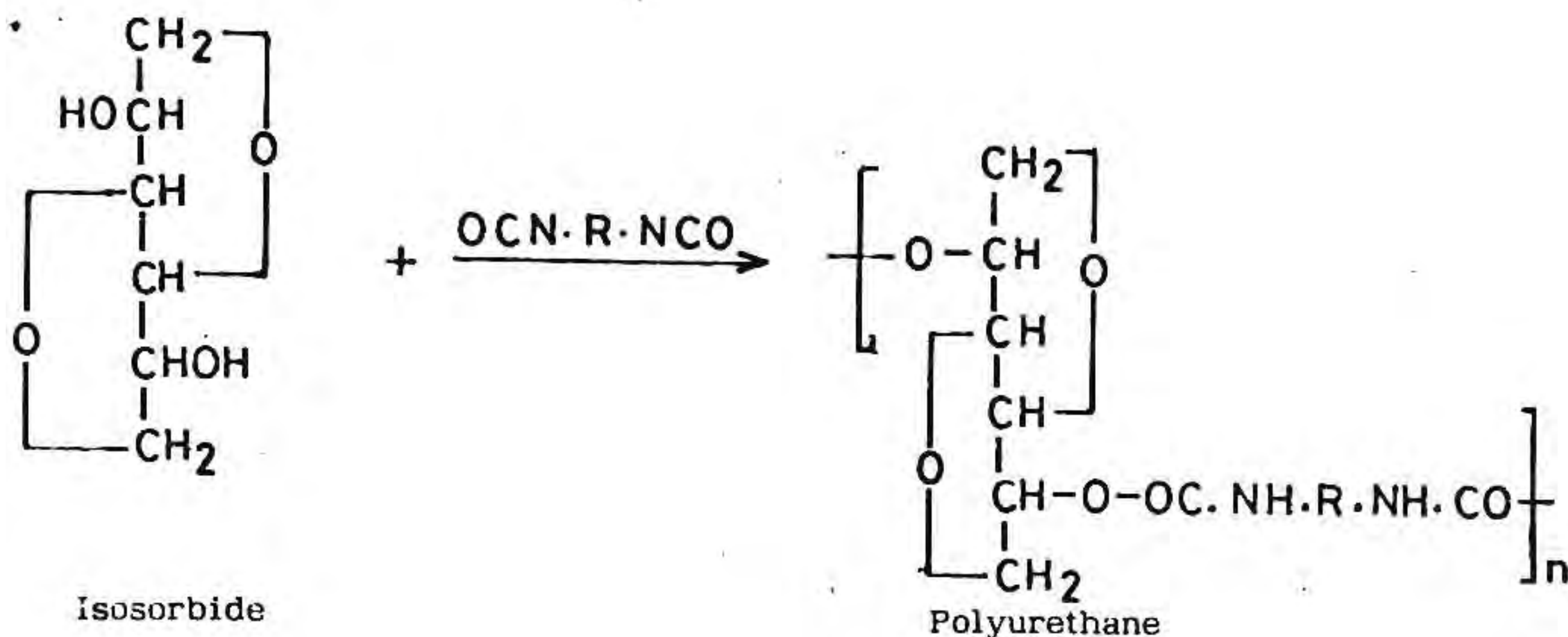


Several polymer-related uses of brassylic acid (BA) have been investigated. For example, a BA/1,3-butanediol/lauric acid oligomer is an effective plasticizer for poly vinyl chloride [80], BA/ethylene glycol and BA/propylene glycol polymers function as polyester based polyurethane elastomers [81]. However, the most detailed studies have involved polyamides [82]. Most properties of polyamide derivatives

of BA, nylons 13, and 13/13 are predictable from properties of commercial engineering plastics such as nylon-11 and nylon-6/10 and the most of which is to impart very low capacity to absorb moisture [83]. This property suggests that these materials may be less affected by water plasticization than other nylons, and has attracted interest in developing BA-based nylons commercially. BA also shows it has potential utility as a monomer for polyester resins designed for industrial coatings.

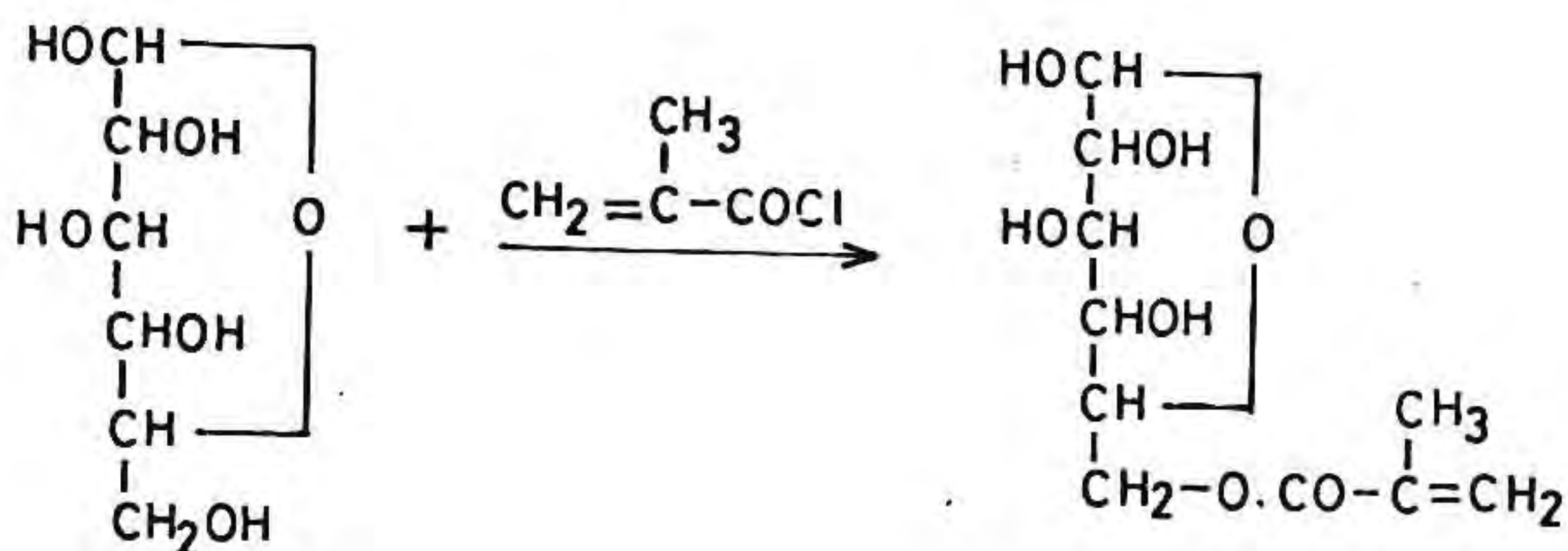
iii. Monomers and polymers based on mono- and disaccharides for the production of speciality polymers [17]

a. Sorbitol is an attractive and inexpensive raw material available from renewable resources. It is industrially produced by hydrogenation of glucose from sugar waste. Sorbitol easily dehydrates into its 1:4 - 3:6 - dianhydro derivative isosorbide in the presence of acid catalysts. A literature search shows that isosorbide has been used in the preparation of polyesters [84] and polycarbonates [85], and is represented in the scheme shown below.



All polyurethanes have been obtained by reacting 1:1 molar ratios of isosorbide and diisocyanate [86]. The products obtained were shown superior properties compared to "synthetic" polymers.

b. D-Glucose methacrylate is the another monomer [17]. Its polymers have many potential application in medicine, secondary oil recovery etc. [87]. The method of preparation of D-Glucose methacrylate is shown below.



Furfural and hydroxy methyl furfural are also examples of naturally obtained monomers that have been polymerised and utilised in industry [88].

Regarding the chemical modification of natural polymers, there are number of excellent reviews on the modification of natural rubber [89], cellulose [90], starch [91], lignin [92,93], protein [63,94] etc. for the preparation of new polymers with improved properties. As it is beyond the scope of this work to sketch all the work on chemical modification in detail, only relevant subject, the chemical modification of cellulose especially grafting of cellulose is reviewed here.

1.5 SELECTION OF NATURALLY OCCURING MONOMER FOR THE PRESENT STUDY

A brief review on natural monomers and natural polymers have been presented. Although there is considerable work being carried out on natural polymers, natural monomers have not been given as much emphasis as it deserves. As is evident from the preceding sections there are a large variety of natural monomers available in nature. Some of these monomers have not even now been polymerised and have not even been recognized as monomers. In a recent study by Manjula and Pillai [95] these monomers have been codified, their sources and polymerisability identified. This study has shown that unsaturated hydrocarbon phenols form an interesting class of biomonomers that possess special structural features for the synthesis of speciality polymers. According to Tyman [96], there are a variety of such phenols present in a number of plant species available in many parts of the world. They are, as shown in Table 1.1 mostly mono and dihydric phenols or phenolic acids, with a hydrocarbon side chain at the meta position, the number of carbon atoms in the side chain varying from C_5 to C_{17} .

Though some of these phenols have certain applications, it appears that use has not been made of the special structural features of these phenols. These phenols could be polymerised either by step-or-chain reaction mechanism or a combination of these techniques[97]. They could also be suitably chemically modified to introduce specific functional groups and polymerised to make specific properties. A survey conducted on the availability of such monomers in India revealed

Table 1.1: List of long chain hydrocarbon phenols

Source	Botanical name	Common name	Main component
Brazil Mozambique India	Anacardium occidentale	Cashew nut shell liquid	Cardanol
Japan China Korea	Rhus vernicifera	Japan lac Chinese lac	Urushiol
North America	Rhus toxicodendron	Poison oak	Urushiol
India	Anacardium semecarpus	Bhilawan nut shell liquid	Bhilawainol
Burma	Melannorrhoea	Burmeselac	
N.W.Australia	Grevilla	A cardol monoene	5-tridecylresorcinol
	Triticum vulgare	Wheat bran phenols	5-nonadecyl resorcinol
Formosa	Semicarpus vernicefera	Formosan lac	
Vietnam	Rhus	Indo china lac	

the existence of two such resources [98]: (1) cashew nut shell liquid (CNSL), and (2) Bhilawan nut shell liquid (BNSL) which are rich in unsaturated hydrocarbon phenols. As CNSL [99] was available in this region, it was selected as the source for bio-monomer for the present study. Thus the present work is centered on cardanol, the distillation product of CNSL [96,100].

1.5.1 Cashew nut shell liquid (CNSL)

Cashew nut shell liquid (CNSL), obtained as a byproduct of cashew industry, is a rich source of unsaturated long chain hydrocarbon phenols [101]. CNSL is selected as a source of monomeric system for the present work because of its ready availability in large quantities, its regional importance. CNSL occurs as a reddish brown viscous liquid in the soft honey comb structure of the shell of the cashew nut, which is a plantation product obtained from cashew tree, *Anacardium occidentale* L which is cultivated in a large number of tropical and subtropical countries [96,102]. 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 [96]. 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 about 3 mm thick and contains CNSL [96]. 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 contain 1.6% water, 10% protein [103], 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 (2%) [104].

1.5.2 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 list of patents that originated from USA, UK, Japan and India upto 1962 [105,106]. It also brought out two other publications [107]. A few reviews have appeared emphasizing the significance of CNSL and its products as versatile industrial raw materials [108-110].

1.5.3 Chemistry of CNSL

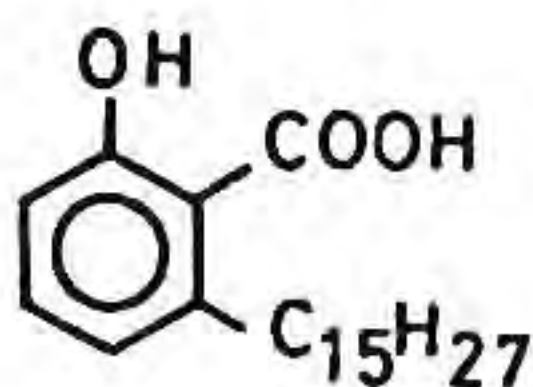
CNSL is said to be the most widely distributed and abundant natural lipids source [96]. The phenolic lipids present in CNSL are (1) phenolic acid - anacardic acid [111,112], (2) dihydric phenol - cardol [111,113], (3) monohydric phenol - cardanol [114] and (4) 2-methyl cardol [115]. Table 1.2 shows the percentage of each component in natural and technical CNSL. Anacardic acid is the major component of natural CNSL but during the hot oil bath process it gets decarboxylated to cardanol [96]. 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 [116].

Table 1.2: Phenolic composition (%) of natural [96] and technical CNSL [117]

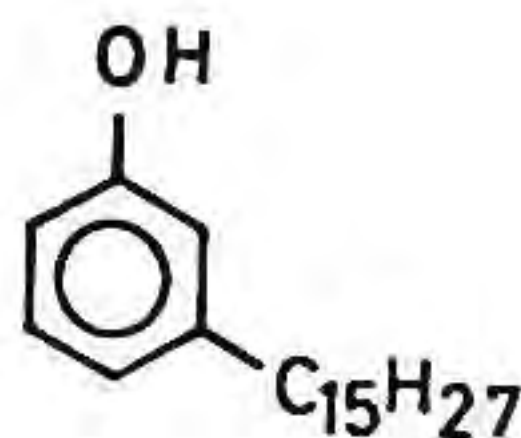
Component	Natural CNSL	Technical CNSL
Cardanol	1.20	62.86
Cardol	11.31	11.25
2-methyl cardol	2.04	2.08
Anacardic acid	64.93	-
Polymer and minor materials	20.3	23.8

1.5.4 Structure of phenolic lipids of CNSL

Städeler in 1847 [111] first investigated CNSL systematically and separated cardol from anacardic acid and decarboxylated anacardic acid. 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 [118]. A.J.H. Smit, in 1931 [119] recognised the presence of salicylic acid system and a pentadecadienyl side chain and P. Von Romburg [120] 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 pelandjanic acid and pelandjanol.



Anacardic acid

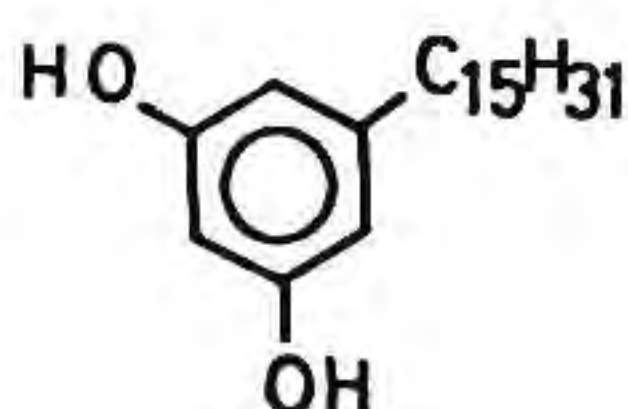


Anacardol
(Cardanol)

Backer and Haack [121] synthesised anacardol and A.A. Durrani and J.H.P. Tyman [122] synthesised anacardic acid.

Städeler first isolated cardanol from natural CNSL and examined its structure followed by Backer and Haack reinvestigated the structure. The hydrogenated material was assigned the following structure since

the oxidation of methyl ether gave 3,5-dimethoxy benzoic acid and palmitic acid.



Later D. Wasserman and C.R. Dawson confirmed the structure in 1948 by synthesis [123].

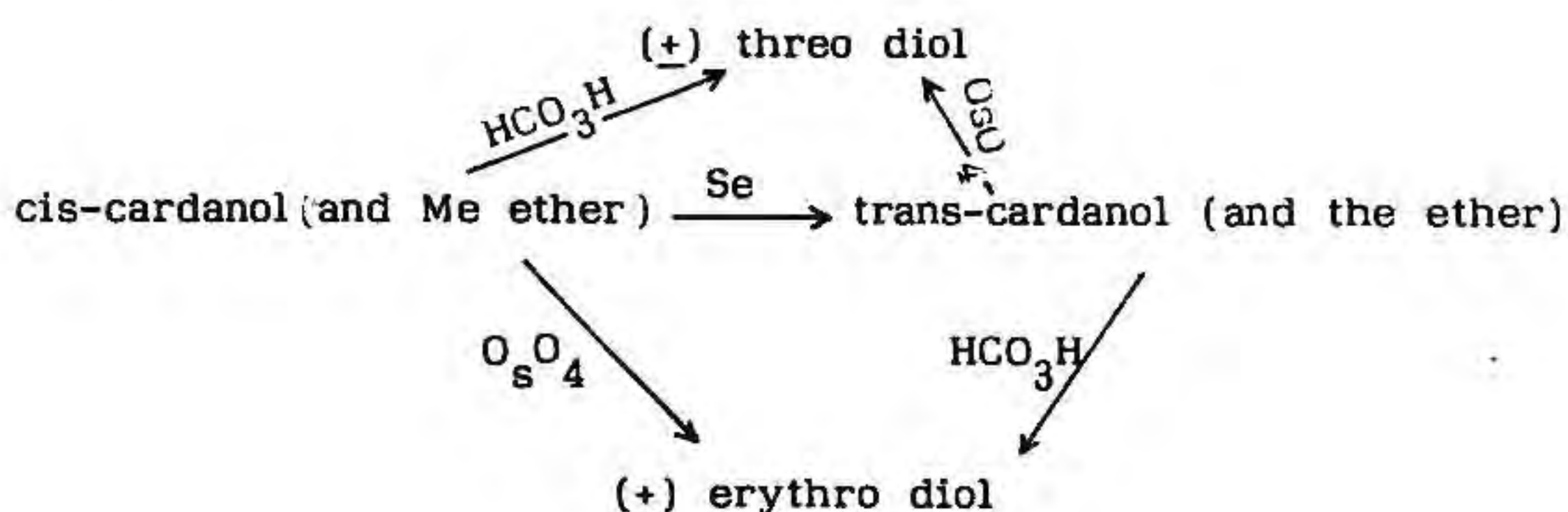
2-methyl homologues of cardol were separated by argentation TLC and are structurally investigated by mass spectrometry and ¹H NMR [115].

Dawson and Wasserman [124] 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. In the early structural work, it was universally believed that a pentadecadienyl side chain was present in the phenols [96]. Later cardanol was shown to consist of a mono- and a di-olefin which formed crystalline glycol separable by fractional crystallisation. B.G.K. Murthy et al [125] 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 characterised

by consideration of their properties and hydrogenation values. In 1953, William F. Symes and C.R. Dawson [113] 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 structure 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 oxidised. Again the pure olefin was oxidised with potassium permanganate and all the products were analysed. The formation of the degradation products indicated the mono-olefin 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 [126]. J.H.P. Tyman and J. Caplin [127] synthesised monoene, diene and triene constituents of cardanol. Paul and Yeddanappalli [126] 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'.

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 which was considered to be the cis isomer because of the final hydroxylation step, was converted into a glycol different in melting point from that derived from cardanol monoene methyl ether [128]. 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 bond 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 isomerisation of cis-isomer with selenium [129]. This is represented in the following Scheme. The existence of unsaturated constituents in the cis configuration had been shown in the ^1H NMR by the J coupling constant values of the olefinic hydrogen [130,131].



1.5.5 Polymerisation characteristics

CNSL can be polymerised in a number of ways [132].

1.5.5.1 Addition polymerisation at the side chain unsaturation

Polymerisation can be effected through the double bonds of the side chain employing ionic initiators. CNSL responds easily to acid catalysts like sulphuric acid, hydrochloric acid and diethyl sulphate [133]. Lewis acids such as AlCl_3 , $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and TiCl_4 easily polymerised cardanol to yield oligomers and polymers [134,135]. For the production of friction dust used in brakelinings, a preliminary

polymerisation of the side chain is carried out with dimethyl or diethyl sulphate. This semi-polymerised material is then polymerised with formaldehyde to get friction dust.

1.5.5.2 Oxidation polymerisation [136]

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 kerosine gives an excellent coating material useful for making paints, varnishes, etc. and for impregnating paper and woven fabrics.

1.5.5.3 Condensation polymerisation

CNSL can be condensed with reactive group 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 brakelinings. Reaction of cardanol and formaldehyde along with tetramethylene pentamine gives derivatives which have been used as weak anionic exchangers [137]. Cation exchange resins have been produced by the sulfonation of CNSL/formaldehyde resins prepared in the presence of hydrochloric acid [138].

1.5.5.4 Metal activated polymerisation

CNSL when activated with metal or metallic compounds acquired drying characteristics [139]. 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 media for paints on further cooking with drying oils [140].

1.5.5.5 Heat polymerisation

When CNSL is heated at 160-300⁰C in presence of certain accelerators, excellent storing enamels are obtained [140].

1.5.6 CNSL based products

Compared to polymers from petrochemical based phenols, CNSL based polymers have many advantages [141]. They have improved flexibility (due to the internal plasticization effect of the long side chain) and hence have better processability [96]. 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 [132]. 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 [142]. In addition to this they possess resistance to cold wear, good electrical and heat resistance, antimicrobial property, termite and insect resistance etc. [97,98]. CNSL polymers are comparable with a wide range of polymers such as plastics and rubbers [143]. 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 [144], chemicals and other useful products have been reported [145].

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, brake-linings, mosquito larvicides [109], detergents [110] etc. Many patents have been taken for using CNSL for lacquers, resins, paints, adhesives, varnishes, canning agents dyestuffs etc.

1.5.6.1 Brakelinings

The major consumption of CNSL is for the production of friction lining materials for automobile brakes and clutches [146]. 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. 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 250⁰C.

1.5.6.2 Surface coatings

Surface coating materials are another outlet for CNSL based polymers [98]. 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.

1.5.6.3 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. Fire resisting and heat insulating paints are based on sodium silicate to which CNSL/chlorinated CNSL were added [140]. CNSL-formaldehyde condensation product in alkaline medium on styrenation gives a resin which can be applied as a varnish to yield an enamel [147]. It can be polymerised on heating in presence of metals like copper, aluminium, lead or their oxides and which form a good media for paints [101].

1.5.6.4 Cashew lacquers

The lacquer made from CNSL could be used for insulation, protective or decorative coatings for furniture, buildings, automobiles etc. [148]. 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.

1.5.6.5 Cashew cements

CNSL polymers react with formaldehyde to give a rubbery gel which can be used as a cement hardner over a period. It can be used for cementing of floor subject to chemical attack [143].

1.5.6.6 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. [101]. Molten mixture of asphalt, rubber and petroleum resin could be used as a "rust proof" tacky composition. Central Building Research Institute, Roorkee, India, developed a surface coating based on CNSL suitable for application for wood based products [148]. Regional Research Laboratory, Trivandrum, India, had developed a coating of CNSL in presence of copper sulphate which could extend the life of coconut leaf thatch from 3-4 years [149].

Gopalakrishna Pillai et al [150] 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. Speciality coatings based on CNSL modified with polybutadiene and epoxy modified CNSL had been reported.

1.5.6.7 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 [101]. Foam plaster based on CNSL have been reported [151].

R.K. Jain et al [152] have reported use of a composition based on CNSL resin and coconut pith for the development of expansion joint filler,

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 70⁰C [153].

1.5.6.8 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.

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 245⁰C [154].

1.5.6.9 Miscellaneous applications

Chen et al [155] reported the synthesis of 6 titanate coupling agents using cardanol which had high reactivity and good hydrolytic stability. Some CNSL based coatings suitable for use in wood and metal were prepared by Muturi Patrick. The gloss flexibility, impact resistance and corrosion of these coatings were compared favourably to those of commercial coating [156].

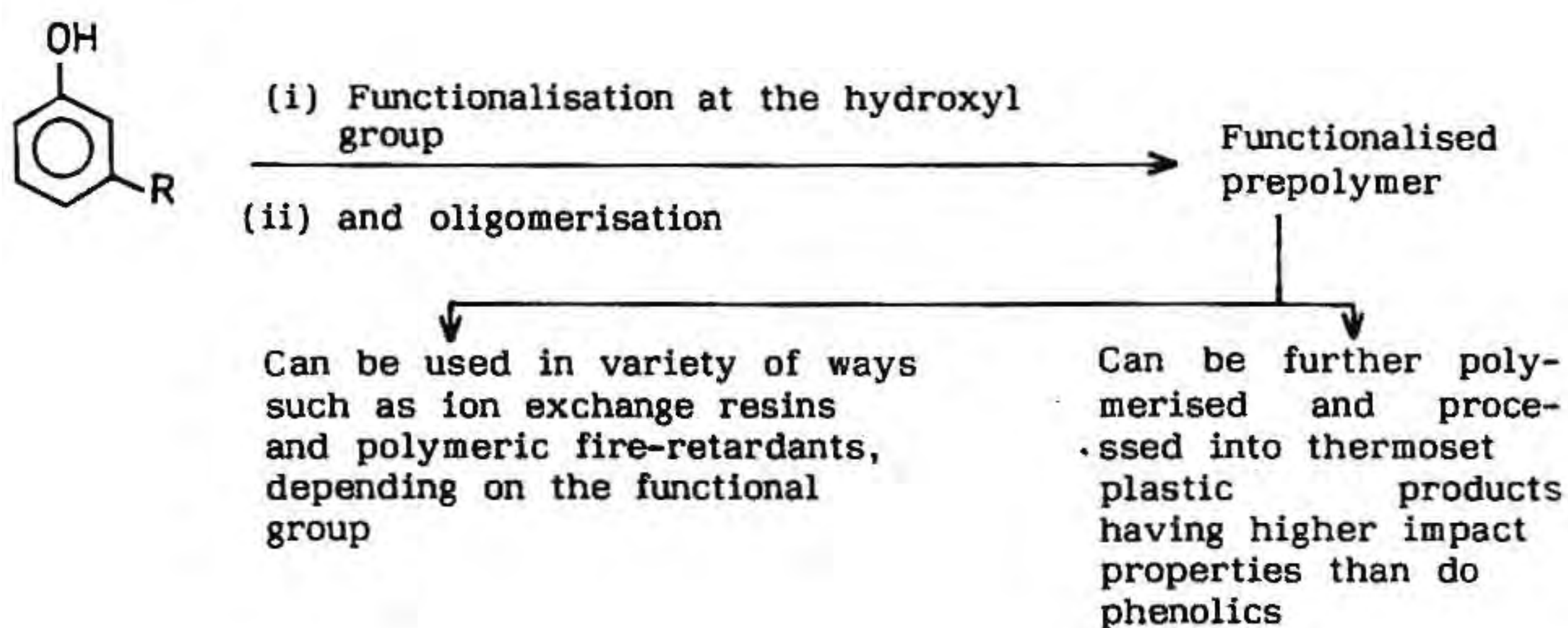
Jayabalan et al [157] prepared slow and fast curing CNSL resins alone and based on novolac/resol by internal condensation methods. The resin had flexibility and form an insoluble rubbery mass on curing. The mechanical properties of glass fiber laminates prepared from modified resins were comparable with those of phenol-formaldehyde resin.

Ghatge et al [158] reported the preparation of a self catalytic resin from cardanol. Formaldehyde and diethanolamine which are blended with polyethylene glycol and resultant blend on treatment with polymeric MDI obtain urethane foams of different densities.

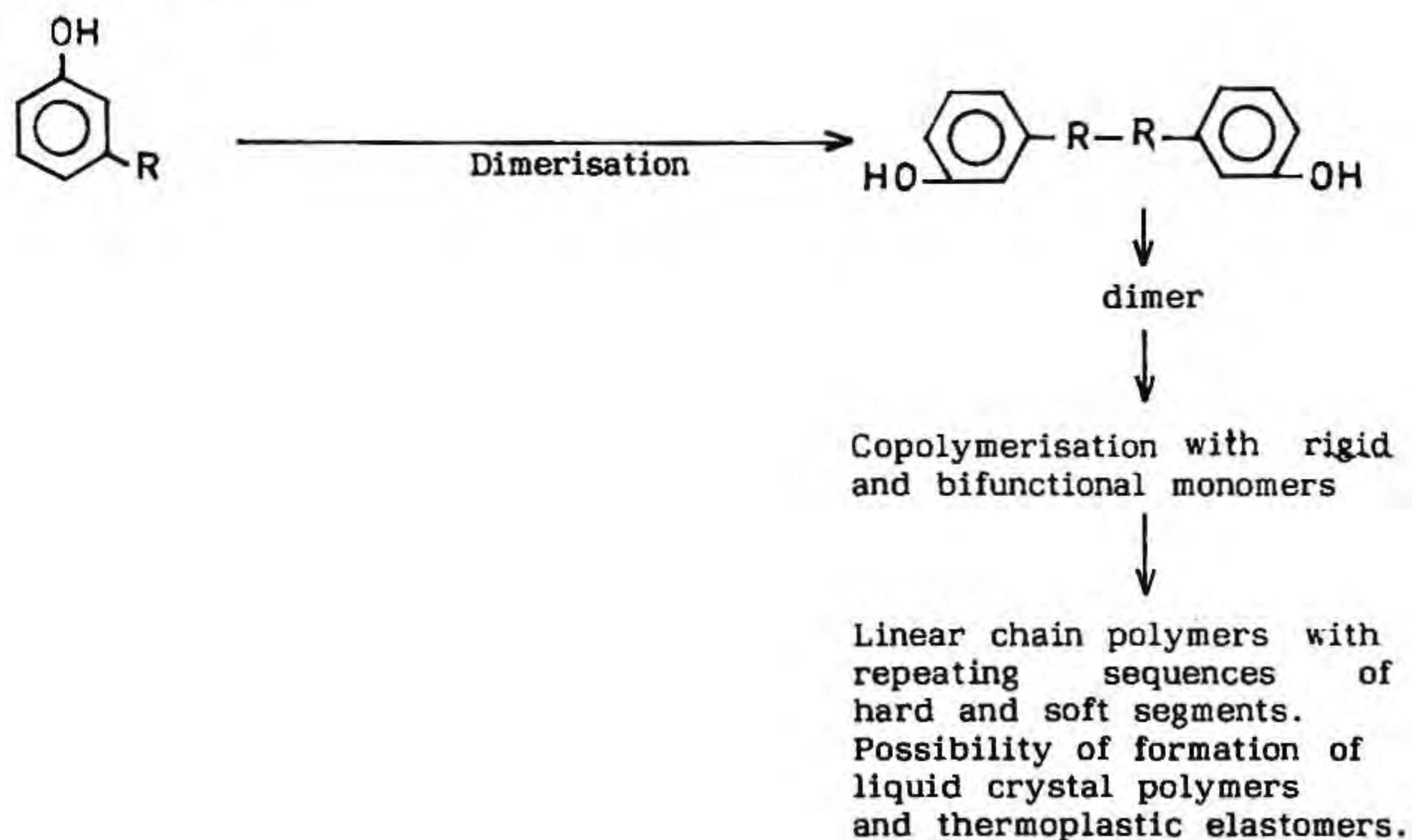
1.6 HIGH PERFORMANCE POLYMERS FROM CARDANOL [159]

The structure of cardanol differs from that of phenol only in having a C_{15} unsaturated side chain. Naturally, cardanol undergoes most of the reactions of phenol. Thus cardanol can be polymerisable with formaldehyde to give resols and novolacs [142]. The presence of the side chain gives it an added advantage that it can be polymerised by chain reaction methods as well. This gives rise to opportunities for selection and control on polymerisation technique for a particular product. For example, the preparation of resins for brake-lining is reportedly made by making use of an acid catalysed side chain polymerisation followed by the conventional formaldehyde condensation. Apart from the variety in polymerisation reactions cardanol can also undergo chemical modifications at the hydroxyl, ring and on the side chain. Moreover, the hydrocarbon side chain itself by its very presence imparts new properties such as internal plasticization, flexibility etc. [96]. Although some of these properties have been put to use in some of the patented products, the special structural features of cardanol were not properly recognised and utilised. A study by Pillai et al [160-162] have shown that high performance and speciality polymers could be produced from cardanol by a variety of methods such as:

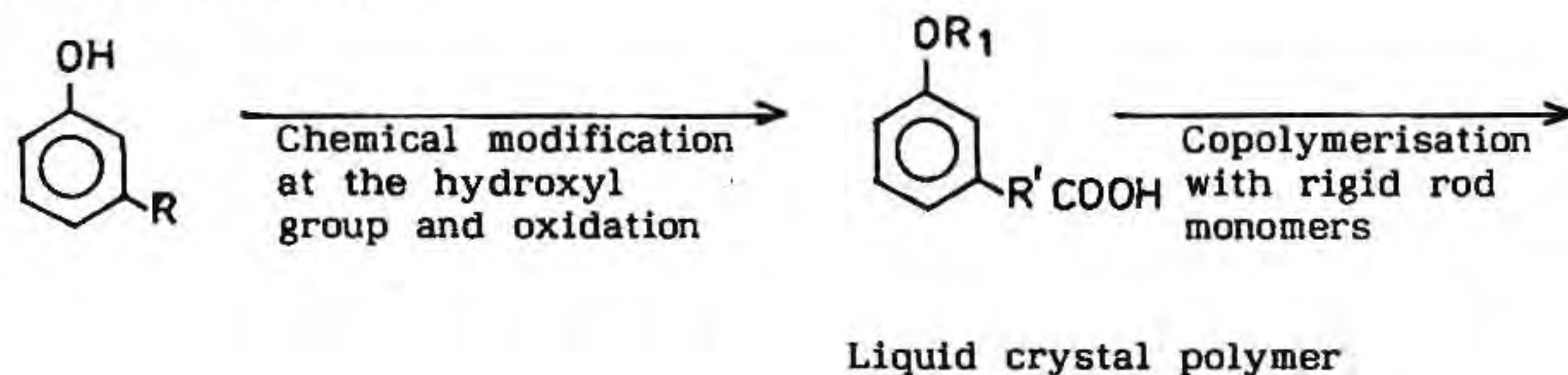
i. Prepolymer route:



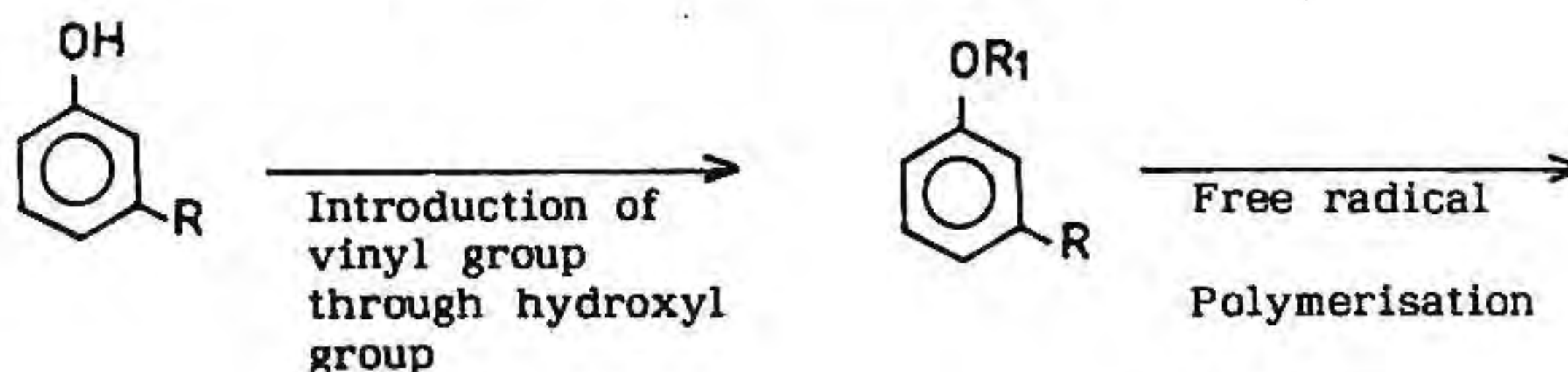
ii. Dimer route:



iii. Oxidation route



iv. Free radically polymerisable monomer route:



Self-crosslinkable polymers

When studies were initiated to develop speciality polymers from cardanol, it became apparent that there exist a wide gap between the processes described in the patents and the scientific understanding on such systems. There has been a total lack of data on kinetics and mechanism of polymerisation of cardanol except the work of Misra and Pandey who reported on kinetics of alkaline catalysed formaldehyde condensation [163]. It is well known that it is not possible to apply modern methods of polymer science and technology for the development of speciality polymers without basic data on polymerisation characteristics and structure property correlations. So, kinetics and mechanism of cardanol were studied using acid catalysts such as H_2SO_4 , H_3PO_4 [135] and Lewis acids such as BF_3 -etherate [134]. These studies showed that cardanol undergoes oligomerisation under acidic conditions through the side chain unsaturation and the oligomerisation is initiated by protonation of the side chain followed by cationic chain growth. These studies led to the development of the prepolymer technology where cardanol was functionalised at the hydroxyl group using orthophosphoric acid [162]. The high acidic conditions simultaneously initiates oligomerisation giving rise to a prepolymer as the phosphorylated product.

It was found that formation of the prepolymer (PCP) is advantageous in the sense that it can be used as a multi-purpose resin because of the possibilities of its different end products as shown earlier. The introduction of the phosphate group raised the LOI value from 21.0 to 35.0 for the amine cured product and the lap shear strength for wood to wood bonding increased 500 fold. (This and other values reported below in Table 1.3 are for the CNSL based polymers, PCNSL).

Table 1.3: Limiting Oxygen Index value of cured PCP/PCNSL resins

Resin	LOI
PCP (HMTA cured)	35.0
PCP (paraformaldehyde) cured	33.0
Brominated PCP	42.0
Cardanol-formaldehyde (novolac)	21.0
Polyethylene	16.9
CNSL-formaldehyde	21.0
PCP/polyethylene	24.5 (16.9)

When it was used as matrix resin for asbestos fibre based brakelinings, a fade value as low as 19% was registered.

The presence of both hydrophilic and hydrophobic groups in the same molecule makes PCP an ideal candidate for wide spectrum [164] polymeric flame retardant. The phosphorylated cardanol prepolymers (PCP)

exhibits unusually high viscosity (200,00-250,00 cP) at 29⁰ C. The viscosity undergoes drastic reduction with increase in temperature reaching a very low value of 82 cP at 150⁰ C. This unusually high viscosity characteristics was studied by George et al [165] and concluded that this might be due to the presence of secondary forces such as hydrogen bonding. PCP resins were found to be compatible with a wide spectrum of polymers such as polyolefins, polyurethane and natural rubber [166]. Table 1.3 shows the limiting oxygen indices of PCP and that of cured products. With polyethylene, the enhancement of LOI from 16.9 to 24.5 is remarkably significant as PCP contains only 8% phosphorus. This behaviour possibly suggests the operation of a different mechanism of flame retardant action. It is possible that (PCP) might act as an antioxidant as well as interfere with surface oxidation of polyethylene.

One of the significant observations has been that introduction of bromine into the phosphorylated prepolymer imparts the property of ablation to the polymer [167]. When tested by oxy-acetylene panel experiments conducted as per ASTM Method, the PCNSL based ablative reinforced thermoset product gave a total burn through time of 97 sec compared to 88 sec for conventional phenolic and 200 sec for a blend of PCNSL with phenolic resin suggesting synergism. Thermal analysis of brominated PCP did not show any significant contribution to ablation from thermal stability and char yield. So it was inferred that the ablation process might arise from the endothermic liberation of vapours of hydrobromic acid followed by transpiration cooling effected through the decomposition gases of the side chain [168].

In a separate study, it was shown that cardanol-formaldehyde (CF resins, both resol and novolac) form semi-interpenetrating networks with PMMA [169]. Although interpenetration of PMMA increases the mechanical properties only marginally, it showed a stabilization in PMMA at 350⁰ C from 50% decomposition to 15%. However, the T_g of CF registered an unusual increase for 128⁰ C to 144⁰ C suggesting restriction in the segmental motion of the CF phase brought about by mixing with another rigid polymer such as PMMA [170].

One of the remarkable achievements in converting cardanol into high value polymer was the successful preparation of a thermotropic liquid crystalline polymer [171]. When cardanol was subjected to phase transfer catalysed KMnO₄ oxidation the side chain was cleaved and oxidised to 3-HPOA. (8-(3-hydroxy phenyl) octanoic acid (3-HPOA). 3-HPOA is a bifunctional monomer possessing both 'Kink' structure and flexible segment $-(CH_2)_8-$ built into the same molecule. These structural features are useful in bringing down the transition temperature of intractable liquid crystalline polymers such as p-HBA so that they could be made processable. While HPOA was copolymerised with p-HBA, the LC copolymers showed a transition at 250⁰ C which is much lower than those of the commercial products Vectra and Xyder.

A number of workers elsewhere have also been applying similar concepts to develop speciality polymers from cardanol. Thus Pillot et al [172] reports the hydrosilylation of cardanol with HMeSiCl₂ followed by hydrolysis to get polysiloxane grafted phenolic resins with thermally stable Si-C linkages. This strategy permits the preparation

of special phenolic resins which are expected to possess improved mechanical properties as well as resistance to chemicals and climatic factors. Trivedi et al [173] studied the dimerisation of cardanol with a view to developing epoxy resins from the dimer. Epoxy resins having improved thermal and mechanical properties have also been developed. Ramsri et al [174] have developed Mannich bases and polyurethane coatings based on card-bisphenol for use in electrodeposition. Specialty coatings based on cardanol-HCHO resins copolymerised with TDI have also been reported by Hu et al [175]. Sitaramam and Chatterjee [176] prepared pressure sensitive adhesives from 3-pentadecylphenol (hydrogenated cardanol) by introducing acrylate/methacrylate moiety through hydroxyl group.

It appears that the opportunities for chemical transformation of cardanol into high value polymers are vast. In a recent report Panda et al [177] reported the preparation of a liquid rocket fuel consisting of 70% cyclopentadiene blended with 30% cardanol which undergo synergistic hypergolic ignition with red fuming nitric acid.

1.7 SELECTION OF NATURALLY OCCURRING POLYMER FOR THE PRESENT STUDY

Among natural polymers, cellulose is the most abundant [178]. Cellulose is photosynthesised in higher plants and synthesised by some bacteria, fungi, algae and unicellular organisms. Whatever be the source of cellulose, the organochemical structure of the polymer is same [179]. Thus, cellulose polymer is unique among natural polymers in that it has a structure that gives rise to high strength and rigidity. It can also be chemically modified by various methods to introduce

speciality properties [180]. The presence of active hydroxyl groups in cellulose has been utilised in a variety of chemical reactions to produce commercially important cellulose derivatives such as cellulose ethers and cellulose esters. Although the practical purpose of cellulose derivatization is by and large to improve various properties of the original cellulose, these cellulose derivatives are often not competitive with many of the petrochemically derived synthetic polymers [181,182]. In order to provide a better market position for cellulose derivatives, there is little doubt that further chemical modification is required. Grafting of vinyl monomers onto cellulose, cellulose derivatives, and lignocellulosic materials may improve the intrinsic properties of these polymers [183].

1.7.1 Cellulose chemistry

In about 1838 the term cellulose was probably first applied to what had become recognised as a common fibrous-like substance in all plant materials. In 1838 Payen isolated and purified a common fibrous substance from cotton and other plants which he named cellulose. The generally accepted empirical formula of cellulose is $(C_6H_{10}O_5)_n$. Cellulose is found in its purest natural form in seed hairs such as cotton fibers.

1.7.1.1 Macromolecular structure

The macromolecular structure of cellulose was proposed by Staudinger in 1920 [184]. Today it is generally accepted that cellulose occurs in nature as an unbranched macromolecule with structure of formula (Fig. 1.2). The values of x (number of cellobiose units) range as high as 2000-2500.

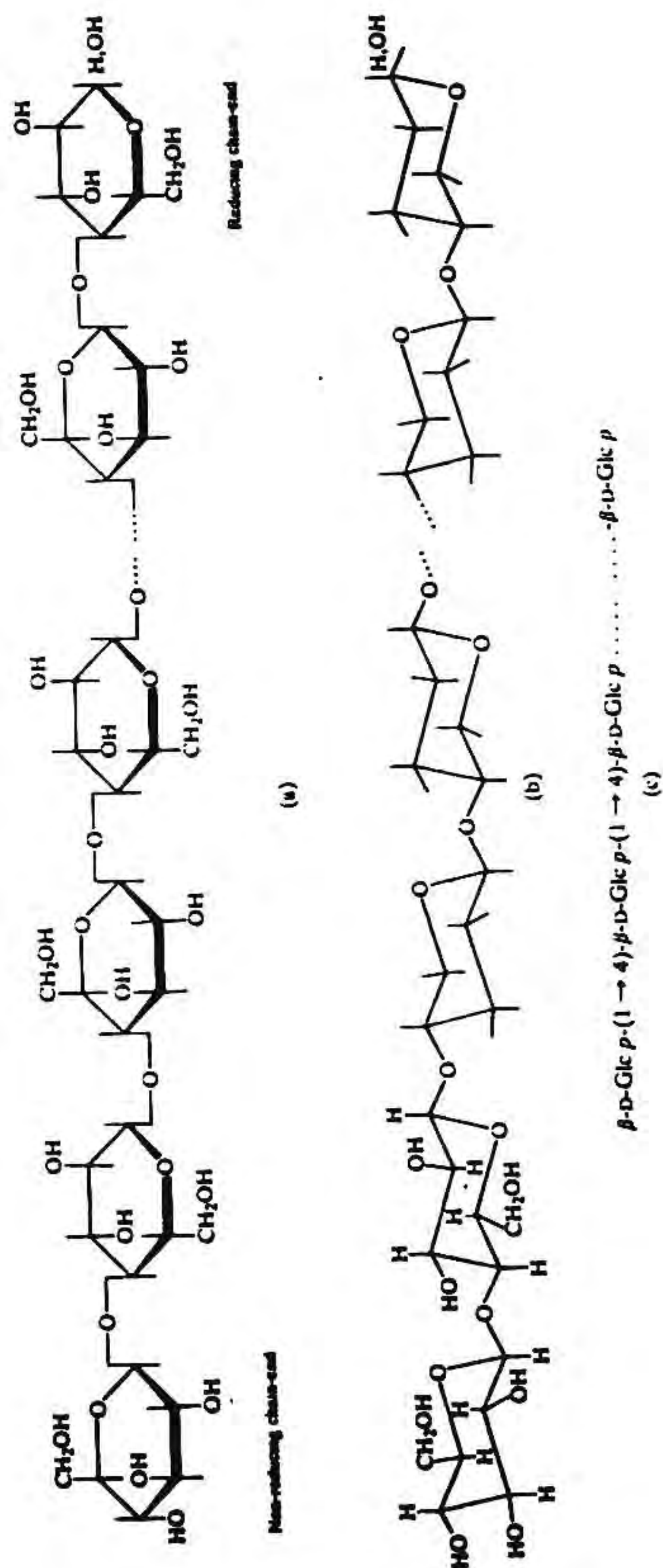


Fig 1.2 : Structure of cellulose (a) using Haworth convention; (b) showing the most stable ring conformation; (c) shorthand form-abbreviations

1.7.1.2 The chemical structure of cellulose can be changed in several ways:

- a. By substitution of the cellulose hydroxyls whereby the cellulose molecules are altered through introducing side groups usually by an etherification or by an esterification reaction [185]. The effect of this is to eliminate or at least to reduce some of the outstanding drawbacks of the cellulose, such as flammability, susceptibility to rot and mildew swellability, etc. and is dependent on the type and extent of the reaction as well as the nature of the substituent.
- b. By reacting cellulose with bi- or polyfunctional compounds, which results in the production of crosslinks or resinification products in the cellulose, thereby stabilising its structure. Such treatments impart crease resistance, shrink resistance, and a number of other properties to the cellulose [186].
- c. By preparing a branched cellulose or what is called a graft copolymer of cellulose, a process in which attempts have been made to combine synthetic polymers with cellulose to produce material with the best properties of both. This process is known as grafting [187], usually done by modifying the cellulose molecules through creation of branches of polymers that will impart certain desirable properties on the cellulose without destroying its intrinsic properties. Important copolymer systems are depicted in figure 1.3.

1.7.2 Graft copolymerisation of cellulose

Grafting reactions provide a potential route for significantly altering the physical and mechanical properties of a substrate polymer [188-190]. Grafting possesses great potential for tailoring material

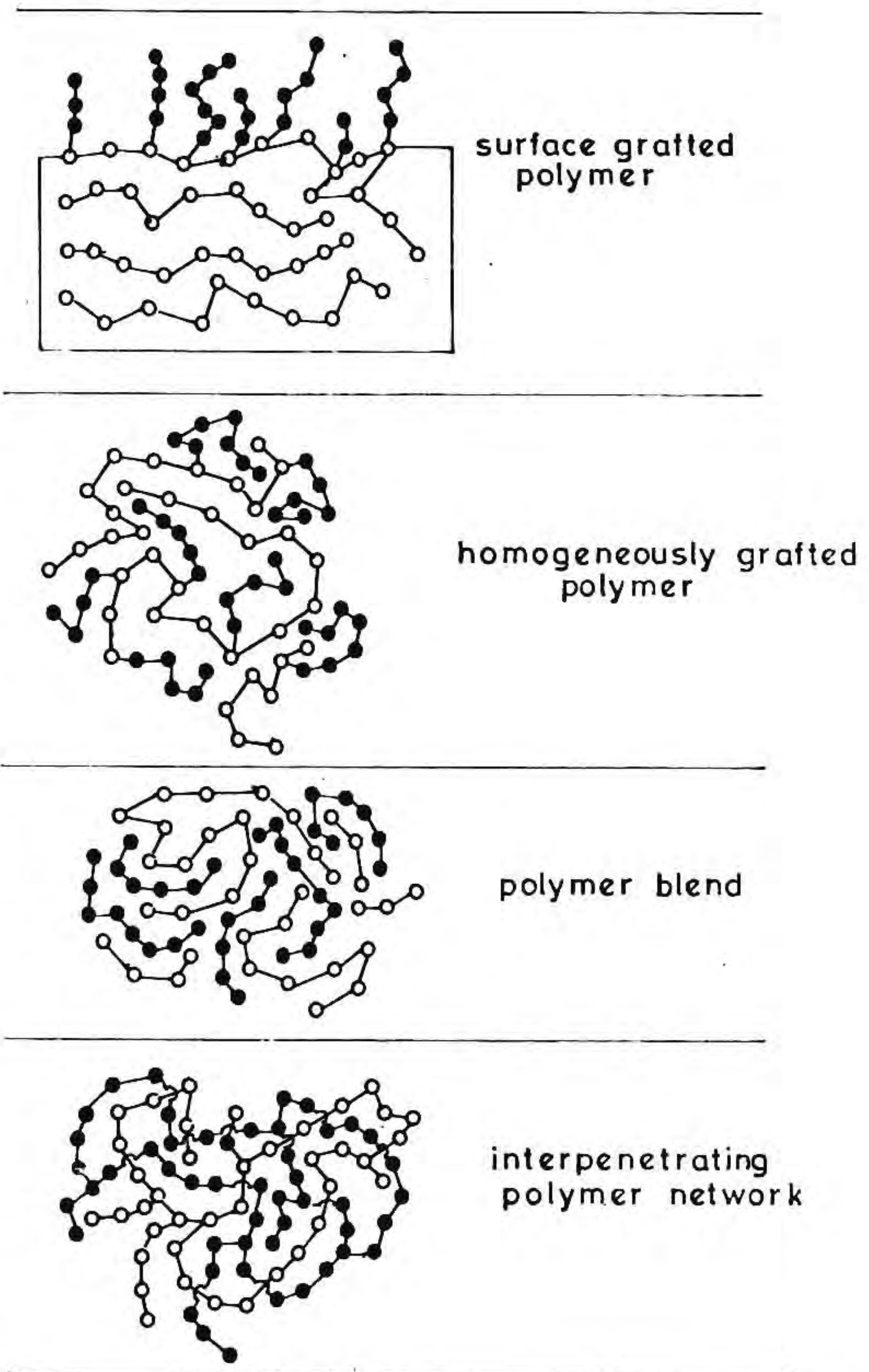


Fig. 1.3: Schematic representation of different copolymer systems

properties to specific end uses [191,192]. Cellulose is transformed into multifarious products affecting every phase of our daily life due to their wide applications as clothing, housing, and industrial products [193,194]. Graft copolymerisation of vinyl monomers onto cellulose, cellulose derivatives, and lignocellulosic fibers has been the subject of extensive studies since 1950, and many hundreds of papers, reviews and patents have been published [193-204]. Processes of combined grafting and crosslinking reactions have been developed to produce cotton-cellulose fabrics with improved wash-wear ratings and wrinkle recovery angle. In some processes the grafting of such multifunctional monomers as allyl acrylates are reported to lead to crosslinking [205]. Methods including combined chemical and free radical linking monomers like methyloyl acrylamide can be grafted onto cellulose materials to improve their end use applications [206]. In spite of all these efforts, there has been comparatively little commercialization of the grafting processes.

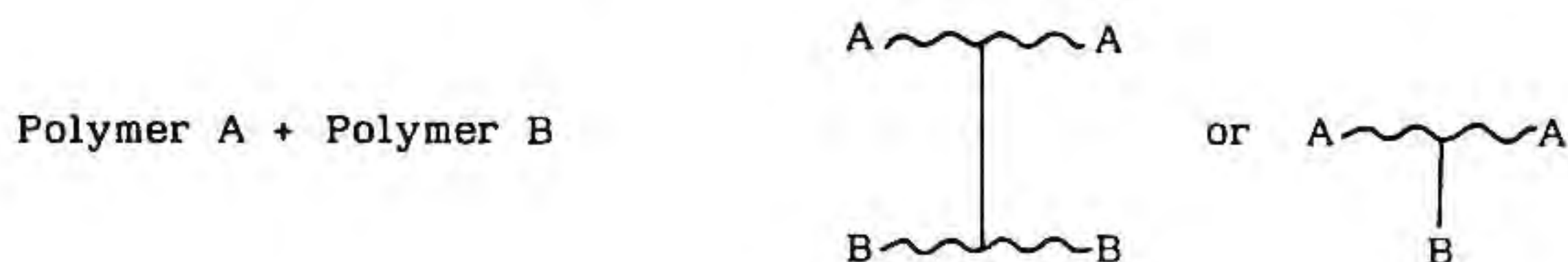
There are a number of methods available for affecting graft copolymerisation onto preformed polymers, each with its own particular advantages and disadvantages. Graft copolymerisation onto cellulose, cellulose derivatives, and lignocellulose is effected through an initiation reaction involving attack by macrocellulosic radicals or ions on the monomer to be grafted. The generation of active sites on cellulose molecules is accomplished by a variety of methods and is briefly discussed in the following sections.

1.7.3 Methods of preparation of graft copolymers

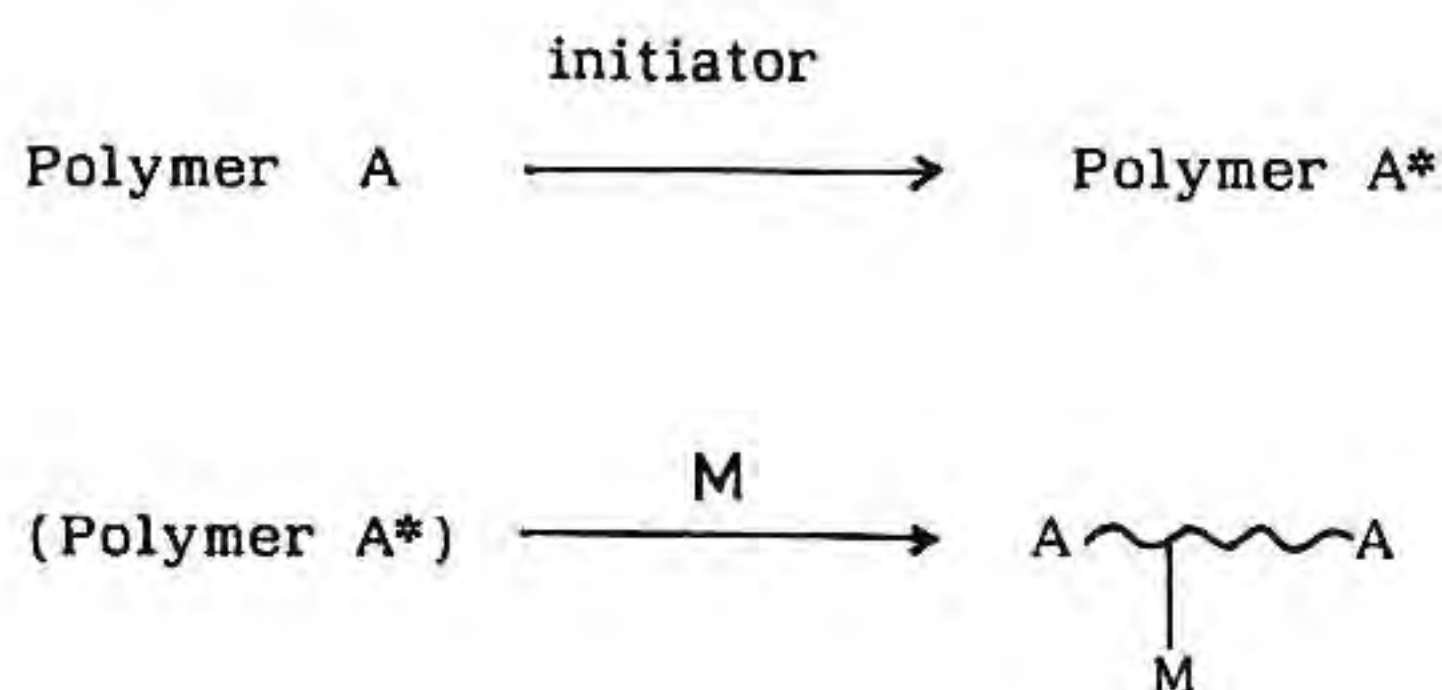
For improving the competitive position of cellulose in comparison with other natural polymers, various specific grafting procedures have been tried. Cellulose graft copolymers have been found to improve a wide variety of cellulosic properties which include tensile strength, resistance to microbial degradation, weathering, abrasion, ion-exchange, acid resistance, dye receptivity, wet strength, adhesion etc. [207-210].

In general, there may be two ways by which graft copolymers can be synthesised.

- (a) Crosslinking reactions of two polymer chains of different types:



- (b) Initiation of active sites on the polymeric backbone (A) when the monomers (M) can be grafted

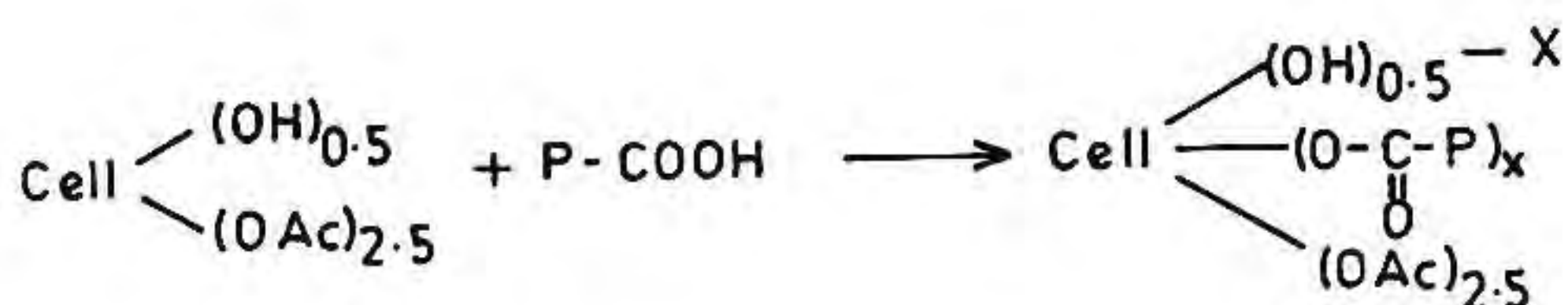


where A* is a polymer having an active site.

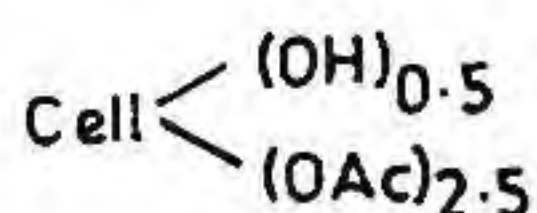
Of the two methods, the second process has attracted the widest attention and initiation has been carried out both by simple chemical means and by using suitable irradiation techniques. The active site may arise from the formation of radicals or ions of which the former again constitutes the main intermediate step by means of which the bulk of graft copolymerisation reaction occurs.

1.7.4 Grafting through crosslinking

In 1970, Mansson et al [211], prepared styrene grafted cellulose esterifying the free hydroxyl groups in cellulose acetate with the polystyrene, having carboxyl group at one end of the chain and then selective removal of acetate groups of the copolymers by aminolysis.



where



represents the cellulose backbone and P-COOH is the polystyrene having one carboxyl group at its chain end. In case of crosslinking initiated by radiation, the two polymers are taken in a common solvent, or they are cast in a film mixture from a solvent and then irradiated.

1.7.5 Grafting through initiation of active sites on the polymer backbone

The second method which aims at initiating graft copolymerisation through intermediate formation of active sites on the polymer backbone, may be carried out by means of high energy or ionizing radiation, or by conventional chemical means. The primary effect of radiation consists of ionization and excitation, the alternate result being the formation of ions or radicals [213]. Now the ions or radicals can subsequently take part in initiating graft copolymerisation [212].

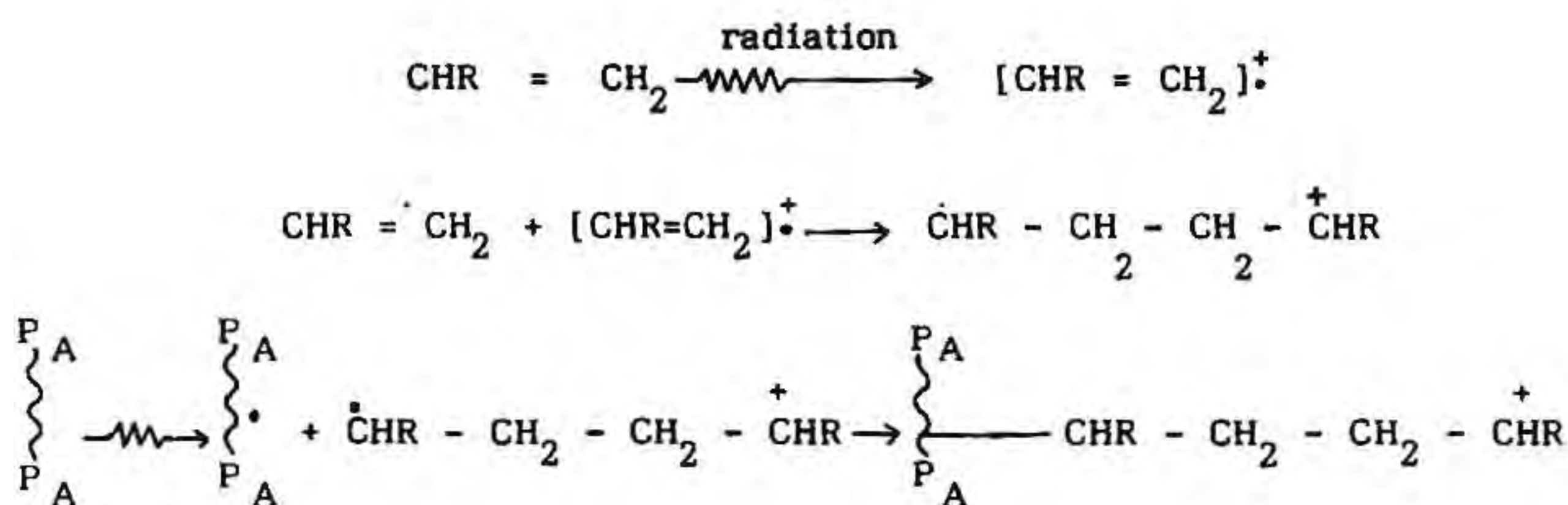
1.7.5.1 Ionic grafting

(a) Ionic grafting initiated by radiation

The overall ionic process initiated by the action of radiation on the monomer can be represented as [214]



Both the positive and negative ions formed in the above reactions may initiate polymerisation and accordingly one can distinguish respectively cationic and anionic grafting. The various monomers such as styrene, *o*-methyl styrene, acrylonitrile, isobutylene, etc. have been grafted to backbone polymers like polyethylene, polytetrafluoroethylene, polyvinyl chloride, cellulose etc. by taking recourse to a radiation induced ionic process. A possible mechanism for cationic grafting of monomer $CHR = CH_2$ to polymer P_A is shown in the following scheme:

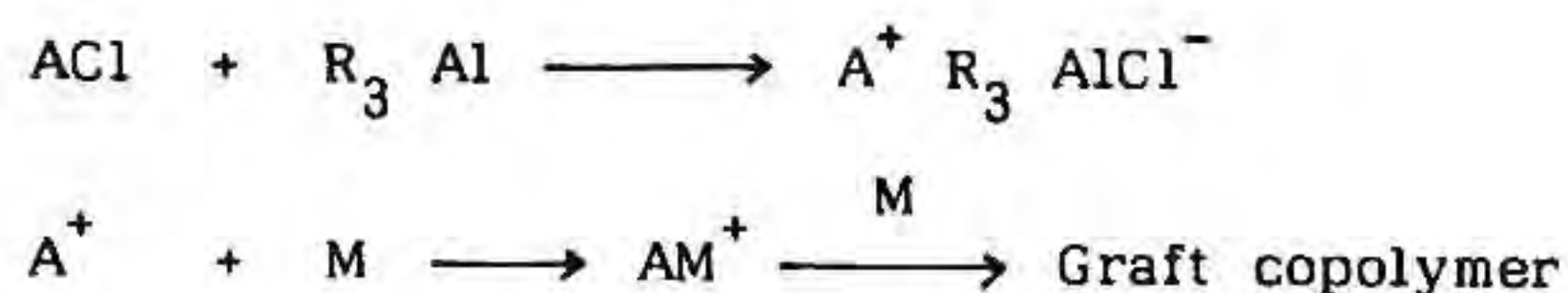


As is evident from the above scheme the plausible intermediate is a monomer radical cation which subsequently forms a dimer. Charge localisation in the dimer occurs in such a way that the dimer radical cation then reacts with the radical produced by the irradiation of the polymer. High reaction rate is the potential advantage of the ionic grafting process. However, experimental difficulty in this process comprise the use of extremely dry conditions.

(b) Ionic grafting initiated by chemical means

The basic requirement in such processes is the selection of a suitable ionic polymerisation initiator. Such initiators may be alkali metal suspensions in liquids that are Lewis bases, organometallic compounds and sodium naphthalenide.

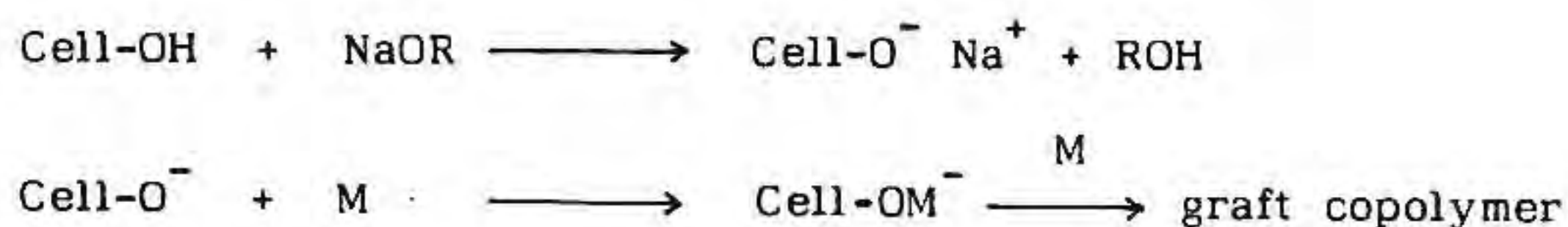
A typical example of cationic polymerisation using alkylaluminium consists of taking the backbone polymer in the halide form, where interaction takes place between the macromolecular halide and the alkyl aluminium compound, resulting in the formation of a carbonium ion along the polymer chain which eventually results in graft copolymerisation.



Various backbone polymers have been grafted with typical monomers using this method [215-219]. In the case of cellulose, however, use of borontrifluoride as the cationic catalyst was reported earlier [215].

Anionic grafting

A typical example of anionic grafting involves the formation of an alkoxide of cellulose by the interaction of the polymer with anionic catalyst such as sodium ammonia or methoxide of alkali metals and subsequently this alkoxide derivative of cellulose is treated with vinyl monomer. The mechanism of such process can be represented as



where Cell-OH represents the cellulose substrate. Cotton [220], amorphous cellulose and rayon can be metalated with alkali metal (Li, Na, K) methoxide in methanol or (1:1) methanol-LMSO and the metalated cellulose is anionically grafted with acrylamide, methacrylamide and crotonamide in various solvents. Richards [221] published a review article on the application of the anionic method for the synthesis of homopolymer and graft copolymer. Ramani Narayan et al [222,223] proposed improved methods for the anionic method of grafting of cellulose.

1.7.6 Free radical grafting

The bulk of graft copolymerisation studies owes its origin to initiation by free radical initiators. Free radicals that are produced as a result of the cellulose substrate then react with the monomers to form the respective graft copolymers. Free radicals can be produced by a number of methods such as chemical method, mechanical degradation, low energy irradiation in the presence of sensitizers or by high energy irradiation.

1.7.7 Grafting initiated by chemical means

Of the various chemical initiation methods the redox system constitutes the most extensively used one. Redox system generally comprise the transition metal ions which occur in various oxidation states [224]. Such oxidised metal ions may directly oxidise cellulose or its derivatives to initiate the formation of free radicals for grafting. There are other types of redox system which initially produce low molecular weight free radicals and these species then induce the formation of free radicals onto the cellulose substrate by chain transfer.

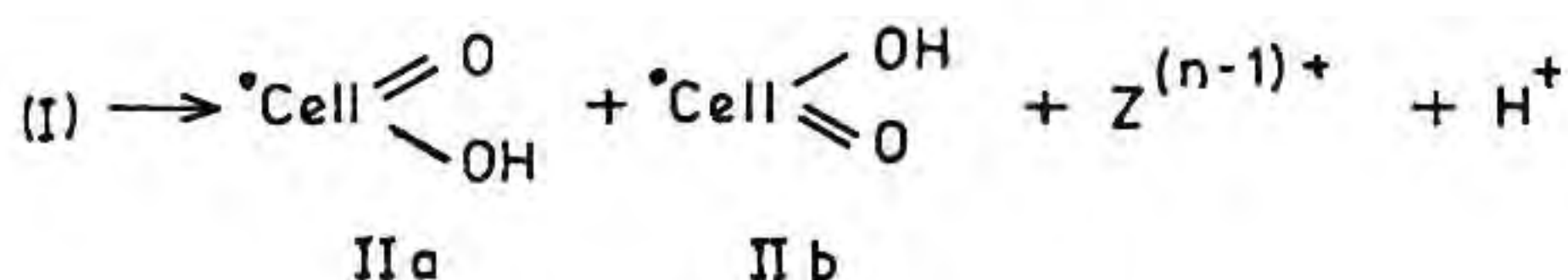
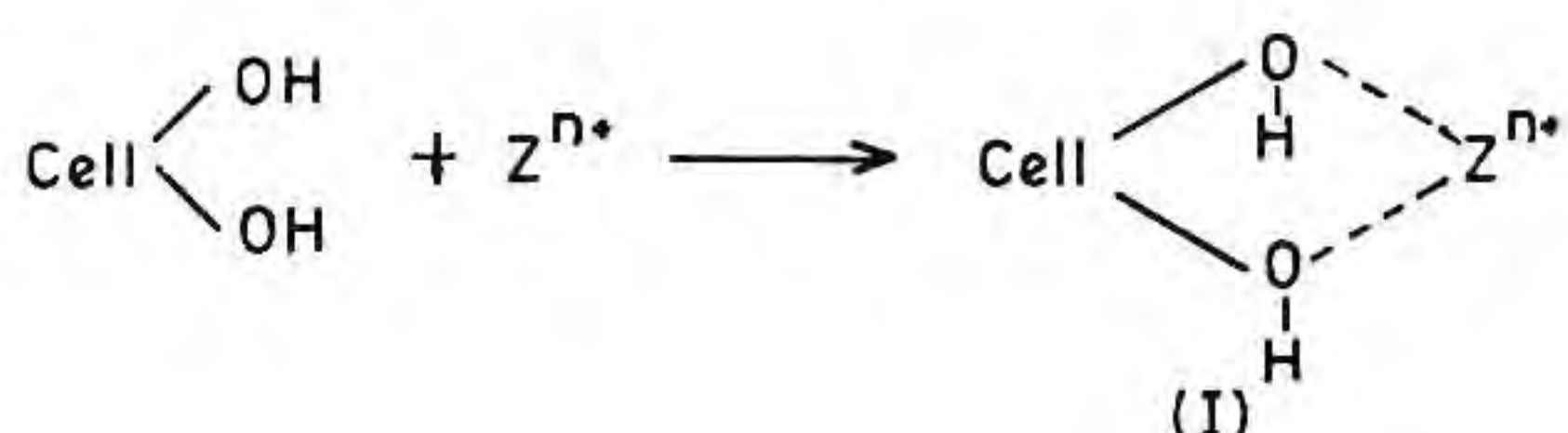
1.7.7.1 Initiation by redox reactions:

Redox initiations can act in two ways, e.g. by direct oxidation or by chain transfer.

(i) Direct oxidation:

Certain transition metal ions eg. Cr^{6+} , V^{5+} , Ce^{4+} , Ce^{3+} , Mn^{3+} , Fe^{3+} , as has already been stated, directly oxidize cellulose as a result of which free radical sites are produced. The proposed mechanism

for such processes has been ascribed to the intermediate formation of a metal ion cellulose complex of chelate type as shown below [224-228] .



where $\text{cell} \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{OH} \end{array}$ represents the cellulose backbone and Z is the transition metal.

Recently Misra et al [229] used metal chelates rather than metal ions as initiator. The novelty of the mechanism in this process lies in the fact that metal ion forms a complex with the monomer rather than with the cellulose matrix. The resulting complex then decomposes to give free radical.

Of all the transition metal ion Ce^{4+} constitutes the most widely used initiator [230,231].

(ii) Chain transfer:

These types of redox initiators form radicals due to the reaction among themselves and the resulting radicals abstract hydrogen



atoms from the cellulose [232-234]. Generally, hydrogen peroxide in the presence of ferrous ion constitutes a frequently used redox chain transfer initiator as shown in equation



where Cell represents cellulose backbone. Similar chain transfer reaction may also occur when organic hydroperoxides, persulphates, Fe^{3+} , Cu^{2+} , etc. are used in place of H_2O_2 together with a reducing agent such as sodium bisulfite, thiosulfate or Ag^+ [235-237].

1.7.8 Initiation through chain transfer using system other than redox ones

This type of initiator on heating produces free radicals which take part in chain transfer to the cellulose substrate to produce free radicals for grafting. Such compounds may comprise peroxides [238,239], hydroperoxide, azo compounds [240-241], metal alkyls, peroxide diphosphate etc. [242].

Chemical pretreatment:

Chemical pretreatment of cellulose backbone may also be induced free radical sites which may serve as potential routes for initiation of grafting. There are several ways by which such treatment can be made and some of them are ozonation [243-245], diazotization [246-248] and xanthation [248-250].

1.7.9 Grafting initiated by mechanical degradation

When a polymer is subjected to an applied shear or stress, the polymer absorbs and stores the mechanical energy in its molecular frame work, as a result of which deformation takes place in the polymer molecule. If the applied stress is sufficiently large, primary bond rupture may take place in the polymer molecule leading ultimately to the formation of the radical fragments which may then react with monomer resulting in the formation of a graft copolymer [251-254].

1.7.10 Plasma radiation-induced grafting

Plasma polymerisation has become relatively very important in recent days. Plasma conditions attained through slow discharge offer about the same possibilities as put forward by ionizing radiation. The accelerated electrons from the plasma have sufficient energy to induce cleavage of the chemical bonds in the polymeric structure to form macromolecular radicals which subsequently initiate graft copolymerisation of vinyl monomers [255-257]. The characteristic feature of this process is that the radiation effect is more limited to the surface than in depth when compared to the more penetrating high energy radiation. Therefore the plasma treatment process would be ideal for surface modification through grafting [258].

1.7.11 Photo-induced grafting

When a macromolecule absorbs light, the result is the formation of an excited state of the molecule. Such an energy rich molecule can either dissociate into reactive free radicals or dissipate its energy

by fluorescence etc. If the former process is operative, the resultant free radical formed in the polymer backbone can be used to initiate copolymerisation. Photosensitizers also were used for the graft copolymerisation reaction of cellulose [259-260].

The photoinduced graft copolymerisation process has been utilised for the grafting of various monomers onto cellulose [261-266]. Takahashi et al exhaustively studied on photoinduced graft copolymerisation of cellulose and cellulose derivatives [267,268].

1.7.12 High energy radiation induced grafting

The use of high energy radiation for the preparation of graft copolymers began to be explored easily in the nineteen fifties and has since then been investigated in great depth [269-272]. Irradiation of organic macromolecules leads predominantly to the formation of free radicals. The free radicals, peroxides, and hydroperoxides formed or trapped in polymeric substrates upon irradiation can be used quite conveniently to initiate block and graft copolymerisation. Three general methods have been successfully developed.

- a. The mutual or simultaneous grafting method
- b. The pre-irradiation grafting method, and
- c. The peroxidation grafting method

There are excellent reviews on radiation grafting of cellulose [269,271,272] and a detailed discussion is beyond the scope of this study.

1.7.13 Free radical grafting without using a free radical initiator

Though an initiator is essential to produce free radical sites into the polymer substrate to initiate graft copolymerisation, a few radical reaction may occur without using a free radical [273-275]. The probable mechanism for such a process has been thought to be due to the formation of a three component complex comprising substrate, water and monomer, which is subsequently rearranged to provide the requisite free radical site with the liberation of atomic hydrogen.

1.8 PROPERTIES AND APPLICATIONS OF CELLULOSE GRAFT COPOLYMERS

Table 1.4 summarises properties and applications of cellulose graft copolymers.

Table 1.4: The main type of cellulose graft copolymers which have found practical application and their uses

Polymer used for grafting	Properties of cellulose graft copolymer	Field of application	References
1	2	3	4
1. a. Polyacrylonitrile	Wool-like appearance; improved resistance to microorganisms, light and wear	Knitted goods, rain coats, tents and textiles	276-278
b. Partially hydrolysed	Poly electrolytes	Non-ionic surfactants and stabilizers	279-280
c. Polyacrylonitrile containing glycol dimethacrylate	Absorption of organic matter	Polymeric absorbent	281

1	2	3	4
2.	Poly(methyl vinyl pyridine)	Decorating and facing materials, theatrical decorations	282-286
a.	Phosphate salt	Non-flammable	
b.	Quaternary salt (eg. with dimethyl sulphate)	Strong anion exchanger and complex compound former	Adsorption of ions, complex formers, dyeing of food products etc. 287-290
c.	Bases	Weak anion exchanger	
3.	Poly(acrylic acid) Poly(methacrylic acid)		
a.	in free state	Weak cation exchanger	Adsorption of metal ions, protein from food products etc. 291-292
b.	in form of calcium salt	Causes coagulation of proteins and blood clotting	Blood-clotting cloth (hemostatic) 293-294
c.	in the form of silver and copper salts	Bactericidal property (destroys bacteria)	Bed linen and underwear in clinics, lab. coats for doctors; work cloths in antibiotics factories and other special plants 295
4.	Poly(acrylamide) Poly(acrylic acid) sodium salt	Super water absorbents	Tampoons, sick bed sheets, other sanitary products 296-300
5.	Phosphorus-containing vinyl polymers	Non-flammable chelating agent	Decorating and facing materials theatrical decoration and adsorption of ions 301

1	2	3	4
6.	Flourine-contai- ning polymers	Water proof and oil resistant properties	Work cloths for works of different trades, tarpaulins, rain coats 302- 304
7.	Polyisoprene and other polyolefins	Hydrophobic (water proof) acid proof	Industrial goods using for oil absorbancy 305- 307
8.	Polypeptide chains or amino acid	Antithrombogenic properties, optical resolution of recemic mixture, perm-selec- tive biomembrane, controlled release drugs	Medicinal use, adsorbents for chromatographic optical resolu- tion of recemic mixture , bio- medical mate- rials; liquid crystalline polymer 308- 312
9.	Siloxane containing functional groups	Good selectivity and flux stability on separation of gases	Semipermeable membranes 313

1.9 SCOPE AND OBJECTIVE OF THE PRESENT WORK

It is clear from the preceeding discussions that recent develop-
ments in polymer science and technology have made available information
necessary for tailormaking polymers with any desired property for any
application and how it can be applied to bio-based systems to bring
out modifications in their structure and properties. This has given
rise to a resurgence of R & D activities all over the world to develop
high performance polymers from natural monomers and polymers. The
possibilities of developing such polymers from cardanol were discussed.

It was indicated that (1) eventhough cardanol possesses the required structural characteristics it has never been polymerised using a free radical initiator, and (2) there is no report existing on grafting of cardanol onto another polymer although such as grafting is expected to give rise to useful properties. So it would be interesting and useful to undertake studies for:

1. Introducing free radically polymerisable vinyl moieties by chemical modification through hydroxyl group.
2. Grafting of cardanol onto another polymer. In this case cellulose has been selected as the polymer because (i) it is a natural polymer abundantly available, (ii) it is amenable to chemical modification, and (iii) high performance properties can be introduced by appropriate modifications.

While studying the grafting reactions onto cellulose, it was found that the xanthate of cellulose is photocleavable and attempts to graft cardanol by this technique failed (may be due to the radical scavenging activity of the phenolic group of cardanol). In order to study the feasibility of the photo-induced grafting of cellulose xanthate, another synthetic monomer MMA was selected for the present study.

Therefore the objectives of the present study are:

1. Synthesis and characterisation of free radically polymerisable monomers, cardanyl acrylate and cardanyl methacrylate from cardanol. Its polymerisation to poly(cardanyl acrylate) and

poly(cardanyl methacrylate) and preparation of crosslinked polymer beads.

2. Autoxidation studies of poly(cardanyl acrylate) and poly(cardanyl methacrylate).
3. Kinetics of cure reaction and kinetics of thermal decomposition of poly(cardanyl acrylate).
4. Cationic graft copolymerisation of cardanol onto cellulose.
5. Photo-induced grafting of methyl methacrylate (MMA) onto cellulose.

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CHAPTER 2

MATERIALS, EXPERIMENTAL TECHNIQUES: GENERAL

2.1 INTRODUCTION

In this chapter, a brief description of the reagents employed for the synthesis of the monomers, polymers and also the analytical and physical measurements used for the characterisation of the monomers and polymers are presented. This includes general methods used for the characterisation of polymers with a view to arriving at information on the nature and structure of the backbone and the functional group and the way they are arranged, molecular size, surface morphology, and thermal behaviour. A description of the instruments used and procedural details are also given here. Further experimental details and specific synthetic procedures for the monomers and polymers are given in appropriate chapters.

2.2 CARDANOL

Cardanol was supplied by M/s. Satya Chemicals, Madras, India, and was purified by distillation at 228-235⁰C under vacuum of 3-4 mm Hg [1]. The fraction having a refractive index of 1.509 and Brookfield viscosity of 45-52 Cps at 30⁰C was collected and used for further experiments.

2.3 CELLULOSE

Sheets of Whatman filter paper (No.1 and 41) were used as

the starting cellulosic material without further purification. Whatman filter paper was used because it has high porosity and absorbability.

2.4 OTHER REAGENTS

The solvents used for the synthesis of monomers and polymers were purified by distillation following standard procedures [2].

2.5 PHYSICAL MEASUREMENTS

2.5.1 Spectroscopic methods

Ultraviolet (~~UV~~) spectroscopy: UV spectra of the samples were measured using a Hitachi-220 spectrophotometer with acetonitrile as the solvent.

Infra red (IR) spectroscopy: IR spectra of the monomers and polymers prepared were recorded on a Perkin-Elmer Model 882 spectrophotometer using KBr disc, neat or nujol smear techniques ($4000-400\text{ cm}^{-1}$).

Nuclear Magnetic Resonance (NMR) spectroscopy: ^1H NMR spectra were obtained on a Hitachi R-24B high resolution NMR spectrometer with CDCl_3 as solvent and tetramethylsilane (TMS) as internal reference.

2.5.2 X-ray diffraction (XRD) method

Unlike inorganic crystalline compounds, polymers in general do not have a perfectly ordered crystal lattice, rather it comprises of both crystalline and amorphous regions. As a consequence, the x-ray diffraction from them are found to be a mixture of sharp as well as diffused patterns [3]. Cellulose gives well defined XRD patterns

which can be used for its identification.

In the present study, XRD patterns were taken in a Philips Model PW-1710 X-ray diffractometer with $\text{CuK}\alpha$ radiations using nickel as filter at a setting of 40 KV and 20 mA. XRD of the polymer films and cellulose (filter paper) was taken by inserting the samples directly in the sample holder.

2.5.3 Gel permeation chromatography (GPC)

Gel permeation chromatography or size exclusion chromatography (SEC) is the widely used method for estimating molecular weight and molecular weight distributions [4]. In the present study, the GPC data were obtained using Hewlett-Packard 1081B HPLC, equipped with an automatic sample injection system and a differential RI detector. The GPC columns used in this work were styrene-divinyl benzene copolymers based microstyragel 100 and 500 Å (Waters Associates) connected in series. An additional column with a large porosity (10^3 Å) was used along with the present set of columns which were calibrated by the linear calibration method (least-square approximation) with monodisperse polystyrene standards, supplied by M/s. H. Knauer & Co., West Germany. Polystyrene standards used had molecular weight in the range of 800-19000 with a polydispersity of 1.08 ± 0.02 .

2.6 MICROSCOPIC TECHNIQUES

Microscopic techniques are used for studying the shape, size, and morphology of polymers [7,8]. Both optical and electron microscopy used for this purpose. While optical microscopy can be

used for measuring the size and shape, electron microscopes (both transmission and scanning) give information regarding morphology also.

In the present study, the scanning electron microscope manufactured by JEOL was used (Model JEOL 35 C). The electron gun is operated at an electron energy of 15 or 20 KeV with a beam diameter of 20-25 nm. The surface of the sample was coated by sputtering with gold (10-20 nm thick) using ion sputtering equipment (JEOL, Fine Coat, JFC 1100 Japan) to make it conductive. The unit is operated at 1 KV and 10 mA current. Initially the bell jar is evacuated to 10^{-4} torr pressure and then the samples are sputtered. The gold coated samples were mounted in the chamber and the system was evacuated. The electron beam is scanned on the samples and the samples are photographed at appropriate magnifications. The polymer beads and grafted polymer samples were mounted on the stud using a suitable adhesive, glue stick or quick fix.

Optical photographs of the polymer beads were taken using a Nikon HFX phase contrast microscope. The unsieved samples were spread on a glass slide and photographs were taken at different magnifications under polarized light.

2.7 THERMAL ANALYSIS

Thermal analysis is a general term which covers a group of related techniques in which the temperature dependence of any physical property of a substance is measured [7]. The physical property is determined as a function of temperature. Among these methods, thermogravimetric analysis (TGA), differential thermal analysis (DTA) [10] and

differential scanning calorimetry (DSC) are important [8,9,10]. In TGA, the mass of a material is determined as a function of time and temperature, while in the case of DTA, differential temperature due to endothermic or exothermic transition or reaction in the sample is plotted as a function of time or temperature with respect to an inert reference powder (eg. alumina). 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 kept at the same temperature throughout and subjected to a controlled temperature programme. DSC is usually used for enthalpy change determination. DSC measurements are considered to be more quantitative than DTA and therefore, the former is more accurate wherever small energy changes are measured. (Thermochemical methods give information due to decomposition of material, oxidation or vaporization, phase transition, reaction, vitrification, crystallization etc.)

The TG-DTG and DTA curves were recorded using a Du Pont Model 2000 thermal analyst in conjunction with 951 thermogravimetric analyser and 1200 DTA cell using a platinum crucible. The experiments were carried out in pure nitrogen or air at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ at various heating rates.

Differential scanning calorimetry (DSC) curves were recorded using a Mettler TA-3000 thermal analysis system equipped with DSC-20 standard cell and TC-10 A TA processor coupled with a Swiss Matrix Printer. The heat flow measurement and temperature calibration were

done using Indium metal as per the recommended procedure given by the manufacturer. Experiments were carried out in air at a rate of $50 \text{ cm}^3 \text{ min}^{-1}$. Aluminium sample pans (40 μ lit) were used for the DSC experiments.

2.7.1 Treatment of data

From the recorded TG-DTG curve, fractional decomposition α was calculated and tabulated as a function of temperature [11]. The values of the procedural decomposition temperature (T_i), the final temperature (T_f) and the DTG peak (summit) temperature (T_s) were noted from the respective curves.

2.7.2 Computational work

Since the manual plotting of data can lead to subjective bias and personal errors, all the curve fittings and subsequent treatment of kinetic data were done using a computer (similarly, area integration for DSC curves was carried out using the Thermal Analysis Software provided by Mettler). The linear curves were drawn by the method of least squares and the corresponding correlation coefficients were calculated as it is an index of the linearity of the curves. All the computation work was done on an IBM-PC/XT using FORTRAN 77 programme.

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P a r t A

CHAPTER 3

FREE RADICALLY POLYMERISABLE MONOMERS FROM CARDANOL: SYNTHESIS AND CHARACTERISATION OF POLY(CARDANYL ACRYLATE) AND POLY(CARDANYL METHACRYLATE) AS CROSSLINKED BEADS*

3.1 INTRODUCTION

There has been much interest in recent years on chemical modification of bio-based materials for imparting speciality functions and properties so that polymers with specific performance profiles could be tailormade [1-2]. Naturally existing monomers and polymers, thus could be transformed into high performance materials to meet specific property requirements [3]. There are quite a good amount of data on the transformations of natural polymers as already mentioned in the introductory chapter, but the literature concerning chemical modifications and polymerisation of bio-monomers is rather limited. A glance through the literature indicate that there exists a wide variety of polymerisable bio-monomers having structural features for imparting speciality properties [4]. Among these bio-monomers, cardanol obtained from the plant *Anacardium occidentale* L., has been shown to possess interesting structural features that can be easily functionalised and polymerised so that speciality properties could be introduced [5-7].

Cardanol is a monohydric phenol with a C_{15} side chain in the meta position and is obtained from technical grade cashew nut shell liquid (CNSL) by vacuum distillation at 3-4 mm Hg and the fraction

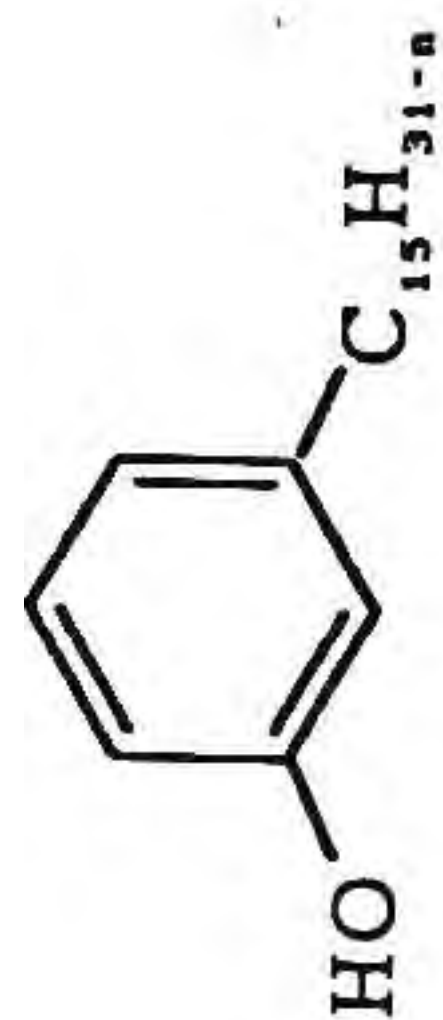
* This work has been partly published in:
Makromol. Chem. Rapid. Commun., **13** (1992) 255.

distilling at 228-235⁰ C was collected [8] (details of CNSL given in chapter 1). The physical properties of cardanol are tabulated in Table 3.1.

Table 3.1: Physical properties of cardanol

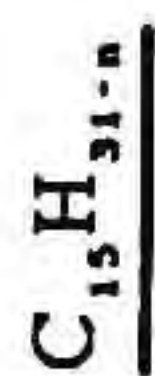
B.P. ⁰ C	228-235 ⁰ C (3-4 mm Hg)
Colour (Lovibond, 1 cm cell)	Red (1.0-3.0)
Freshly distilled	Yellow (1.5-3.5)
Viscosity 30 ⁰ C cP	45-52
Refractive index	1.509

Cardanol is a mixture of four components differing in the degree of unsaturation of the side chain (Figure 3.1) [5]. Molecular formula, molecular weight and percentage composition of each component of cardanol are given in Table 3.2. The percent composition however may vary depending upon the source, method of extraction etc. There have been many attempts to separate the components of cardanol and foremost among them is the work of Tyman [9-11] (see introduction for details). Attempts in this laboratory to separate the components of cardanol did not yield polymerisable quantities [12].



Cardanol

(mixture of compounds)



n=0	$-(CH_2)_{14}CH_3$	
n=2	$-(CH_2)_7CH=CH(CH_2)_5CH_3$	8'(Z)
n=4	$-(CH_2)_2CH=CHCH_2CH=CH(CH_2)_2CH_3$	8'(Z), 11'(Z)
n=6	$-(CH_2)CH=CHCH_2CH=CHCH_2CH=CH_2$	8'(Z), 11'(Z)

Fig. 3.1: Structure of cardanol

Table 3.2: Chemical composition of cardanol

Component	M.Wt.	%	Molecular formula
Cardanol with saturated side chain	304	5.4	$C_{21}H_{36}O$
Cardanol with one double bond in the side chain (monoene)	302	48.5	$C_{21}H_{34}O$
Cardanol with two double bond in the side chain (diene)	300	16.8	$C_{21}H_{32}O$
Cardanol with three double bond in the side chain (triene)	298	29.3	$C_{21}H_{30}O$

The structure of cardanol (Figure 3.1) was established through the painstaking efforts of a series of workers such as Dawson and Wasserman [13], Paul and Yeddanappalli [14], Tyman [15] and his group, Gedam et al [16] etc. One of the significant aspects of its structure as mentioned earlier is its amenability to chemical modifications and polymerisations. An examination of Figure 3.1 shows that cardanol can undergo chemical modifications at the hydroxyl group, substitution reactions on the phenolic ring, and oxidation/addition reactions at the side chain. The presence of active hydrogens of the phenolic ring and the unsaturation in the side chain make it polymerisable either by step reaction polymerisation or by chain reaction polymerisation or a combination of both as is being practiced in the preparation of

resins for brakelinings [17]. The presence of allylic structure in the side chain will induce oxidative coupling polymerisation that has been largely used in surface coating applications [18]. As discussed in the introductory chapter, cardanol, thus possess interesting structural features for development of speciality polymers.

One of the interesting features of the polymerisation of cardanol has been the fact that it resisted polymerisation by the conventional free radical initiation. Experiments conducted with initiators such as benzoyl peroxide, azobisisobutyronitrile and also with high temperature initiators such as cumenehydroperoxide, tert-butylhydroperoxide failed to initiate polymerisation. This could be understood from the radical scavenging activity of the phenolic moiety which is known to be an effective antioxidant [19]. This led to initiating work on introducing free radically polymerisable vinyl moiety by chemical modification of the hydroxyl group. Sitaramam and Chatterjee [20] reported that hydrogenated cardanol modified with acrylate/methacrylate moiety on polymerisation gives rise to pressure sensitive adhesive property. It occurred to us that conversion of cardanol into an acrylate/methacrylate monomer might be more useful in terms of (i) cost effectiveness, (ii) preparation of crosslinked beads in the absence of crosslinking agents as a matrix for supported reactions, and (iii) as a comonomer-cum-crosslinking agent in copolymerisation reactions. This chapter, therefore, deals with the study on (a) synthesis and characterisation of cardanyl acrylate, cardanyl methacrylate, and pentadecylphenyl acrylate as monomers, (b) their polymerisation characteristics,

(c) transformation of poly(cardanyl acrylate) and poly(cardanyl methacrylate) into crosslinked beads in the absence of any crosslinking agents and (d) a comparison of these polymers with the saturated analogue ie. poly(3-pentadecylphenyl acrylate).

3.2 EXPERIMENTAL

3.2.1 Materials

Acryloyl chloride: acryloyl chloride was prepared by the procedure of Stempel et al [21] and distilled before use.

A mixture of 72 g (1 mole) of acrylic acid, 280 g (2 moles) of benzoyl chloride and 0.5 g hydroquinone was distilled at a fairly rapid rate through an efficient 25 cm distilling column. The distillate at temperature between 60-80°C was collected in a receiver containing half a gram of hydroquinone immersed in ice. The crude product weighing between 75-78 g was then redistilled through the same column and fraction boiling 72-74°C at 740 mm was collected. The weight of the final product was 58-60 g.

Methacryloyl chloride: The same procedure as above was followed (86 g, 1 mole methacrylic acid) for the preparation of methacryloyl chloride. The fraction boiling at 92-96°C was collected.

Benzoyl peroxide (BPO): BPO was purified by recrystallisation from methanol.

Azobisisobutyronitrile (AIBN): AIBN was purified by recrystallisation from methanol.

Benzoin ethyl ether (BEE): BEE (Aldrich Chemicals) was used as such without further purification.

Poly vinyl alcohol (PVA): PVA (Nice Chemicals) was used as such supplied.

Hydroquinone: Recrystallised from water and was used.

Solvents used were purified by distillation.

3-Pentadecylphenol: Distilled cardanol was hydrogenated in a Paar medium pressure hydrogenator using the procedure described below. Cardanol 80 g (0.26 mol) was weighed into the hydrogenation flask, 50 mg of platinum oxide was added as catalyst and diluted with 50 mL of dry distilled methanol. The solution was washed with hydrogen by purging H_2 gas three times. The hydrogenation reaction was conducted at a pressure of 50 psi for 3 h. The black coloured solution obtained after the hydrogenation reaction was filtered through a sintered crucible using Whatman No.42 filter paper. The filtrate obtained was allowed to settle, decanted and concentrated in a rotavapor and distilled to remove any solvent present. The hydrogenated cardanol obtained was purified by distilling under reduced pressure. The fraction collected between $198-200^{\circ}C$ at 1-2 mm Hg. was twice recrystallised from n-hexane to give ($> 99\%$) 3-pentadecyl phenol. m.p. $50.5-51^{\circ}C$.

3.2.2 Methods

3.2.2.1 Synthesis of monomers

(i) Cardanyl acrylate (CA):

Cardanol (30 g; 0.1 mol) in toluene (200 mL) was taken in a three necked flask (500 mL) equipped with an efficient stirrer, a dropping funnel, and a Dean-Stark trap. An aqueous solution of sodium hydroxide (4.4 g, 0.11 mol in 5 mL H_2O) was slowly added to it while the solution was vigorously stirred and heated to reflux. Refluxing was continued upto the azeotropic removal of water was complete (3-4 h). The contents of the flask were cooled to $45^{\circ}C$ and hydroquinone (1% of the weight of cardanol) was added to it. Later freshly distilled acryloyl chloride (10.86 g, 0.12 mol) was added dropwise in the stirred solution. The reaction was monitored by TLC and the maximum conversion attained within 5 h reaction. The contents of the flask were filtered to remove the sodium chloride formed. The filtrate was freed from toluene under reduced pressure. The crude product was purified by column chromatography using hexane as eluting solvent.

Yield: 20 g (67%), n_D^{25} : 1.485

UV (CH_3CN): λ_{max} = 205 nm

IR (neat): 3020 ($-CH=CH-$), 1750 ($-C=O$) 1658 ($C=C$, acrylic)
1600 (Ar, $C=C$), 1290 (vinyl) and 1025, 980 cm^{-1}
(acrylic ester)

^1H NMR (CDCl_3) δ_{ppm} : = 0.8(t, CH_3), 1.11-1.5(m, $\{\text{CH}_2\}$),
 1.7-2.2(nr, $-\text{CH}_2-\text{CH}=\text{CH}-$)
 2.2-2.8 (nr, $-\text{CH}_2-\text{Ar}$)
 5.2-5.5 (m; $-\text{CH}_2-\text{CH} =$, $-\text{CH}=\text{CH}-$),
 5.7-6.6 (m; $-\text{CH}=\text{CH}_2$, acrylic) and
 6.8-7.3 (m, ArH)

(ii) Cardanyl methacrylate (CMA):

The same procedure as that for CA was followed using methacryloyl chloride (12.55 g, 0.12 mol), freshly distilled, in place of acryloyl chloride. The crude product obtained was purified by column chromatography using hexane as eluting solvent.

Yield: 22 g (73%), n_D^{25} : 1.487

UV (CH_3CN): λ_{max} = 206 nm

IR (neat): 3020 ($-\text{CH}=\text{CH}-$), 1740 ($-\text{C}=\text{O}$),
 1640 ($\text{C}=\text{C}$ methacrylic), 1600 (Ar, $\text{C}=\text{C}$),
 1290 (vinyl) and 1320 and 940 cm^{-1} (methacrylic ester)

^1H NMR (CDCl_3), δ_{ppm} : = 0.8 (t, CH_3), 1.11-1.5 (m, $\{\text{CH}_2\}$)
 1.84 (s, CH_3)
 1.7-2.2 (nr, $-\text{CH}_2-\text{CH}=\text{CH}-$),
 2.2-2.8 (nr, $-\text{CH}_2-\text{Ar}$)
 5.2-5.5 (m; $-\text{CH}_2-\text{CH}=\text{CH}-$, $-\text{CH}=\text{CH}-$),
 5.6-6.3 (s, $=\text{CH}_2$, methacrylic) and
 6.8-7.3 (m, Ar-H)

(iii) 3-Pentadecylphenyl acrylate (PPA):

The monomer (PPA) was prepared by the procedure reported earlier [20].

Yield: 20 g (67%), n_D^{25} : 1.482
 IR (neat) 3040 (acrylic vinyl unsaturation), 1750 ($-\text{C}=\text{O}$),
 1600 (Ar, $\text{C}=\text{C}$), 1025 and 980 cm^{-1} (acrylic ester)
 ^1H NMR (CDCl_3): δ_{ppm} : 0.8 (t, CH_3), 1.11 (m, $-(\text{CH}_2)_{13}$),
 2.2-2.6 (nr, $-\text{CH}_2-\text{Ar}$),
 5.1-5.4 (m, $=\text{CH}_2$), 5.6-5.9 (m, $-\text{CH}=\text{CH}-$),
 6.1-6.6 (m, Ar-H)

3.2.2.2 Synthesis of polymers

The polymers were prepared, following the general procedures i.e. (a) solution polymerisation, (b) bulk polymerisation, and (c) suspension polymerisation, as detailed below:

(a) Solution polymerisation

One molar solution of the monomer in toluene was used for the polymerisation reaction. 5 mL of the stock solution was pipetted into a 25 mL round bottomed flask and 0.5% (Wt/Wt) initiator, benzoyl peroxide (BPO), was added to the solution. The flask was closed with a rubber septum and then purged with pure argon to exclude any dissolved oxygen. The polymerisation was carried out in a thermostat at 80°C with constant stirring for 24 h. The reaction mixture was cooled to room temperature and poured into excess of methanol to precipitate the polymer. The polymer was purified by reprecipitation from acetone and dried in vacuum.

The yield and spectral data of the polymers are given below:

(i) Poly(cardanyl acrylate):

Yield: 1.25 g (70%)

IR (neat): 3020 (-CH=CH-), 1750 (-C=O), and
1600 cm⁻¹ (Ar, C=C)

¹H NMR (CDCl₃) δ_{ppm}: 0.8 (t, CH₃), 1.11-1.5 (m {CH₂}),
1.7-2.2 (nr, -CH₂-CH=CH-),
2.2-2.8 (nr, -CH₂-Ar),
5.2-5.5 (m, -CH₂-CH=, -CH=CH-) and
6.8-7.3 (m, ArH)

(ii) Poly(cardanyl methacrylate):

Yield: 1.4 g (75%)

IR (neat): 3020 (-CH=CH-), 1740 (-C=O) and
1600 cm^{-1} (Ar, C=C)

^1H NMR (CDCl_3) δ_{ppm} : 0.8 (t, CH_3), 1.11-1.5 (m, $\{\text{CH}_2\}$),
1.84 (s, CH_3), 1.7-2.2 (nr, $-\text{CH}_2-\text{CH}=\text{CH}-$),
2.2-2.8 (nr, $-\text{CH}_2-\text{Ar}$),
5.2-5.5 (m; $-\text{CH}_2-\text{CH}=\text{CH}-$, $-\text{CH}=\text{H}-$) and
6.8-7.3 (m, Ar-H)

(iii) Poly(3-pentadecylphenyl acrylate):

Yield: 1.4 g (75%)

IR (neat): 1750 (-C=O), 1600 (Ar, C=C)

^1H NMR (CDCl_3) δ_{ppm} : 0.8 (t, CH_3), 1.11-1.5 (m, $\{\text{CH}_2\}$),
2.2-2.6 (nr, $-\text{CH}_2-\text{Ar}$), 6.1-6.6 (m, Ar-H)

(b) Bulk polymerisation

1 g batch of monomer was used for the bulk polymerisation reaction. Benzoyl peroxide (BPO, 0.5 Wt/Wt-%) as initiator was added and purged with pure argon to remove the dissolved oxygen. The degassed sample was kept in a constant temperature bath with gentle shaking at 80°C for 10 h. The viscous or solid products thus obtained were washed free of monomers by precipitation and washing using acetone.

The yield and spectral data of the polymers are given below:

(i) Poly(cardanyl acrylate):

Yield: 0.959 (95%), Insoluble product

IR(KBr): 1750 (-C=O) and 1600 cm^{-1} (Ar, C=C)

(ii) Poly(cardanyl methacrylate):

Yield: 0.95 g (95%), Insoluble product

IR (KBr): 1740 (-C=O) and 1600 cm^{-1} (Ar, C=C)

(iii) Poly(3-pentadecylphenyl acrylate):

The polymer obtained was soluble in most of the solvents.

Yield: 0.7 g (70%)

Spectral data same as that of solution polymerisation products.

(c) Suspension polymerisation

The polymerisation was carried out either by thermal or photo-initiation.

Thermal: In a typical experiment, 50 mL of a 2 wt % poly vinyl alcohol (PVA) solution was used as the suspension medium. The monomer (1 g) and benzoyl peroxide (BPO) (0.8 wt % with respect to the monomer) as initiator were dissolved in 2 mL of chlorobenzene (diluent), and the monomer mixture was thoroughly flushed with nitrogen and was added to the degassed suspension medium, dropwise using a syringe, while stirring at a constant speed. The polymerisation was allowed to proceed for 5 h at 80°C in a thermostat. After that, the

suspension mixture was taken into water and stirred with a glass rod for a few minutes, allowed to settle, and then decanted. The beads were washed with distilled water, acetone, and dichloromethane to remove unreacted monomer and soluble polymers. Finally, the beaded polymers were filtered through a sintered glass funnel by applying suction and were dried in vacuum oven overnight at room temperature.

Photoinitiation: In photopolymerisation, benzoin ethyl ether (BEE) (10^{-2} molar of the monomer) was used instead of BPO as initiator. The reaction temperature was maintained at 30°C by circulating water. The polymerisation was carried out using a high pressure mercury UV lamp.

The beads of poly(cardanyl acrylate) PCA, and poly(cardanyl methacrylate) PCMA, were collected.

The suspension polymerisation method for the preparation of beads using 3-pentadecylphenyl acrylate was not successful in the absence of crosslinking agents. The spectral data of the polymer obtained by suspension polymerisation were identical with those of bulk polymerised products.

3.2.2.3 Swelling ratio measurements

Solvent imbibition of the crosslinked polymer beads was carried out using a centrifuge method [22]. A sample of the resin (1 g) was introduced into a glass disc of porosity No.3. The sample in the glass tube was weighed and then 15 mL of the solvent was added to the tube, which was closed with a rubber cerum cap to prevent solvent evaporation. It was kept at room temperature for 1 h to allow the solvent

to imbibe into the bead. Then, the sample was centrifuged at 500 rpm for 5 min using a laboratory centrifuge. After removing the excess solvent, the filter tube was weighed. Using this procedure, the swelling of the polymer beads in chloroform and toluene was carried out. The swelling ratio were calculated from the weight changes noted [23].

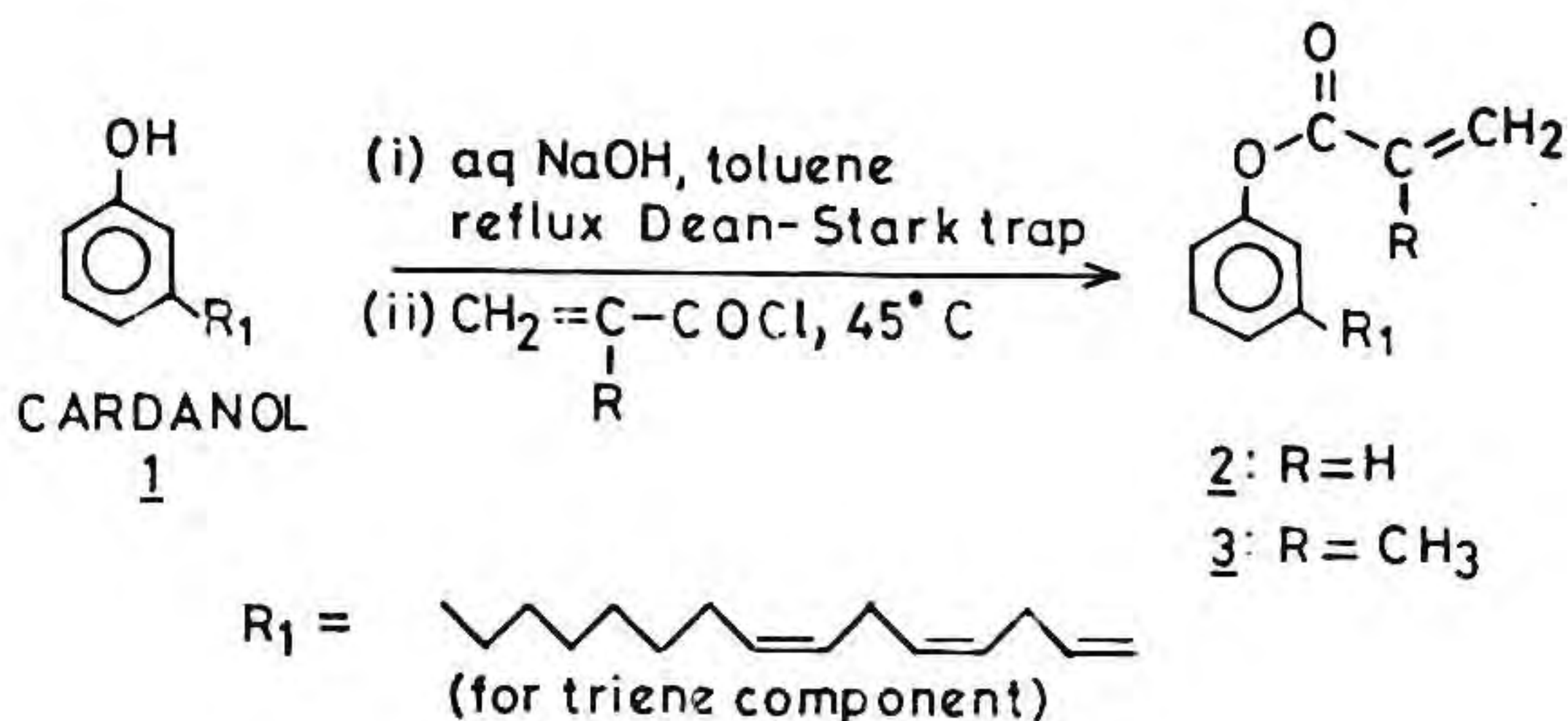
3.2.2.4 Instruments

IR spectra were recorded on a Perkin-Elmer Model 882 spectrophotometer. UV spectra were recorded on a Hitachi - 220 spectrophotometer with acetonitrile as the solvent. The ^1H NMR spectra were obtained on a Hitachi R-24B high resolution NMR spectrometer with CDCl_3 using tetramethyl silane as internal reference. Number- and weight-average molecular weights (\bar{M}_n and \bar{M}_w) were determined using GPC (Hewlett-Packard 1081 B HPLC equipped with RI detector). The polymer beads were observed with a transmission optical microscope Nikon HFX at various (20, 40 and 80) magnifications. Scanning electron micrographs of the polymer beads were taken on a Jeol-JSM 35 C instrument with the sample sputtered with gold. The refractive index values of the monomer samples measured using an Abbe refractometer. Further details regarding the instrumentation are given in chapter 2.

3.3 RESULTS AND DISCUSSION

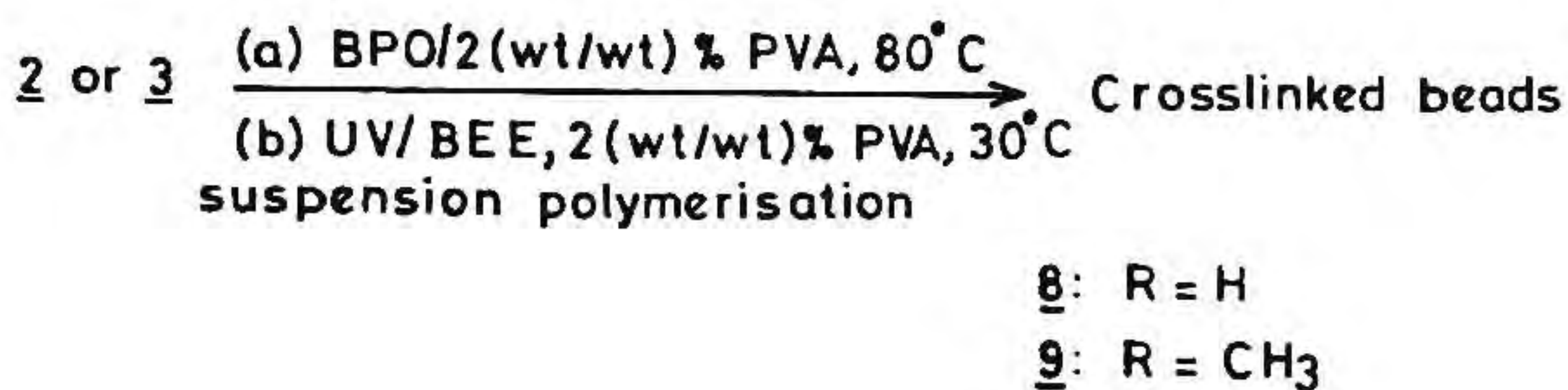
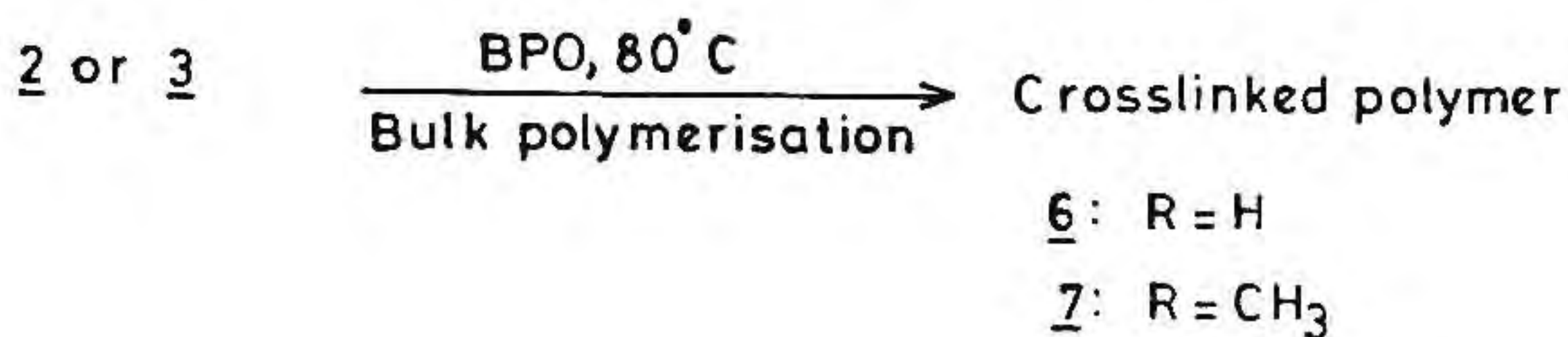
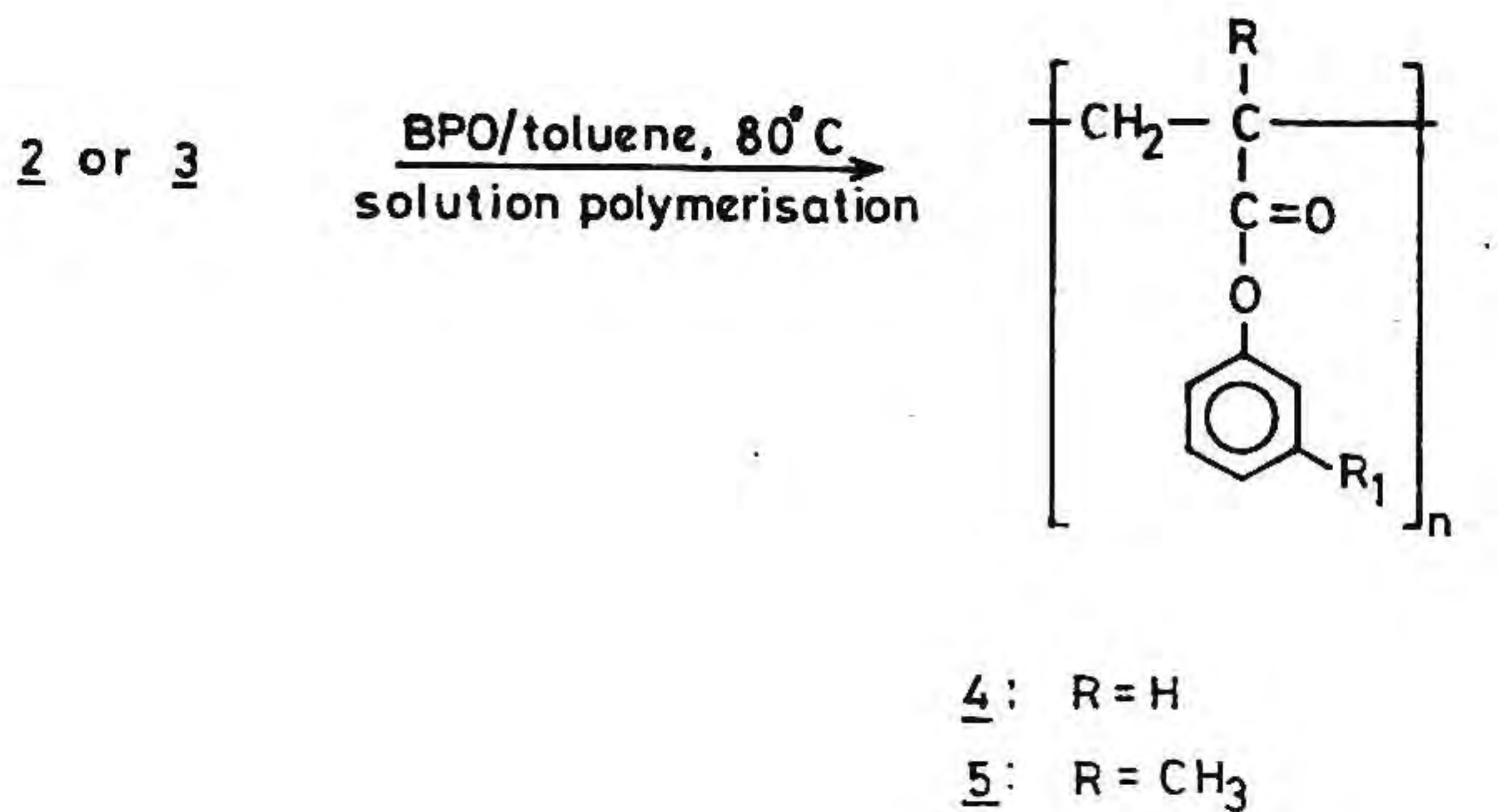
Cardanol on reaction with acryloyl chloride and methacryloyl chloride yields corresponding acrylate and methacrylate (Scheme 3.1). The monomers prepared, cardanyl acrylate 2 and cardanyl methacrylate 3 were stable and could be stored at 0°C for a few months without

undergoing any polymerisation reaction.



Scheme 3.1: Synthesis of monomers cardanyl acrylate (CA) 2 and cardanyl methacrylate (CMA) 3.

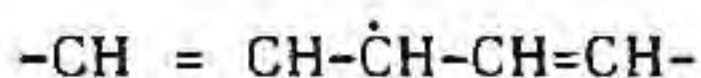
Generally, simple acrylic monomers undergoing free radical polymerisation reactions yield soluble polymers in the absence of crosslinking agents. But in the present case polymers prepared by solution polymerisation showed physical properties and spectral features different from those obtained by bulk and suspension polymerisation. The insoluble nature of cardanyl acrylate/cardanyl methacrylate polymers by bulk and suspension polymerisation can be due to crosslinking reaction as shown in Scheme 3.2.



Scheme 3.2: Polymerisation reaction of CA, 2 and CMA, 3.

3.3.1 Solution versus bulk polymerisation

The monomers 2 and 3 could be easily polymerised by solution polymerisation to yield a soluble polymer with an average molecular weight $\bar{M}_n=3000-5000$ and a weight-average molecular weight $\bar{M}_w=10000-15000$. This low molecular weight and the high molecular weight distribution may be due to the influence of the long unsaturated side chain of the monomer. This can be compared to the study of Harrison and Wheelers [24] who have shown that the degree of polymerisation decreases as the degree of unsaturation in the fatty vinyl monomers increases. In emulsion polymerisation using linoleate and linolenate soaps as surfactants, the isolated double bonds in the fatty chain retard the reaction. This is caused by the susceptibility of the allylic methylene hydrogen to abstraction by a growing free radical, together with the stabilisation of the resulting soap by resonance as follows:



The linolenate soap interferes with the vinyl polymerisation more than the linoleate soap. Port et al further confirmed that even 5% vinyl oleate in vinyl palmitate retards the polymerisation rate of the latter considerably [25].

The IR spectra of polymer 4 and 5 (Fig 3.2&3.2a) exhibit the characteristic stretching frequency of the ester group at 1750 cm^{-1} and

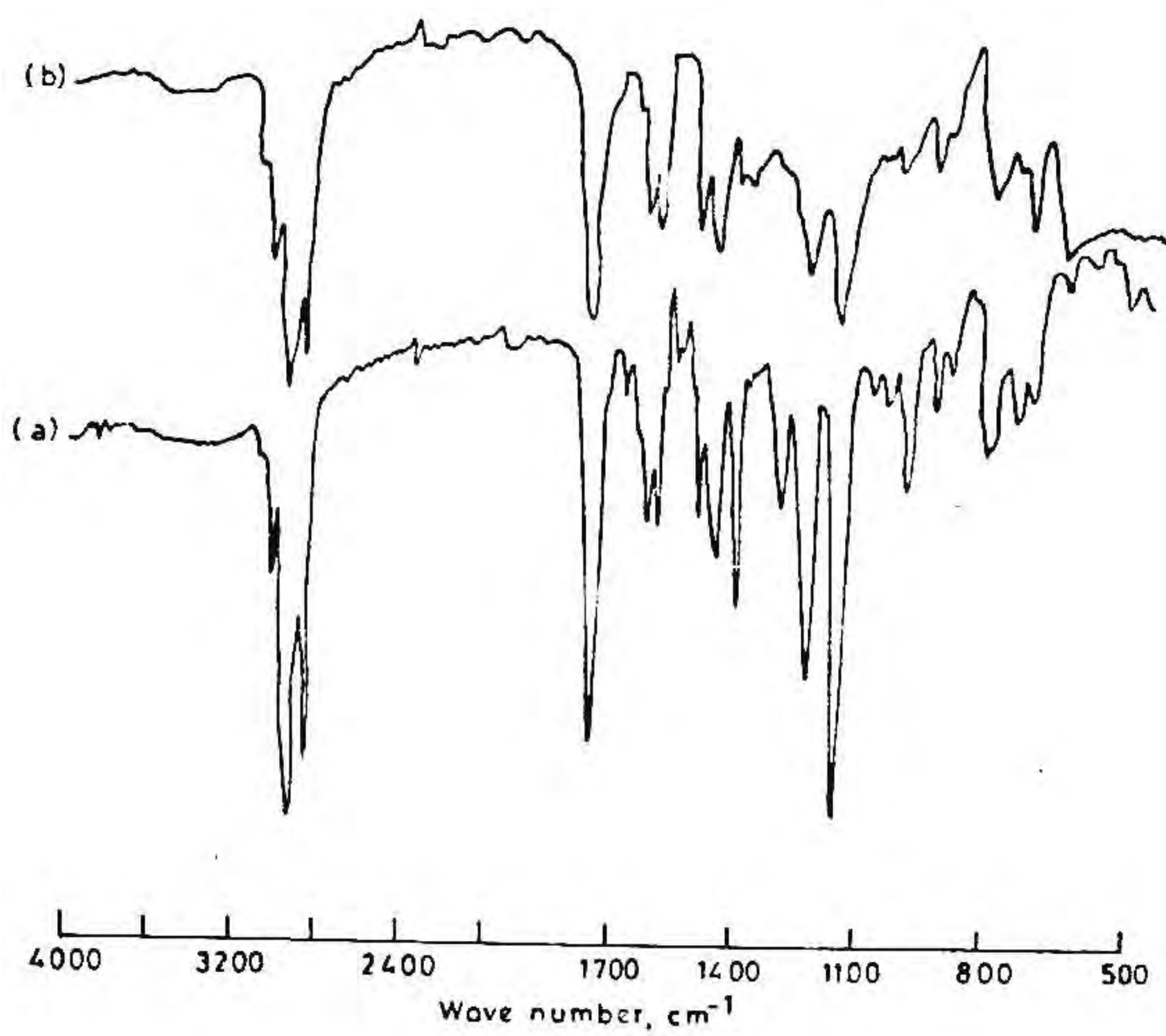
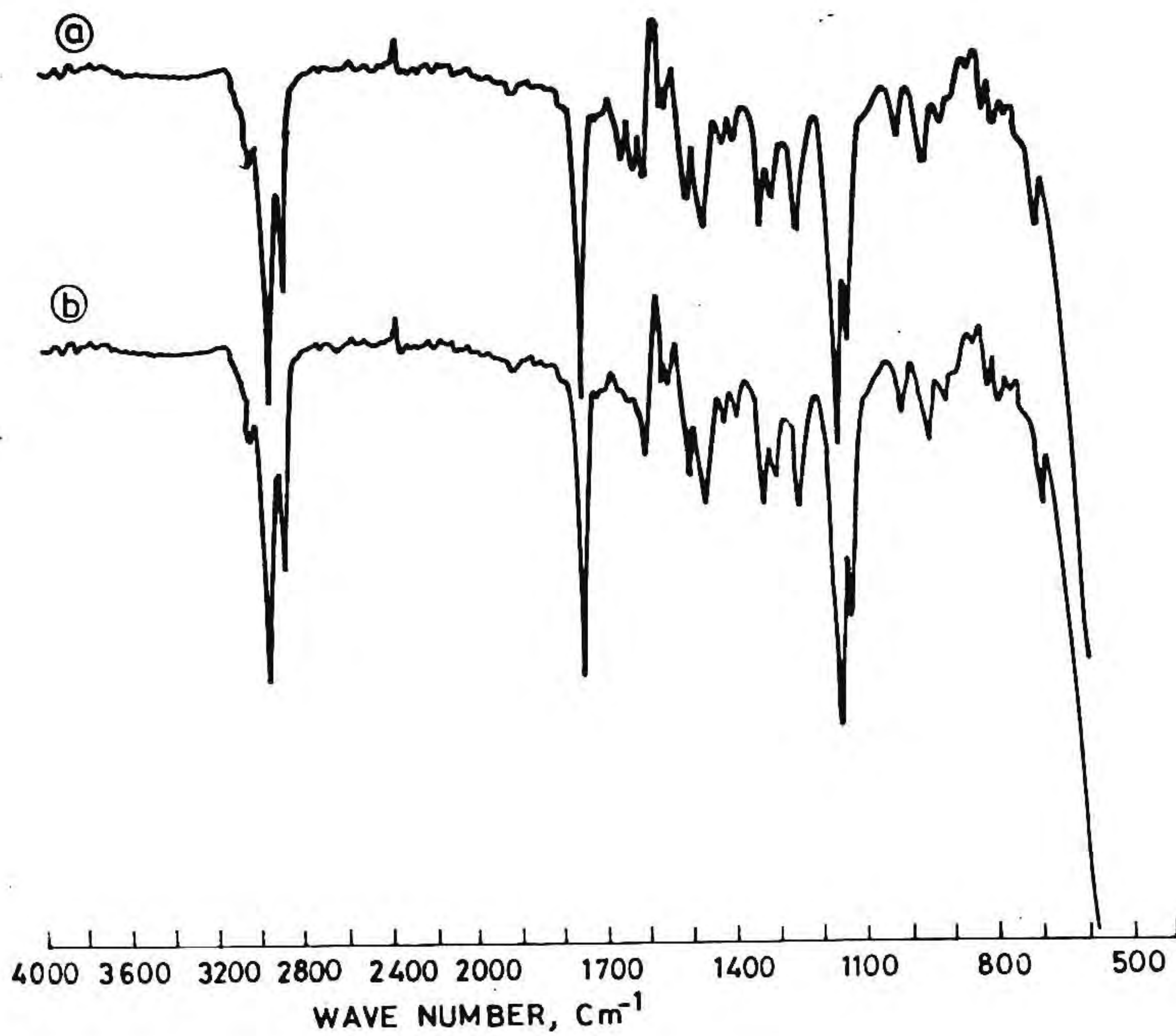


Fig. 3.2: IR spectrum of (a) cardanyl acrylate (CA) monomer, (b) poly(cardanyl acrylate)



• Fig. 3.2a: IR spectrum of (a) cardanyl methacrylate (CMA) monomer, and (b) poly(cardanyl methacrylate)

1740 cm^{-1} respectively. A sharp peak at 3020 cm^{-1} which is characteristic for a disubstituted olefinic bond, viz. $-\text{CH}=\text{CH}-$ might represent the stretching vibration of the unsaturated side chain (R1) of 1. This is further evidenced from the observation that this peak is absent in saturated cardanyl acrylate in which the side chain has no double bond. In the IR spectrum of the polymer, no peak was observed at 1658 cm^{-1} due to the conversion of acrylic $\text{C}=\text{C}$ to $\text{C}-\text{C}$. The polymers 4 and 5 on removal of solvent and keeping at ambient conditions for 12 h yielded a transparent film which is insoluble. This is typical of drying oils and might be caused by the well known autoxidation reaction at the unsaturated side chain present in the polymer. This phenomenon of autoxidation reaction will be described in detail in next chapter.

In contrast to the solution polymerised products, bulk polymerised systems were insoluble in almost all common organic solvents. The IR data also showed the absence of the characteristic absorption due to side chain unsaturation indicating that it takes part in polymerisation reaction possibly giving crosslinked structures. The formation of soluble polymers only in the case of 3-pentadecylphenyl acrylate as monomer confirmed this argument.

3.3.2 Suspension polymerisation

The beads of 2 and 3 were prepared in aqueous suspension medium at $80 \pm 1^\circ \text{C}$. Suspension was maintained by magnetic stirrer and with the help of suspension stabilizers. However, it was further

observed that same results were obtained even in the absence of suspension stabilizers. Details are given in Table 3.3. In the present work calcium phosphate was used as the stabilizer. Suspension polymerisation yields beads which are insoluble in organic solvents as in the case of bulk polymerised, crosslinked products. The resulting polymer beads were dried in vacuum and were sieved with mechanical sieves. Generally, the range obtained was 100-500 mesh (BSS). The polymer beads were characterised by IR, optical, SEM, and solvent imbibition studies.

Table 3.3: Suspension polymerisation of cardanyl acrylate (CA) and cardanyl methacrylate (CMA)

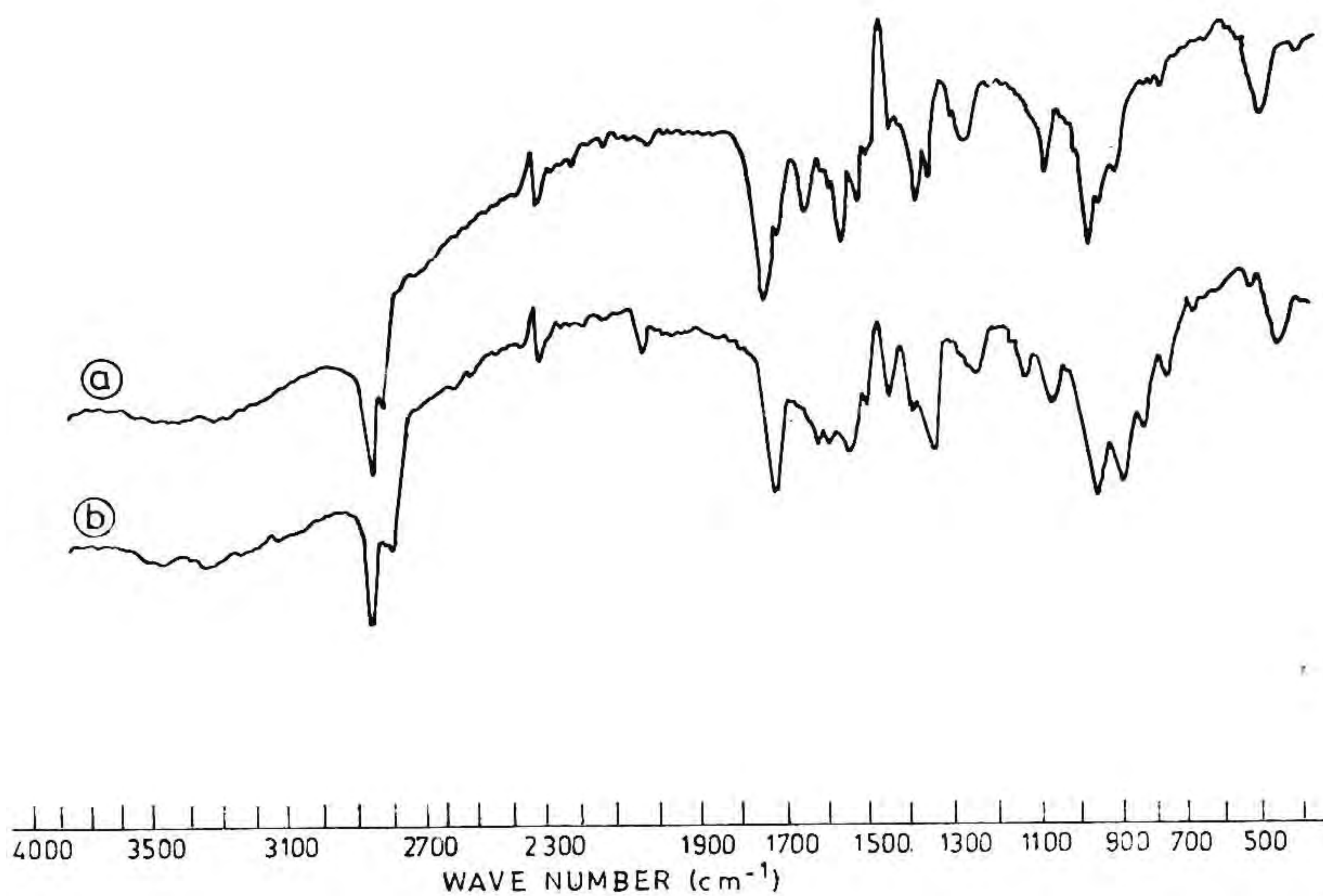
Polymer	Monomer (g)	Crosslink- ing agent (g)	Diluent (g)	Initiator (mg)	2% PVA in water (g)
Poly(cardanyl acrylate) PCA	1	0.0	2	20	50
Poly(cardanyl methacrylate) PCMA	1	0.0	2	20	50

3.3.3 IR spectroscopy

Infra red spectroscopy is the most widely employed technique not only for following the chemical reactions carried out on crosslinked polymers but also for structure identification. IR spectra of the polymers 6 and 7 (Figure 3.3) exhibit the characteristic stretching frequency of the ester group at $1750/1740\text{ cm}^{-1}$ respectively. The unsaturated side chain of the monomer has the grouping $-\text{CH}=\text{CH}-$ characteristic of olefinic double bonds which gives a sharp peak at 3020 cm^{-1} in the IR spectrum. As expected this peak was absent in the IR spectrum of the crosslinked beads suggesting that the side chain double bonds have got involved in the crosslink formation. It appears, therefore that, in solution, the polymerisation takes place through the acrylate group with the side chain double bonds of the monomers 2 and 3 remaining unchanged, but in suspension polymerisation, participation of the side chain of the 2 and 3 in the polymerisation is inferred because crosslinked beads were obtained.

3.3.4 Optical microscopy

The optical micrograph of the polymer beads is shown in Figure 3.4. Based on visual appearance, beads were classified as (1) transparent and (2) translucent. The optical photograph of the polymer beads 6 and 7 shows the spherical nature of the beads. It can be seen from the figure that different sizes (Figure 3.4) of the particles are formed in the course of polymerisation. The small size particles are seen in greater number, as the stirring rate employed



**Fig. 3.3: IR spectrum of crosslinked (a) poly(cardanyl acrylate),
(b) poly(cardanyl methacrylate) beads**

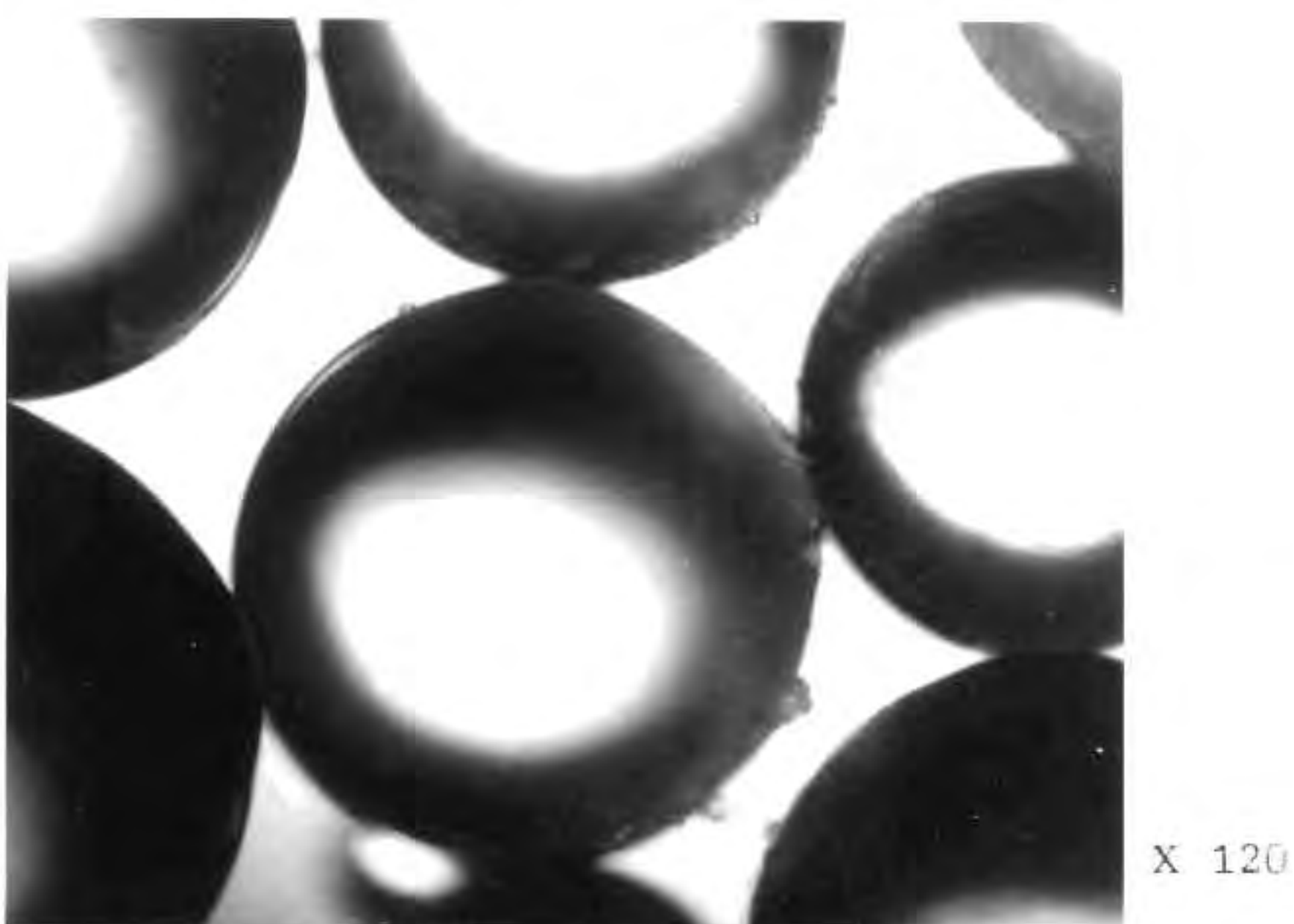
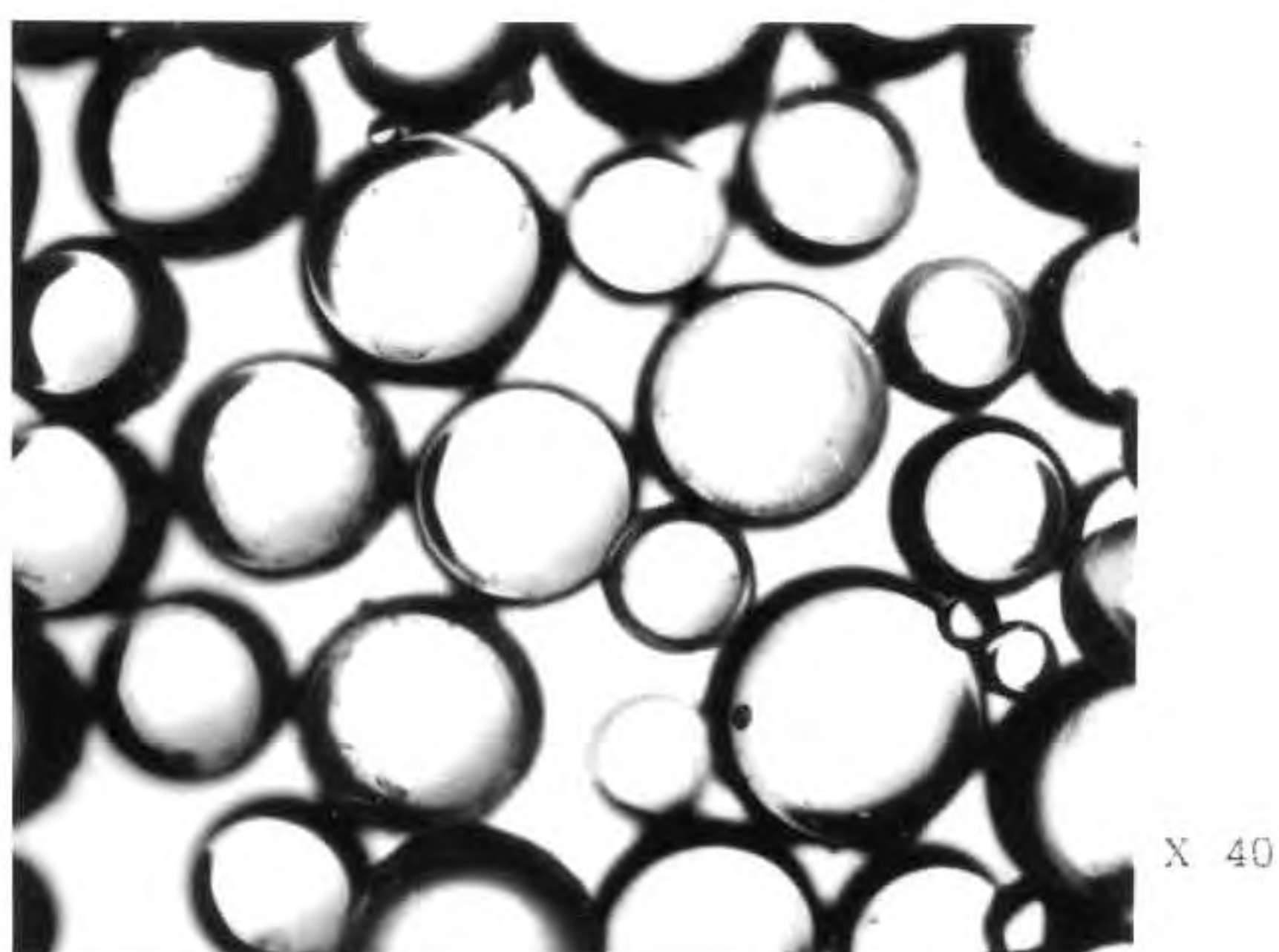
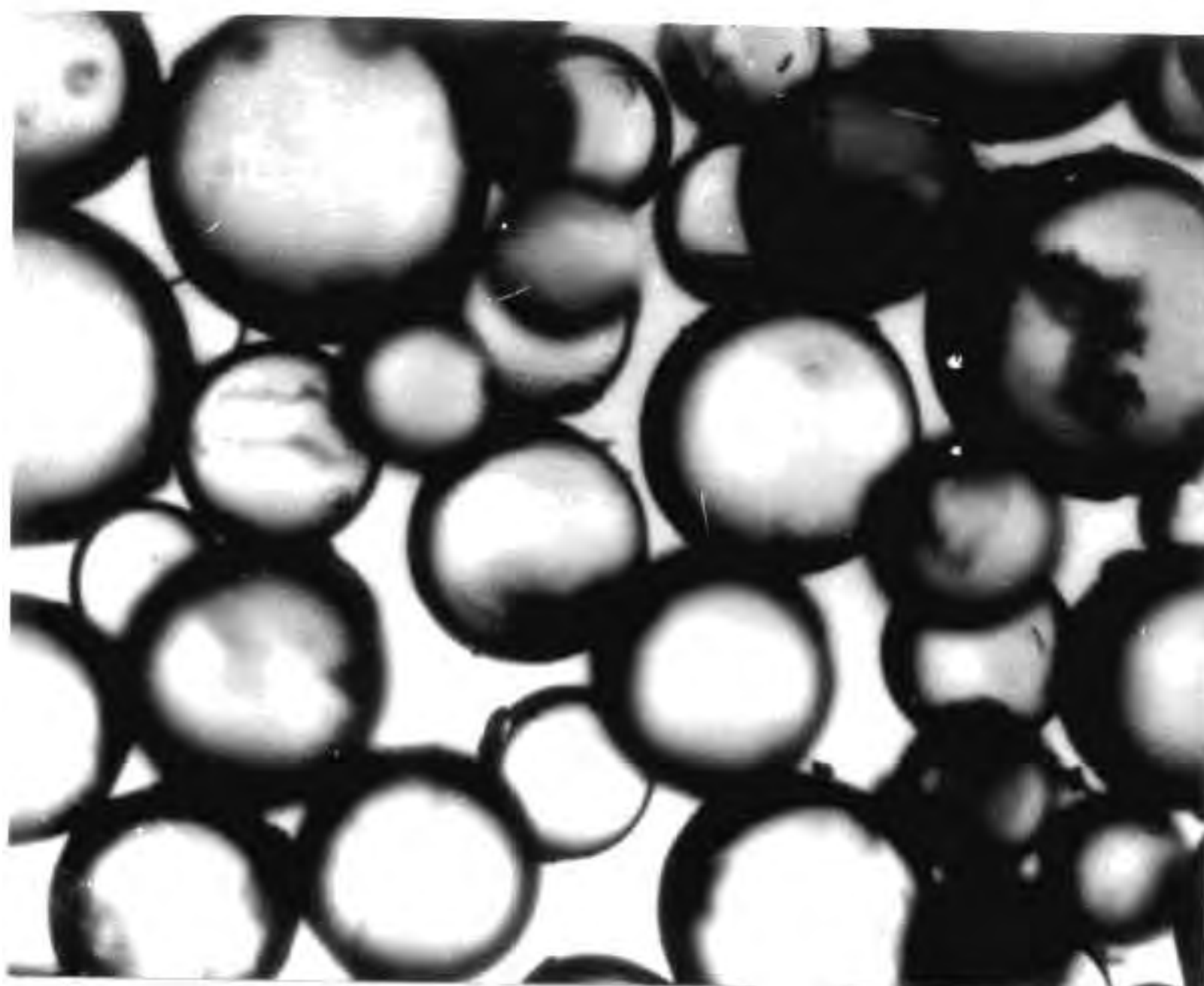
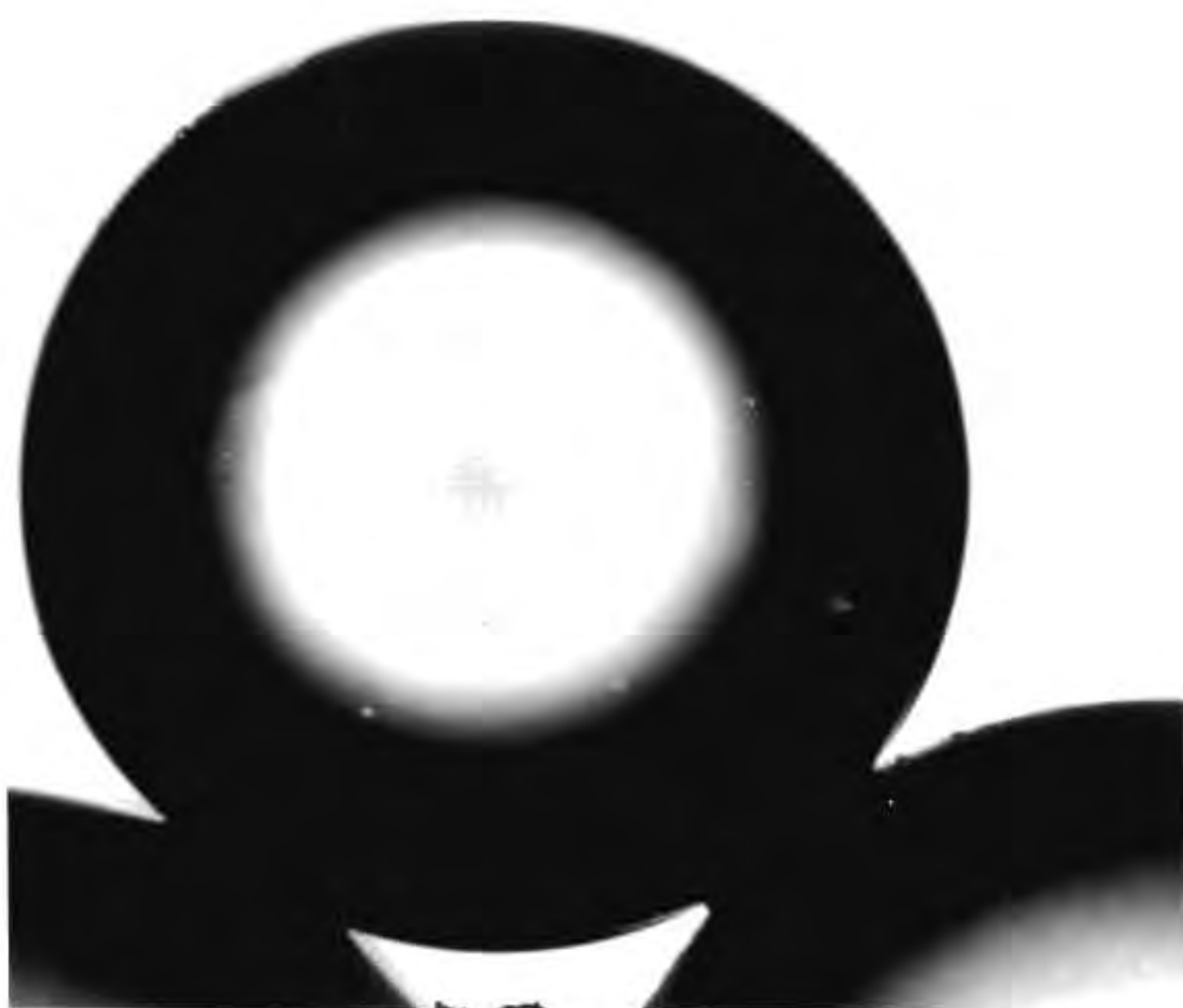


Fig. 3.4: Optical photograph of crosslinked poly(cardanyl acrylate) beads



X 40



X 120

Fig. 3.4: Optical photograph of crosslinked
poly(cardanyl methacrylate) beads

was high during the polymerisation. The transparent and translucent nature of the beads (Figure 3.4) obtained in the present experimental conditions demonstrate that the diluent employed in the synthesis of polymer beads is a good solvent [26].

3.3.5 Scanning electron microscopy

Scanning electron micrographs of the typical polymer beads are shown in Figure 3.5. The bead size, shape and surface can be observed from these micrographs. SEM was used for the determination of porosity characteristics of ion-exchange resins. Guyot et al [27] used the SEM technique extensively for studying the morphological features and the mechanism of formation of the beads. The micrographs show that almost all particles are perfectly spherical and almost uniform in their sizes and that the surface is even and smooth. The even and smooth surface of the particles also demonstrate that the monomer diluent is a good solvent for the resulting beads.

3.3.6 Swelling studies

One of the applications that could be thought for the use of the crosslinked beads of cardanyl acrylate and cardanyl methacrylate is in the area of polymer supports [28-31]. Among the factors that influence the accessibility of functional groups in crosslinked copolymers is the phenomenon of swelling. Generally the swelling properties of the polymer support depends on two factors, (i) crosslink ratio, and (ii) chemical nature of the polymer support employed. It is known from literature that microporous resins possess porosity only in a

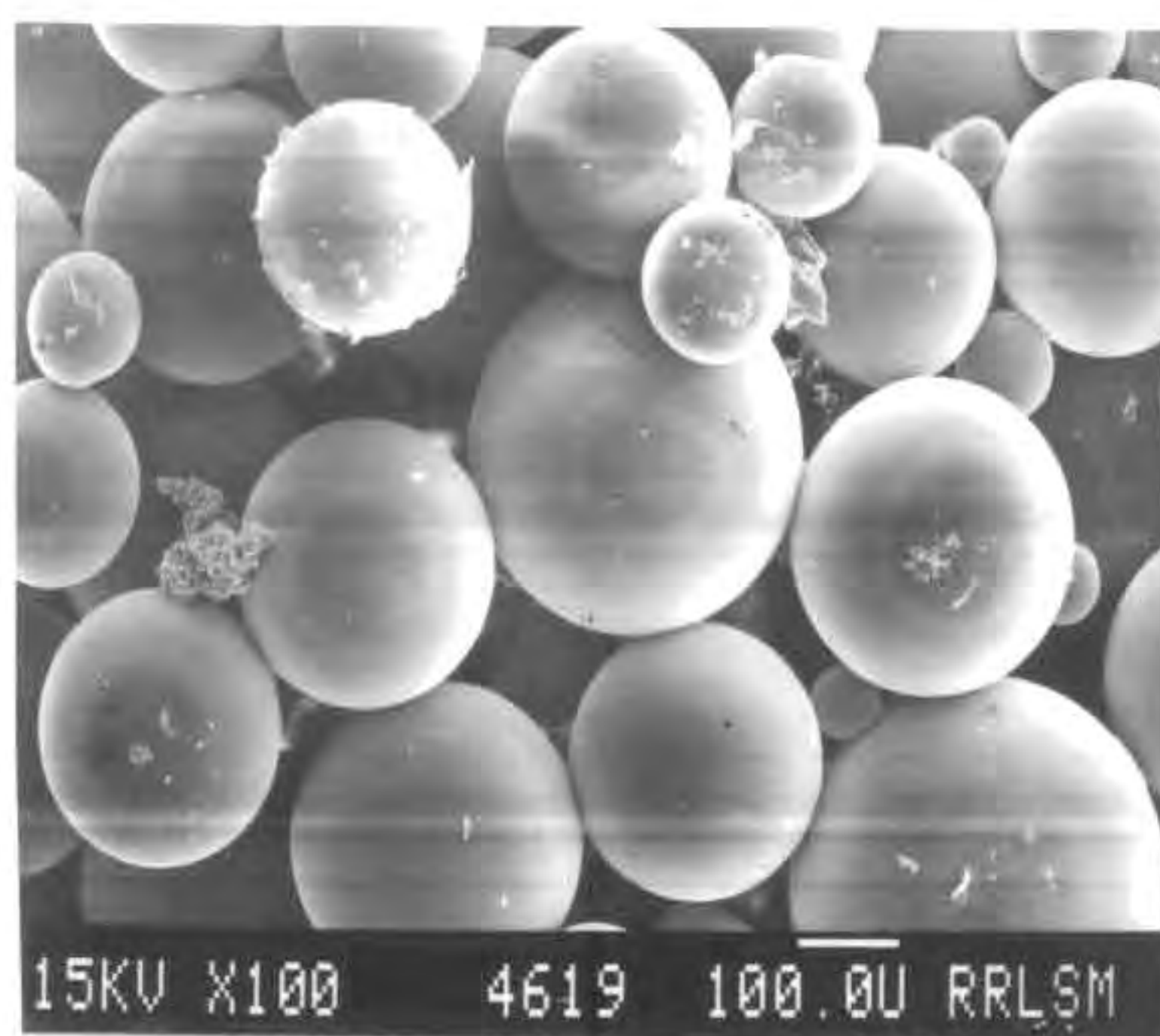
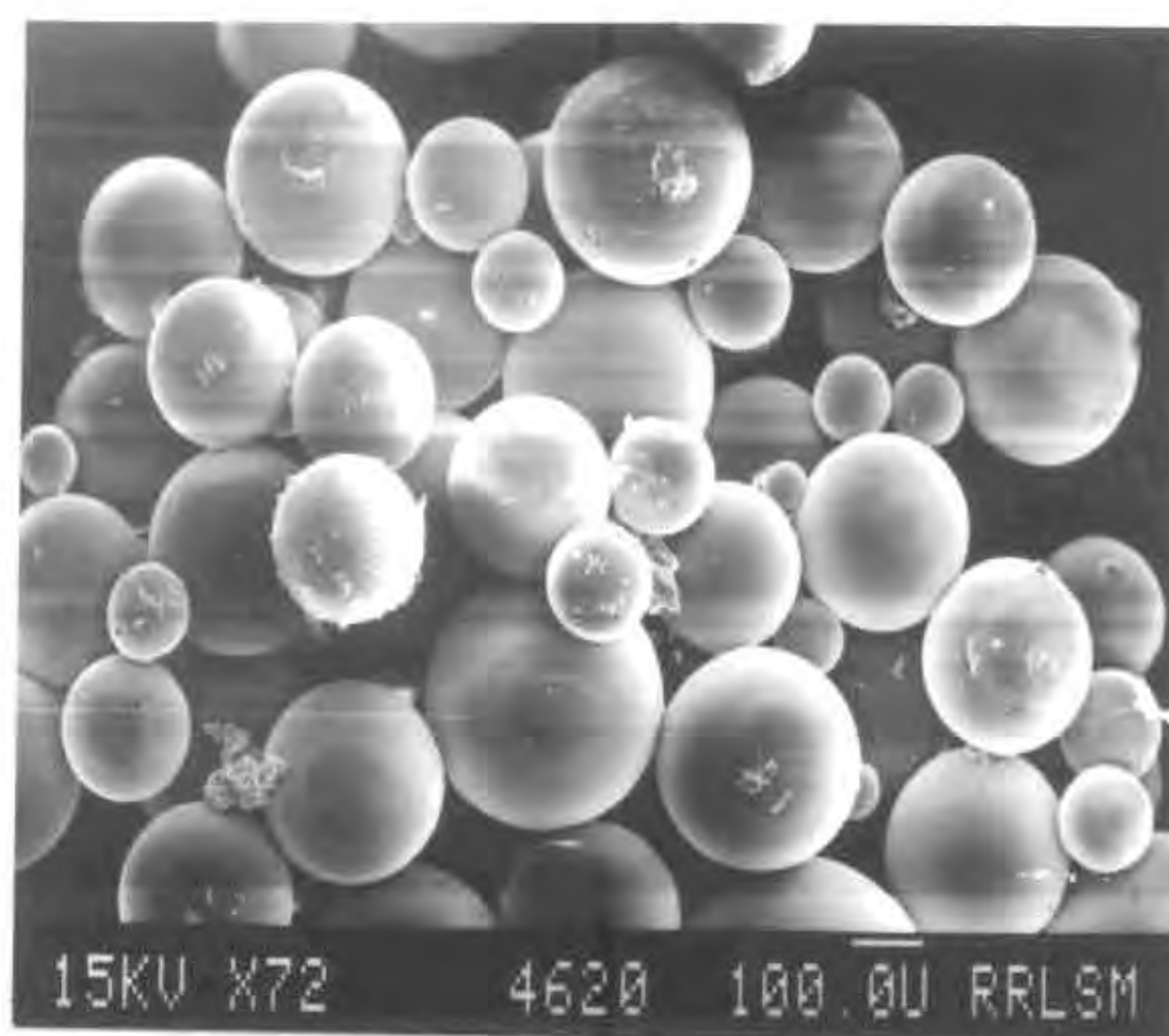


Fig. 3.5: Scanning electron micrograph of crosslinked poly(cardanyl acrylate) beads

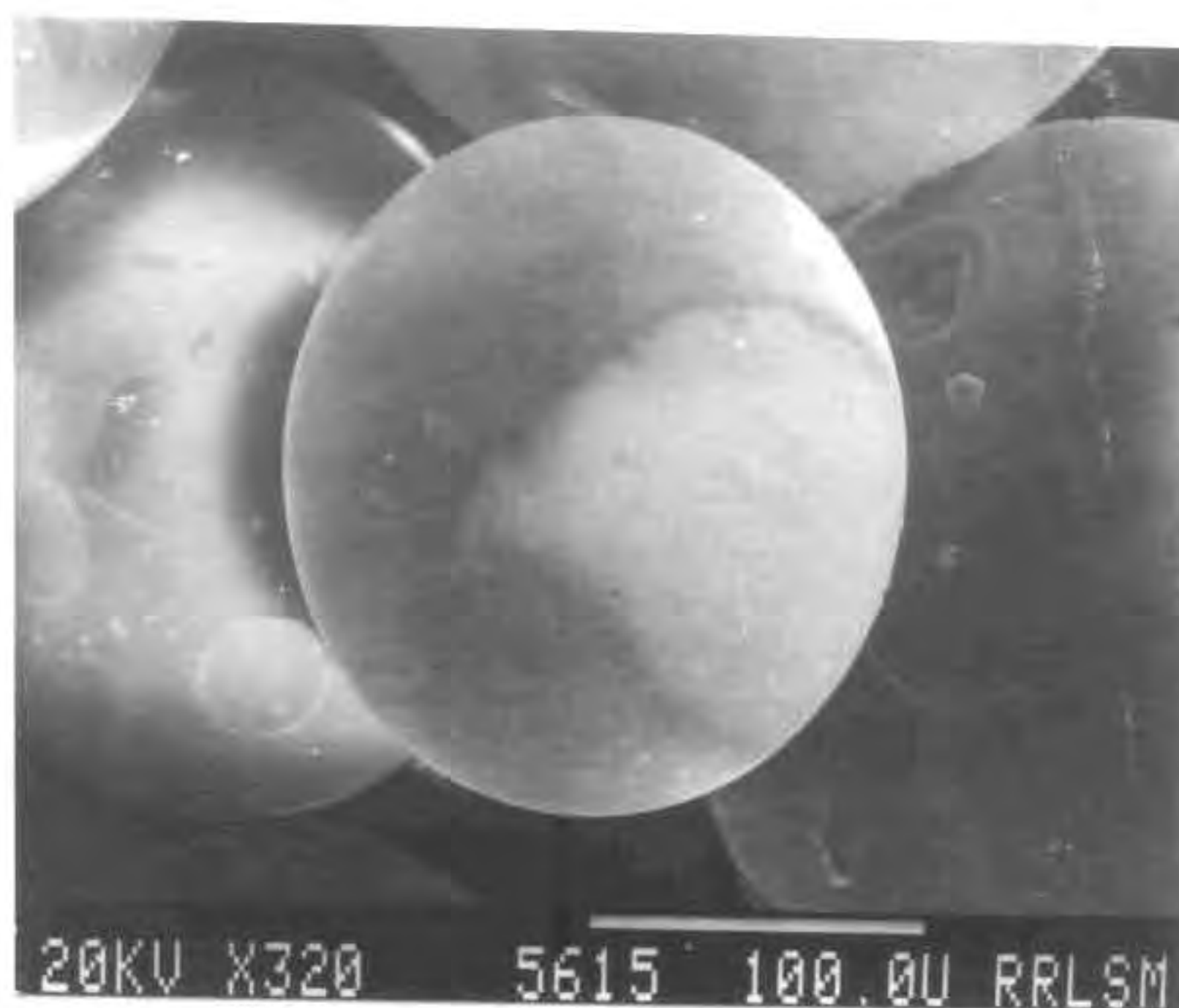


Fig. 3.5: Scanning electron micrograph of crosslinked poly(cardanyl methacrylate) beads

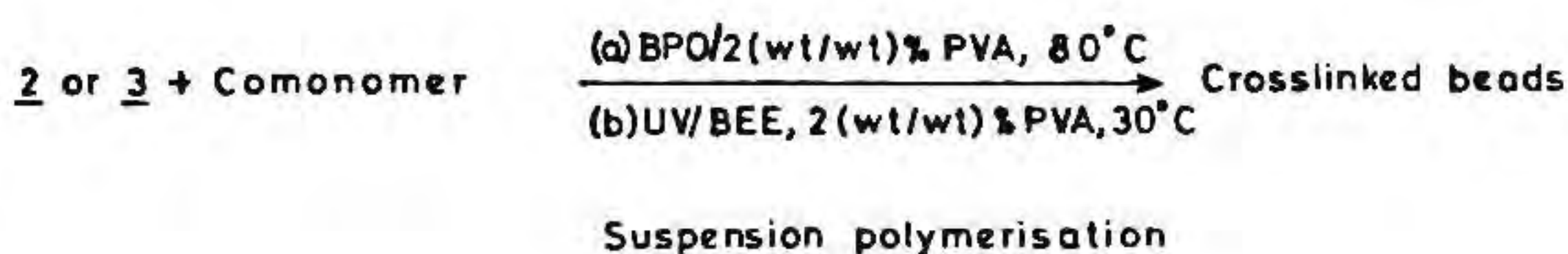
swollen condition and is called as gel porosity. Since the resins under study are microporous in nature, the swelling studies are important for identifying the good solvent in order to select the suitable reaction medium for performing reactions on polymer supports [32,33]. To investigate the swelling behaviour of these polymer beads, solvent imbibition studies were undertaken. (The samples were allowed to swell for 1 h, in chloroform, toluene, ethyl acetate and methanol which are common solvents used for the supported reactions.) (The excess solvent was removed by the centrifugal method, and the results were expressed as the weight of the solvent absorbed per weight of the dry resin. The swelling of the resin in chloroform, toluene and ethyl acetate are comparatively higher than that in the other solvents studied,) thereby showing the hydrophobicity of the supports (Table 3.4).

Table 3.4: Swelling studies of polymer beads

Polymer	Solvent (g)			
	Chloroform	Toluene	Ethyl acetate	Methanol
Poly(cardanyl acrylate) PCA	2.43	1.72	3.65	0.727
Poly(cardanyl methacrylate) PCMA	2.51	1.75	1.70	0.750

3.3.7 Copolymerisation studies

Preliminary studies have shown that monomers 2 and 3 were copolymerised with styrene or MMA in a suspension medium yielded uniform beads as in the case of suspension polymerised homopolymers of 2 and 3 (Scheme 3.3).



Scheme 3.3: Copolymerisation of monomers 2 and 3 with other vinyl monomers

3.4 CONCLUSION

Novel crosslinked polymer beads based on cardanyl acrylate 2 and cardanyl methacrylate 3 were synthesised successfully without using any crosslinking agents by employing aqueous suspension polymerisation technique. The polymer beads thus obtained were characterised

using different instrumental techniques. The swelling index indicates that the polymer beads studied in the present investigation are basically hydrophobic in nature and could be useful as a matrix for supported reactions. This is significant because interest has been expanding in the application of crosslinked acrylate polymer beads in packing materials for liquid chromatography and as a support for solid- or liquid-phase reaction. The monomers were also useful as comonomer-cum-crosslinking agent in vinyl polymerisation reactions.

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CHAPTER 4

STUDIES ON AUTOXIDATION OF POLY(CARDANYL ACRYLATE) AND POLY(CARDANYL METHACRYLATE)*

4.1 INTRODUCTION

Polymers of fatty acid/long chain acrylates and their copolymers with styrene, methyl methacrylate and other vinyl monomers have shown considerable promise as plasticizers, adhesives, chewing-gum bases and lubricating oil additives [1]. However, only a few attempts have been made to polymerise unsaturated fatty acrylates and methacrylates because unsaturation in the fatty chain adversely affects the polymerisation of these monomers [2-4]. This was clearly evident in the polymerisation of cardanyl acrylate 2 and cardanyl methacrylate 3, both possessing unsaturated fatty side chains in their structures. The side chain unsaturation in both the system was found to affect the polymerisation reaction and the nature of the end product formed. When polymerised in solution, both the monomers 2 and 3 gave only low molecular weight linear polymers contrary to the high molecular weight polymers reported by Sitaramam and Chatterjee in the case of pentadecylphenyl acrylate and methacrylate [5]. However, when polymerised in bulk/suspension 2 and 3 gave directly crosslinked transparent beads. Although no crosslinking was observed in solution polymerisation, the polymers on exposure to air was found to undergo crosslinking to give a transparent insoluble film. The transformation from the linear to the crosslinked network structure is thought to take place through the

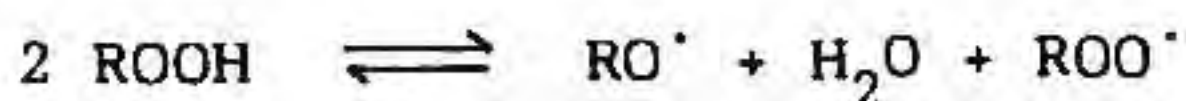
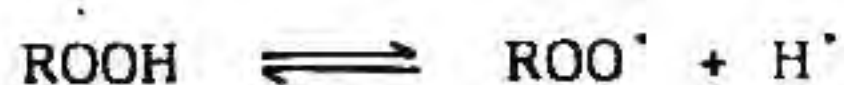
* Part of this work has been accepted for publication in:
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well known autoxidation reaction occurring as in the case of unsaturated fatty acids and related compounds through the unsaturated centers [6]. This chapter discusses autoxidation of poly(cardanyl acrylate) PCA, and poly(cardanyl methacrylate), PCMA and their curing mechanism.

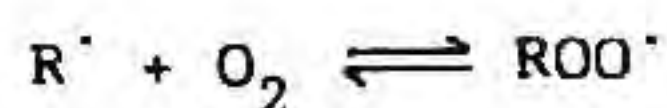
4.1.1 Autoxidation

The phenomenon of autoxidation is well known with systems such as linseed oil or resins containing unsaturated fatty acids [7-9]. In general, the term autoxidation refers to chemical reaction that usually takes place at ambient temperatures between atmospheric oxygen and an organic compound. Autoxidation is a phenomenon which concerns mainly with unsaturated compounds. When spread as a thin film, these materials absorb oxygen from air and changes from a liquid (viscous) state to a crosslinked network [10-11]. The process of such film formation involves production of peroxides and their decomposition leading to intermolecular bonding through oxygen-carbon and carbon-carbon bonds. A general description of the mechanism of autoxidation as being applied to unsaturated fatty systems is depicted as follows [11-12].

initiation



propagation

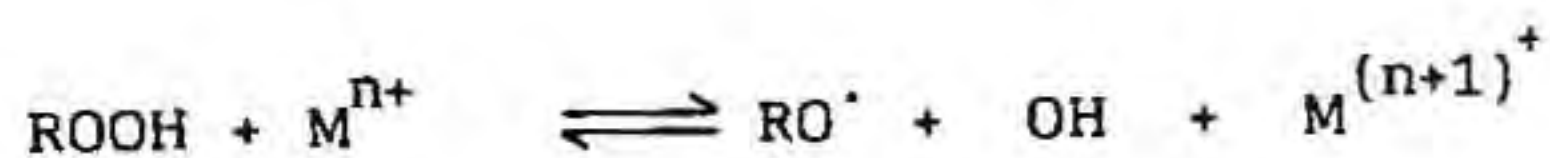


termination



Autoxidation is a free radical chain reaction, the main initiation reaction being the decomposition of hydroperoxides which are unstable above 150^oC [13]. The hydroperoxides also decomposes slowly below this temperature, especially in the presence of traces of metal ions which act as catalysts. Cobalt, copper and iron are effective both in their oxidised and reduced forms and will catalyse the decomposition at levels below 1 ppm.

The action of metal ions in the decomposition of hydroperoxides is [8,14]



The polymers 4 and 5 undergo autoxidation to give a crosslinked transparent film and an attempt is made here to understand its mechanism.

4. 2 EXPERIMENTAL

4.2.1 Methods

4.2.1.1 Polymerisation and preparation of crosslinked film

The monomers cardanyl acrylate, CA 2, and cardanyl methacrylate

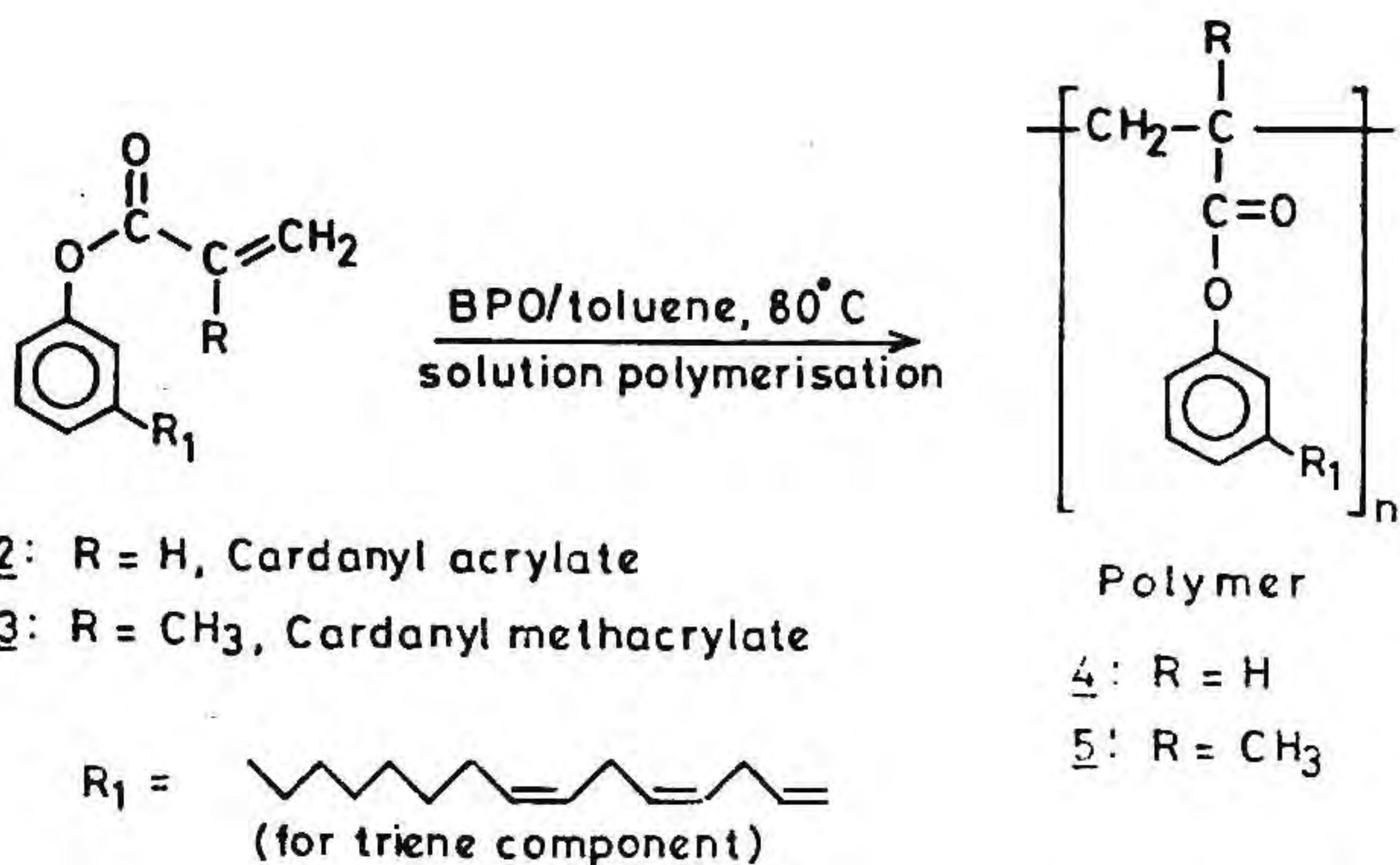
CMA, 3 were synthesised by the procedure described in the chapter 3. Polymerisation of 2 and 3 were carried out in solution at 80⁰ C using toluene as solvent and 0.8% BPO as initiator, in nitrogen atmosphere for 24 h. The polymer was precipitated in methanol and purified by redissolving in toluene and reprecipitation from acetone. Yield: 65-70%. A concentrated solution of polymers 4 and 5 obtained were cast into a thin film and exposed to air at ambient conditions for 12 h or at 60-80⁰ C or UV irradiation for 30 min. yields non-sticky, insoluble, infusible, transparent film. Scheme 4.1.

4.2.1.2 Thiobarbituric acid (TBA) test

The TBA test is perhaps the most widely used method for detecting lipid peroxides in food and other biological samples [8,15]. Although it is an empirical assay, it has gained wide use because of its simplicity and sensitivity. The general procedure, involves heating a small quantity of the test sample in an aqueous acidic solution of thiobarbituric acid and then measuring the absorbance at 535 nm.

4.2.1.3 Instruments

IR spectra were recorded on a Perkin-Elmer Model 882 spectrophotometer. The ¹H NMR spectra were obtained on a Hitachi R-24 B high resolution NMR spectrometer with CDCl₃ using tetramethylsilane as internal reference. Number-and weight-average molecular weights (\bar{M}_n and \bar{M}_w) were determined using (Hewlett-Packard 1081 B HPLC equipped with RI detector). DSC was recorded using a Mettler TA-3000 system in air at a heating rate of 5⁰ C/min from 30⁰ C to 200⁰ C. (Further details regarding the instrumentation are given in chapter 2).



Scheme 4.1: Preparation of poly(cardanyl acrylate)/poly(cardanyl methacrylate) and its crosslinked film

4.3 RESULTS AND DISCUSSION

The number- and weight-average molecular weights (\bar{M}_n and \bar{M}_w) of the polymers 4 and 5 as determined by GPC were in the range of 3000-5000 and 10,000-15,000 respectively.

The IR spectrum of cardanyl acrylate, 2 and cardanyl methacrylate 3 monomers and polymers 4 and 5 (given in chapter 3) showed the carbonyl stretching frequency of ester group at 1750 cm^{-1} . The C-H stretching vibrations of $-(\text{CH}_2)-$ groups present in the side chain of cardanyl acrylate/cardanyl methacrylate were obtained at 2925 cm^{-1} and 2855 cm^{-1} . The C-H stretching vibrations of the unsaturated part of the side chain of the monomers 2 and 3 were observed at 3020 cm^{-1} which is characteristic of disubstituted olefinic system. This is further clarified from the observation that this peak is absent in saturated cardanyl acrylate where the side chain has no double bond. The $-\text{C}=\text{C}-$ stretching vibrations of the acrylic/methacrylic moiety were observed at $1658/1640\text{ cm}^{-1}$ in the monomers, and as expected, this peak was not observed in the polymers 4 and 5, due to the conversion of acrylic $\text{C}=\text{C}$ to $\text{C}-\text{C}$. As the side chain unsaturation was not involved in polymerisation, the peak at 3020 cm^{-1} remain unchanged in the polymers. These observations were supported by the ^1H NMR spectrum. The protons involved in the acrylic/methacrylic unsaturation were prominently seen at $\delta\text{ (ppm)} = 5.7-6.6$ in the ^1H NMR spectrum of the monomers, whereas this peak was absent in the spectra of the polymers 4 and 5 as $-\text{C}=\text{C}-$ was converted to its saturated analogue on polymerisation (Figure 4.1a&b). At the same time, the peak at $\delta\text{ (ppm)} = 5.2-5.5$ which is attributed to the unsaturated protons of the side chain

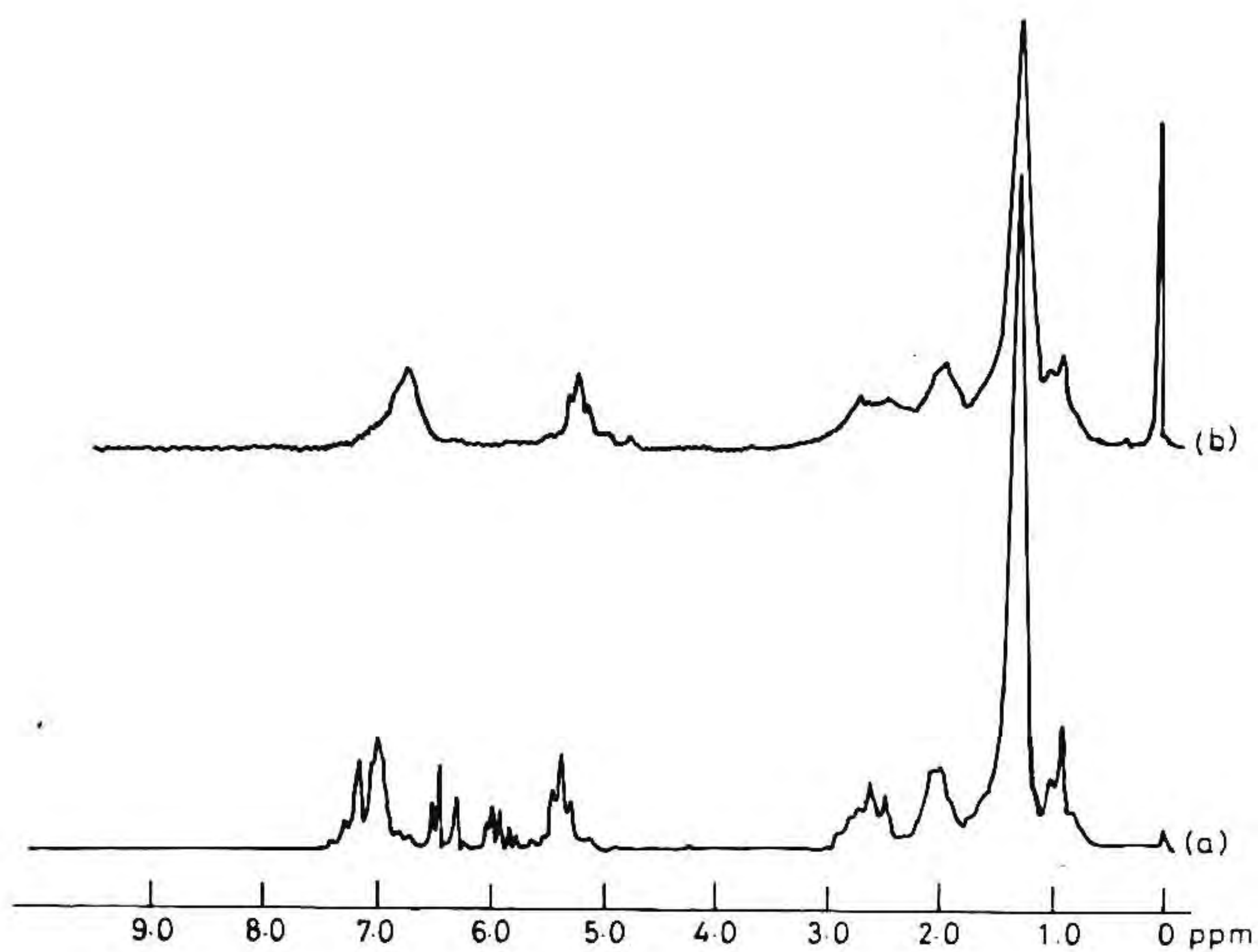


Fig. 4.1(a): ^1H NMR spectrum of (a) cardanyl acrylate (CA), 2,
(b) poly(cardanyl acrylate) (PCA), 4.

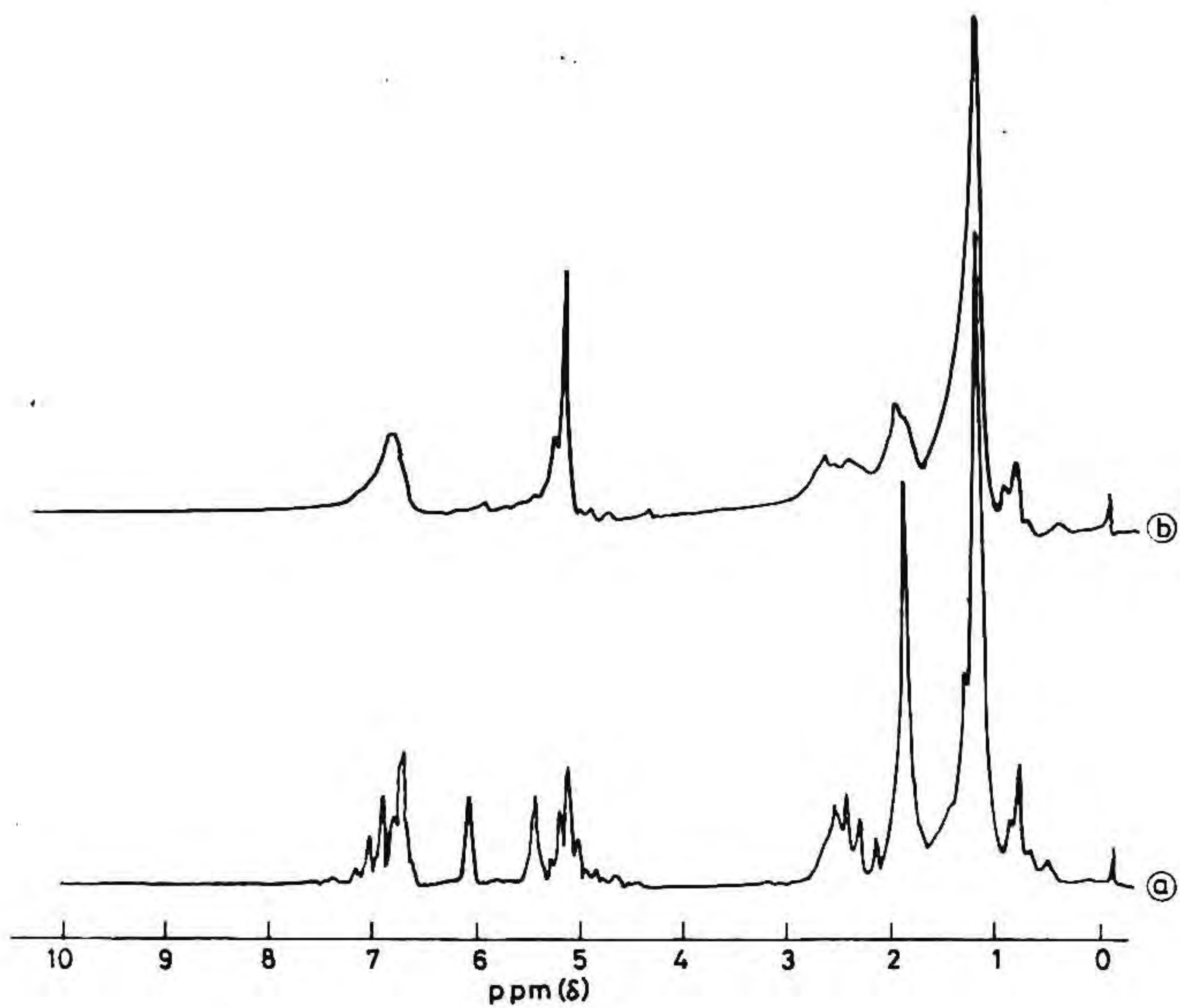


Fig. 41(b): ^1H NMR spectrum of (a) cardanyl methacrylate, (CMA), 3,
(b) poly(cardanyl methacrylate) (PCMA), 5.

indicating that it was not involved in polymerisation.

4.3.1 Crosslinking reaction

A concentrated solution of polymers 4 and 5 obtained were cast into a thin film and exposed to air at ambient conditions for 12 h or at 60-80^o C for 30 min or UV irradiation for 30 min, the film gets changed to an insoluble, infusible state and this change takes place in the absence of initiators.

The DSC curve (Figure 4.2) for polymer 4 shows an exotherm at 80-185^o C and a peak maxima at 132.1^o C indicating crosslinking reaction. In all possibility this might be through the double bonds present in the side chain by oxidative curing as there is no other possibility for a polymerisation reaction. This was confirmed by IR spectroscopy. The characteristic peak at 3020 cm⁻¹ for the disubstituted olefinic bond of the side chain of the monomers 2 and 3 was nearly absent in the IR spectrum of the crosslinked film (Figure 4.3). Similar results were obtained for the crosslinked polymer/beads prepared by bulk/suspension polymerisation of cardanyl acrylate, CA, 2 and CMA, 3. Occurrence of crosslinking was further supported by solubility studies. The crosslinked system was found to be insoluble in almost all organic solvents.

4.3.2 Crosslinking mechanism

One of the interesting aspects of the chemistry of polymerisation of cardanol is that it does not undergo polymerisation by the conventional free radical initiators such as benzoyl peroxide (BPO) or

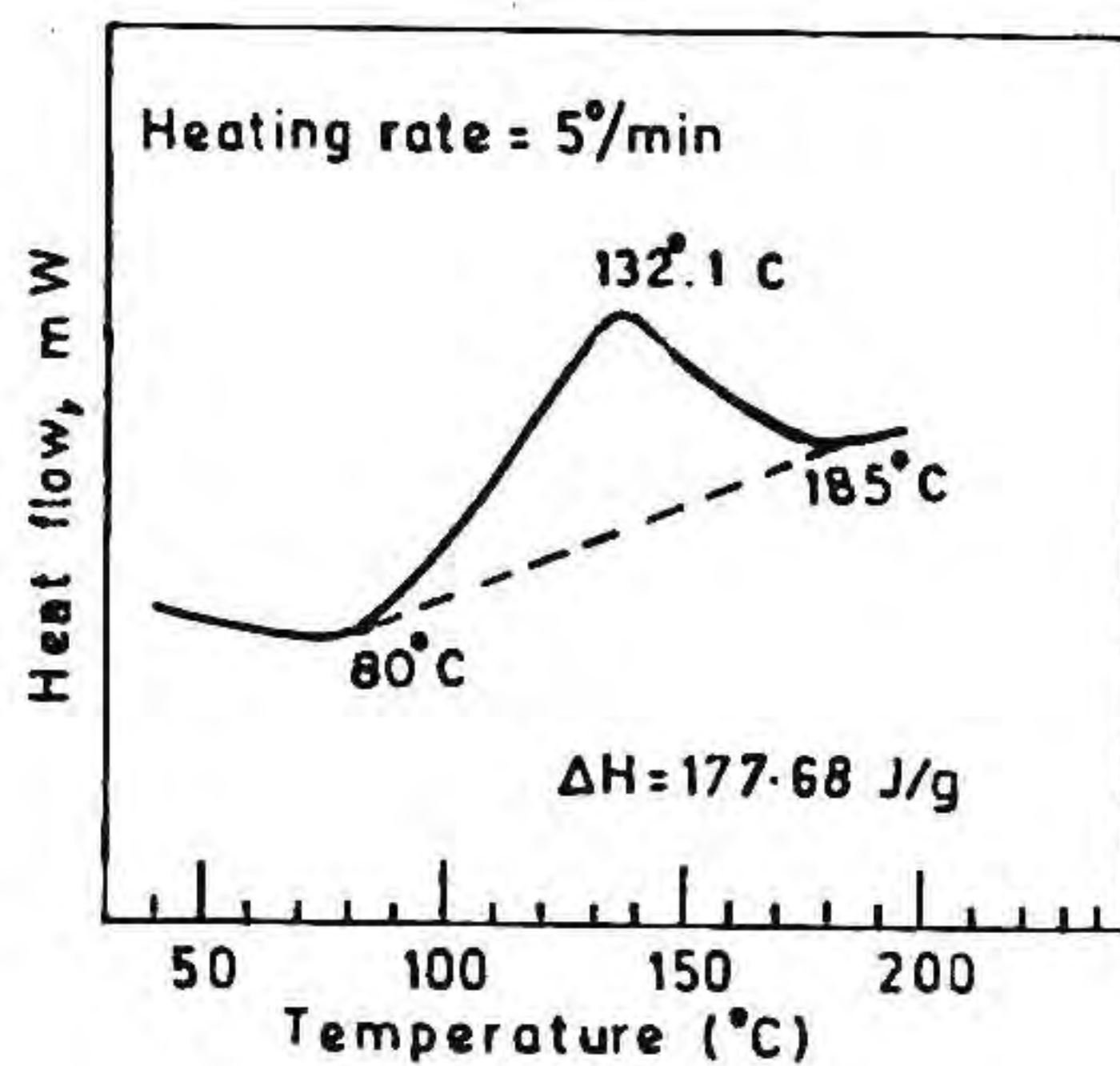


Fig. 4.2: DSC curve of poly(cardanyl acrylate) in air

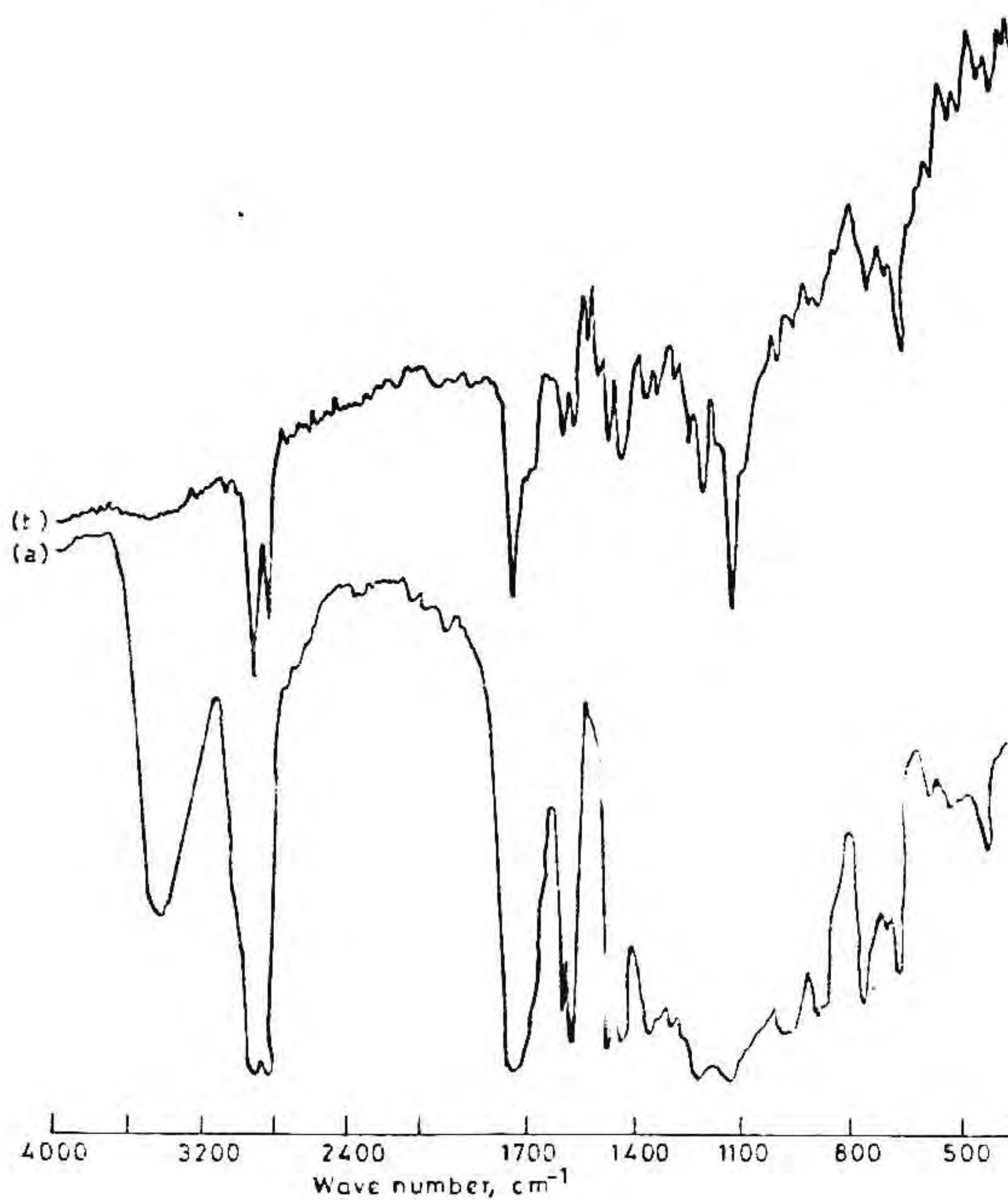
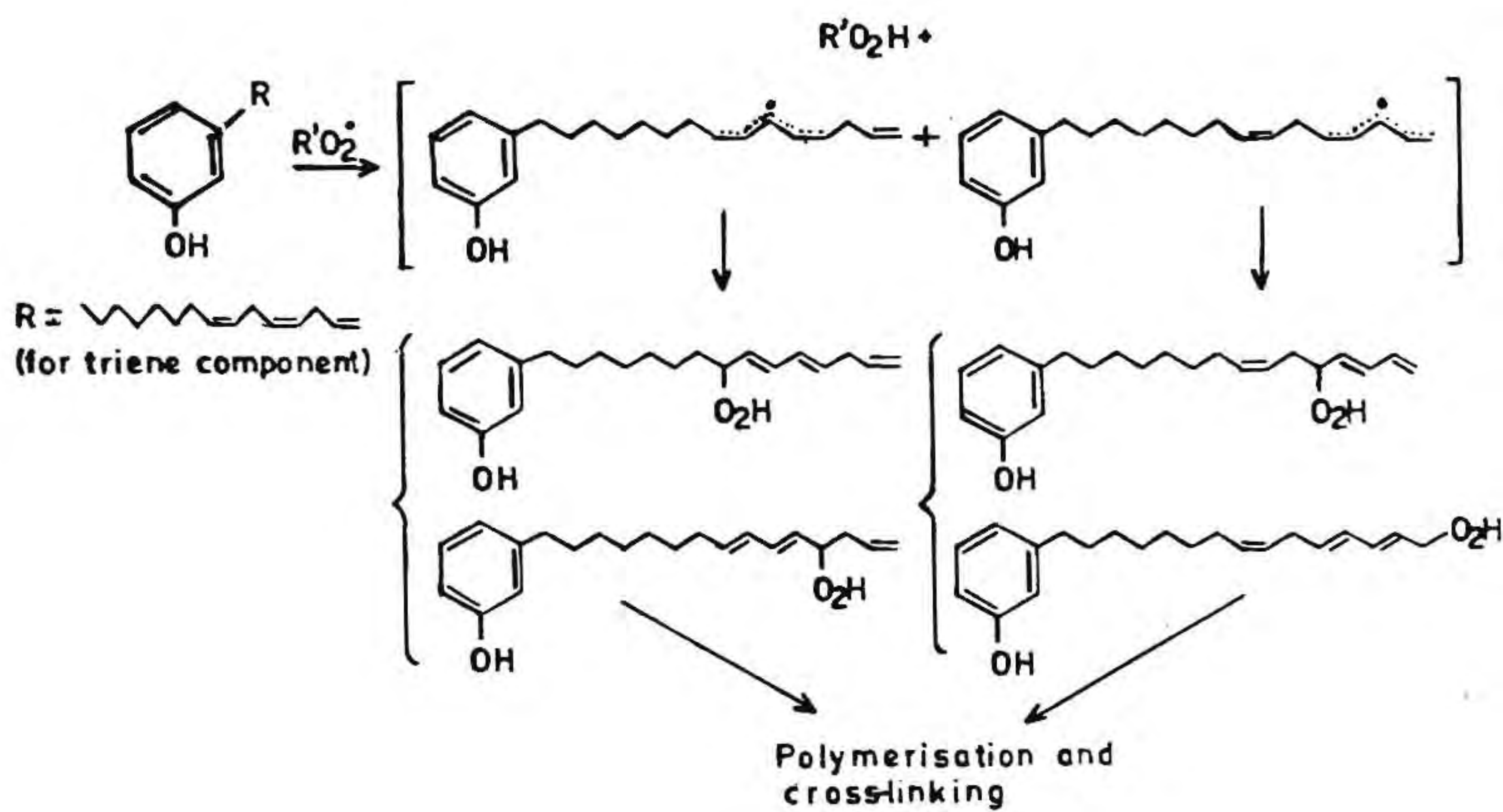


Fig. 4.3: IR spectrum of (a) autoxidised poly(cardanyl acrylate) film, (b) crosslinked beads

azobisisobutyronitrile (AIBN). The phenolic moiety of cardanol which by its antioxidant nature can act as a radical scavenger during the initiation step [16]. However, it is reported that cardanol is susceptible to autoxidation leading to polymerisation giving rise finally to crosslinked products [17] (Scheme 4.2). Cardanol with its hydrophobic unsaturated side chain and hydrophilic phenolic moiety can be considered as an unsaturated nonconjugated lipid [18]. It is well known that nonconjugated lipids undergo oxidative polymerisation through the formation of hydroperoxide groups as intermediate reactive species that can give rise to active centres for further reaction and polymerisation. Similar mechanisms are operating in the drying process of lacquers made from urushiol [9,10], in the drying oils such as triglyceride of linoleic acid [6] (Scheme 4.3), and in the autoxidation of nonconjugated cyclic dienes [19]. Tyman suggested that cardanol on exposure to atmospheric oxygen can undergo hydroperoxidation through the triene double bonds giving rise to allylic radical centers that would combine to form conjugated intermediates leading to propagation reactions and crosslinking.

In the case of cardanol it takes several days for the normal drying process to complete so that a crosslinked network is obtained. But polymer 4 or 5 on exposure to atmospheric oxygen at 60-80°C gives a totally insoluble crosslinked product within 2 h (at ambient conditions 12 h required). The acrylate moiety situated far away from the unsaturated centers in the side chain might not be activating the side chain here and the crosslinking might be taking place due to certain ordered arrangements of the side chain in near proximity to each other brought

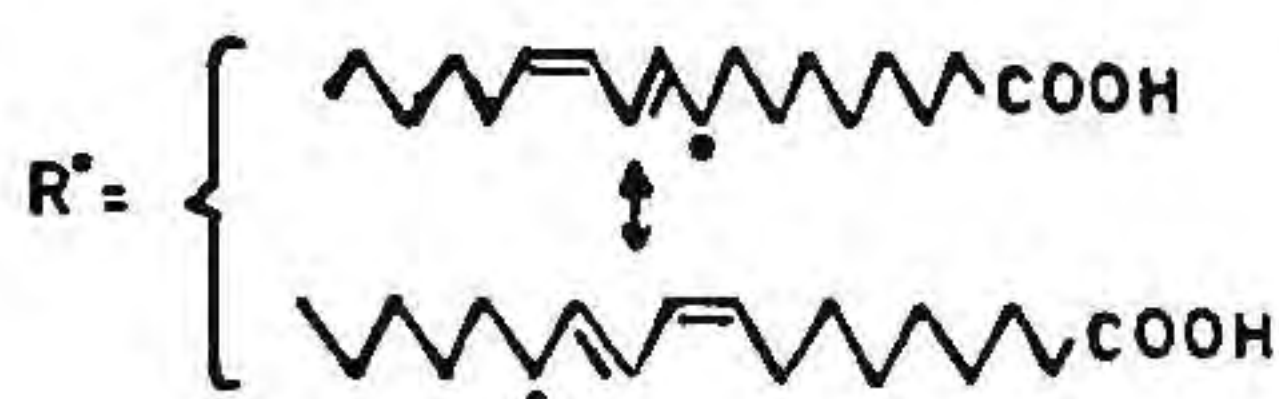


Scheme 4.2: Hydroperoxidation of allylic radical centres of cardanol

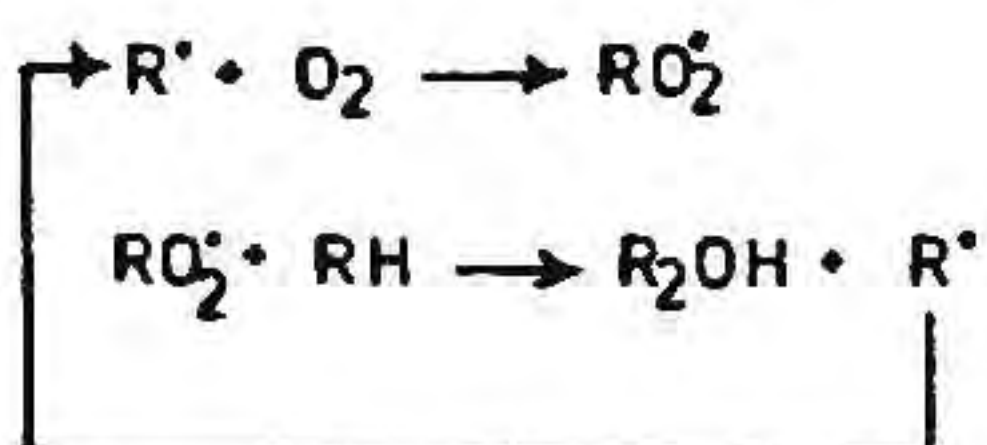
initiation



linoleic acid

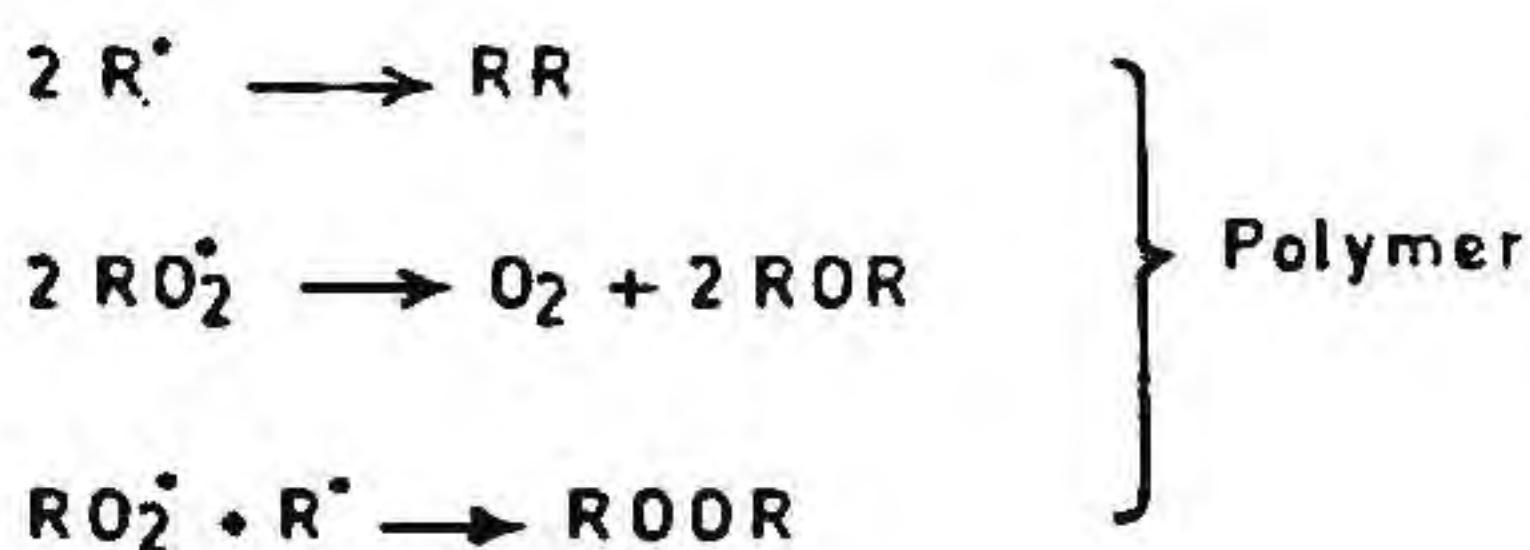


propagation



Where RH may be starting substance

termination



Scheme 4.3: Classical mechanism of autoxidation of linoleic acid

about by the polymer backbone of polymers 4 and 5. This is analogous to a model study of autoxidation of biomembrane lipid bilayer using adsorbed unsaturated fatty acid monolayers onto silica gel [20,8].

In short, the side chains are brought closer to each other by the acrylate polymer support and such a structure is schematically presented as in Figure 4.4.

4.3.3 Evidence for hydroperoxidation

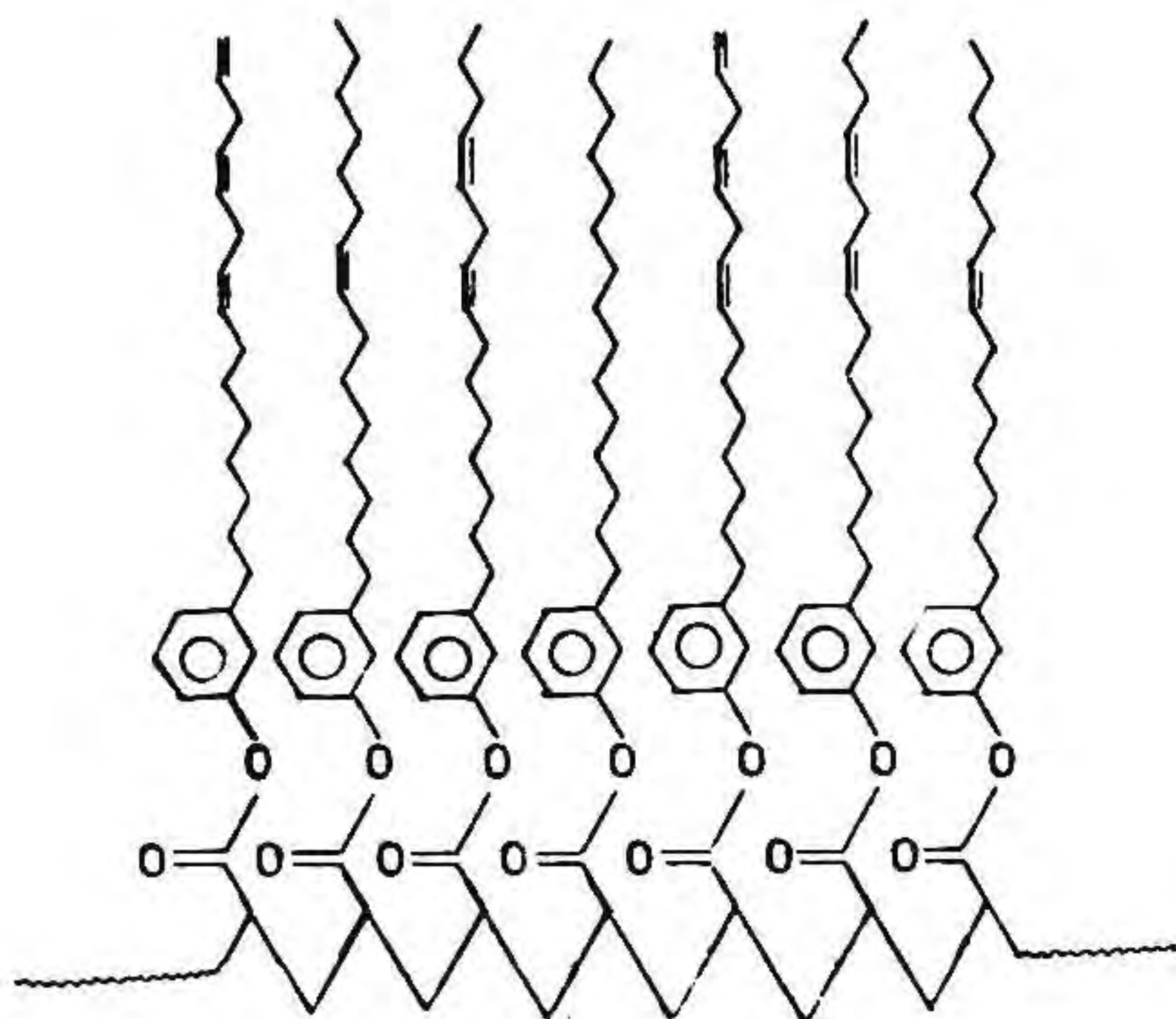
The formation of hydroperoxides and crosslinking reaction of polymers 4 and 5 were confirmed by various analytical and spectroscopic methods.

4.3.3.1 Thiobarbituric acid test

The thiobarbituric acid test imparts red colour with autoxidised systems. The pigment produced in TBA reaction has been characterised by formation of an adduct produced by condensation of two moles of TBA with one mol of malondialdehyde formed by decomposition of lipid peroxides under the conditions of test [8,15].

4.3.3.2 Catalytic action of metals on autoxidation

Organic metal salts are well known to catalyse the autoxidation reaction of allylic systems [21,22]. Heavy metal salts particularly those that exist in two or more valency states and that possesses suitable oxidation-reduction potentials (such as copper, iron, manganese, cobalt, and nickel) are among the most powerful catalysts of lipid autoxidation, and allylic systems initiating the oxidation chain reaction.



**Fig. 4.4: Schematic representation of poly(cardanyl acrylate), PCA
(an isotactic structure is given for simplicity)**

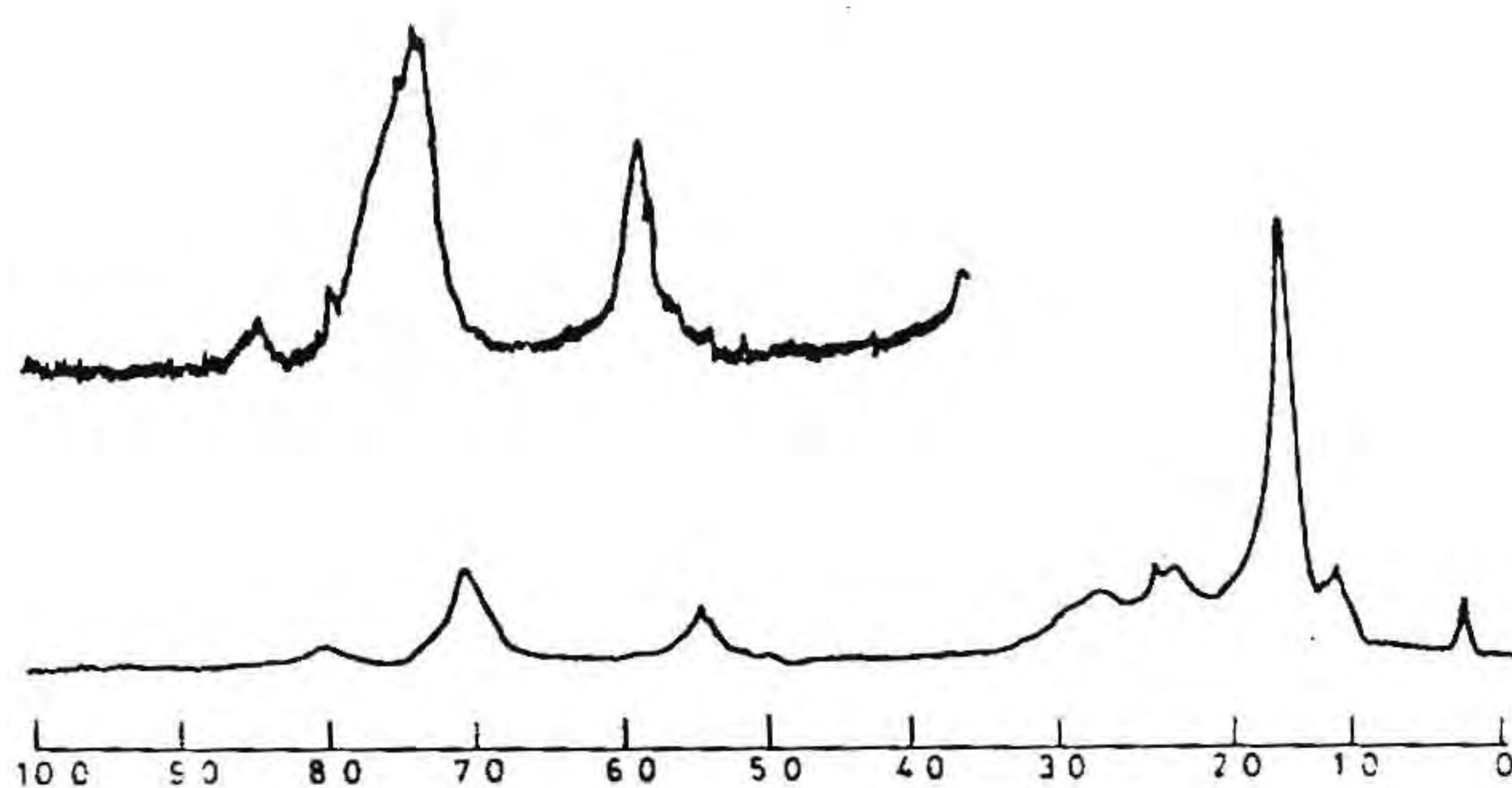


Fig. 4.5: ^1H NMR spectrum of the autoxidised poly(cardanyl acrylate)

Since cobalt catalysts are active driers [23,24] cobalt naphthenate was used in the present study.

When polymers 4 and 5 were subjected to autoxidation in the presence of cobalt naphthenate, it was found that the crosslinking reaction was complete within 45 min. instead of 12 h at ambient condition.

4.3.3.3 Spectral evidence

Spectroscopic data clearly supports the autoxidation of polymers 4 and 5. In the IR spectrum a broad peak at $3450-3550\text{ cm}^{-1}$ indicates the presence of OH groups in the crosslinked polymer, whereas this peak is absent in the crosslinked polymers by suspension/bulk polymerisation shown in Figure 4.3. ^1H NMR (Figure 4.5) showed a broad singlet at $\delta(\text{ppm}) = 7.9-8.2$ ppm for an exchangeable proton which is characteristic for the hydroperoxide group. The sample was prepared by dissolving partially cured (polymers 4 or 5 on solution casting and autoxidation at ambient conditions for 2-3 h, which is still soluble in CDCl_3) polymer in the required solvent [8,15,19].

4.4 CONCLUSION

Two vinyl monomers, cardanyl acrylate CA, and cardanyl methacrylate, CMA, were synthesised from cardanol. The monomers CA, and CMA gave soluble polymers in solution polymerisation. The linear polymers on exposure to air/UV/heat, undergoes autoxidation and crosslinking to give an insoluble transparent material. This phenomenon

was explained by hydroperoxide theory. This polymer could find use in air drying application as a substitute for allyl ethers and as a model polymer for autoxidation studies of lipid membranes.

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CHAPTER 5

THERMAL CHARACTERISATION OF POLY(CARDANYL ACRYLATE): KINETICS OF CURE REACTION AND KINETICS OF THERMAL DECOMPOSITION

5.1 INTRODUCTION

Thermal analysis is now established as an invaluable and rapid method for the characterisation 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 properties 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 [1-4]. 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 [4,5]. Thermal analysis has been treated mainly as a chemical analysis tool till the middle of this century [6]. In recent years, it has grown 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 (heterogenous kinetics).

The most widely used techniques on thermal analysis are, thermogravimetric analysis (TGA), differential thermal analysis (DTA) (see chapter 6) differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Among these tools, TGA and DSC have been successfully applied in the case of poly(cardanyl acrylate), PCA, to arrive at an understanding on cure kinetics and evaluation of kinetic parameters for the thermal decomposition. The synthesis and characterisation of poly(cardanyl acrylate) was discussed in chapters 3 and 4. It was found interesting that PCA on exposure to air, absorbs oxygen and undergoes autoxidative crosslinking reaction. PCA with its ability to give a transparent film by autoxidation might find applications in speciality coatings and hence a study on its thermal behaviour is warranted. This chapter discusses the findings on the oxygen absorption and subsequent crosslinking of poly(cardanyl acrylate) monitored by thermal methods, DSC and TGA. A general discussion on TGA, DTA and DSC and their use in the evaluation of kinetic parameters are also provided.

5.1.1 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 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. [4,5].

The main parts of a thermobalance are (1) recording balance, (2) furnace, (3) furnace temperature programme 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, mineralogy, food technology, inorganic and organic chemistry, polymer chemistry, biochemistry and geochemistry. TG is the most widely used thermal technique to study the heterogenous reaction kinetics [4,5].

The greatest number of applications of thermogravimetry during the past few years have been in the characterisation of polymeric materials which have been useful not only in the applied areas, but also in the theoretical aspects of polymer chemistry [7-9]. 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, etc. In studies of thermal oxidative degradation, TG can reveal the molecular structure and arrangement of repeating units, existence of crosslinks 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]. There are a number of books and reviews describing the thermal stability of polymers in terms of TG [12]. This method is also very useful in identification of plasticizers [13]. Numerous TG studies had been made on the characterisation 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.

5.1.2 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 basic components of DTA are (1) furnace, (2) sample holder, (3) temperature sensor, (4) property sensor, (5) recorder, and (6) furnace temperature programmer [16]. A large number of DTA instruments are available and they have been discussed in several monographs and books [17]. DTA is a useful thermal technique for studying reaction kinetics and characterisation of inorganic materials [18]. DTA has found many applications in the polymer field also. It is used to measure melting points, degree of crystallinity, heats of fusion, etc.

It can be used to identify the individual polymers from a physical mixture of compounds [19]. It is an effective tool to study the curing reaction of resins [20]. 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 degradation mechanism studies.

5.1.3 Differential Scanning Calorimetry (DSC)

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 reference are subjected to a controlled temperature programme [21].

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

DSC measurements are considered to be quantitative and kinetics and mechanisms of solid state thermal decomposition reaction can be studied by DSC [22]. A bibliography of literature in DSC has been compiled by Perkin-Elmer Corporation [23].

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 reaction, heats of adsorption, heats

of reaction, Curie point determination, thermal stability, oxidation stability, glass transition temperature etc. [4-5]. 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 [4,5].

DSC is widely used to study a variety of polymeric substances. Among them are rubber [24], molded resins [25], polymer films [26], engineering thermoplastics [27] etc. It is successfully used to measure glass transition temperature, melting points, degree of crystallinity, heats of fusion and crystallization, decomposition temperatures, and numerous other parameters. DSC is also used to predict the potential explosive hazard of materials in an ASTM method [4]. The thermal oxidative stability of a resin can be studied using DSC [4,8]:

5.1.4 Kinetic analysis of reactions

DSC and TG 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 programmed temperature conditions [15,28]. The present study involves only non-isothermal techniques.

5.1.5 Non-isothermal kinetics

Flynn [29] 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 Arrhenius 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 [30], Horowitz and Metzger [31].

The advantage of determining the kinetic parameters by non-isothermal methods have been listed by Wendlandt [4] and they are: (1) results can be obtained from a single 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 methods have 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 [15,28]. However, non-isothermal method is used more commonly because it required only a single TG experiment to compile the results.

The developments in non-isothermal kinetic methods have close parallels in the study of luminescence of materials, thermal desorption, thermally stimulated conductivity and several other reactions.

5.1.6 Kinetic equations for DSC curve analysis

Recently DTA and DSC curves have been extensively used for the evaluation of kinetic parameters. The methods for the evaluation of kinetic data from DTA and DSC have been reviewed by Satava [32], Wendlandt [33,34], Sestak and Berggren [35], Friedman [36] and others [37].

The evaluation of kinetic parameters by these methods is based on the area under the DTA or DSC curve of the reaction under investigation. Several equations relating the differential temperature ΔT , to the reaction rate, which enables the calculation of kinetic parameters from DTA and DSC experiments, have been proposed.

Almost all the kinetic methods used in DTA and DSC are based on the equation,

$$(d\alpha/dt) = f(\alpha, T) \quad (5.1)$$

where $d\alpha/dt$ is the rate of reaction and $f(\alpha, T)$ has the same meaning as in the TG studies. It is also assumed that the rate of heat generation H , is directly proportional to $d\alpha/dt$; the equality is

$$H = B \rho (d\alpha/dt) \quad (5.2)$$

where B = heat per unit volume and ρ = sample density. Therefore,

the kinetic equation can be used in DTA and DSC studies as well.

Differential scanning calorimeter is uniquely suited to the studies of enthalpy changes accompanying phase changes and chemical processes [38]. The heat of reaction is recorded as endotherm or exotherm against temperature (thermograms). Similar studies can be carried out at constant temperature (isothermal). Knowledge of the amount of heat liberated during the course of reaction can be utilised to estimate kinetics of curing in thermosetting resins. It is used not only for isothermal mode but also in the dynamic mode at different heating/cooling rates. The isothermal cure curve is obtained by stepwise integration of the thermogram as function of time. It is necessary to express heats of reaction as a function of total heat change (H/H_0), where H is fraction of heat change and H_0 is total heat change. This is because the total heat of reaction varies with the curing temperature.

In the present work, Roger's method [38,39] is used for obtaining kinetic parameters. The necessary data required are, distance measured between the reaction curve and the base line (scanning) at associated absolute temperatures. The distance measured is proportional to the rate of heat evolution or absorption at that temperature which in turn is proportional to the rate constant. As many distances as possible are measured between the onset and maximum of the curve. The logarithm of the distance is plotted against $1/T$ in degrees K. The best straight line portion is chosen. The distance at the extremes, d_1 and d_2 with corresponding temperatures $1/T_1$ and $1/T_2$ are put into the

equation

$$-E = \frac{4.58 \log (d_1/d_2)}{(1/T_1) - (1/T_2)} \quad (5.3)$$

The distance enter only as a ratio, so that proportionality constants cancel. Neither mass nor heat of reaction needs to be known. The Arrhenius plot should be linear over a reasonable range. E will appear as Kcal/mol. Caution must be exercised not to exceed dynamic range of the DSC and to contain the reaction and products within the sample cell. Some consideration of phase of the sample during the reaction must also be made, especially when the data are compared to literature values.

Given E from the previous calculation, the heating rate ϕ , and the temperature at maximum T_{\max} , it is possible to calculate the pre-exponential factor A with

$$A = \frac{E e^{E/T_{\max}}}{R T_{\max}^2} \quad (5.4)$$

The method is totally independent of sample mass and is operable so long as the kinetic order of the reaction is not significantly different from one and the above precautions are observed.

5.1.7 Nonisothermal kinetic equations for the analysis of TG data

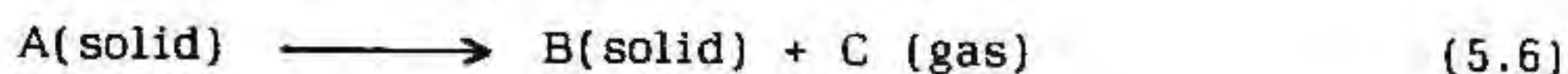
Nonisothermal (i.e. dynamic) thermogravimetry has been widely used to study the kinetics of thermal decomposition reaction. As

pointed out by Doyle [40], a single mass loss curve is equivalent to a large number of isothermal mass loss curves. This large amount of information is gained without sample-to-sample error, since the same sample is used throughout the run in dynamic thermogravimetry.

TG is indeed the most widely used thermal technique to study heterogeneous kinetics [41].

$$d\alpha/dT = A/\phi e^{-E/RT} (1-\alpha)^n \quad (5.5)$$

The general equation (5.5) made for the study of kinetics is relating the parameters A, E and n. Several authors have given the solution of above equation in simpler and more practically useful forms for calculating the kinetic parameters for the thermal decomposition of solid-state reactions of the type:



For monitoring the reaction from mass loss, various forms such as concentration C, weight fraction w, number of atoms N, volume fraction V, etc. have been used. However for uniformity, a dimensionless quantity, the fractional decomposition, α , which at time t, is defined as the fraction of the sample decomposed, is employed.

Therefore,

$$\alpha = w_t/w_\infty = (m_0 - m_t)/(m_0 - m_\infty) \quad (5.7)$$

where

w_t = mass loss at time t

w_∞ = maximum mass loss in the TG experiment for the reaction under investigation

m_0 = initial mass of the sample

m_t = the mass at time t and

m = the mass at the end of the reaction

Most of the existing evaluation methods for obtaining the kinetic parameters utilise the eqn. (5.5) in some form or other. Three different approaches have been made in this context.

- a. Differential methods
- b. Integral methods, and
- c. Approximation methods

Using the three approaches, there are a number of equations derived by different authors and they have been cited in the thesis of Madhusudanan [42].

Integral methods: Integral methods are generally accepted as the most accurate among the methods available for the determination of kinetic parameters from TG data.

5.1.8 Determination of order parameter n

The order parameters were evaluated for the different stages of decomposition using the Coats-Redfern equation by an iteration

method. Using computer, linear plots of $\ln [g(\alpha)/T^2]$ versus $1/T$ were drawn by the method of least-squares, taking the α and the corresponding T values from the TG curves. Linear curves were drawn for different values of n , ranging from 0 to 2, in increments of 0.01. The value of n which gave the best fit was chosen as the order parameter for each stage of decomposition.

5.1.9 Mathematical treatment of data

The kinetic parameters were calculated from the TG curves using four non-mechanistic equations. The forms of these equations used are given below, wherein the integral form of $g(\alpha)$, has been introduced for convenience and is defined as

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1-n} \quad (5.8)$$

where α = the fractional decomposition at time t , related to the sample mass from TG as m_t/m_∞ (m_∞ refers to completion of reaction); n = order parameter.

Coats-Redfern [43] equation:

$$\ln [g(\alpha)/T^2] = \ln [AR/\phi E(1-2 RT/E)] - E/RT \quad (5.9)$$

MacCallum-Tanner [44] equation

$$\log_{10} g(\alpha) = \log_{10} (AE/\phi R) - 0.485 E^{0.435} - \frac{(0.449 + 0.217 E) \times 10^3}{T} \quad (5.10)$$

Horowitz-Metzger [45] equation

$$\ln g(\alpha) = \ln (ART_s^2/\phi E) - E/RT_s + E\theta/RT_s^2 \quad (5.11)$$

MKN [46] equation

$$\ln [g(\alpha)/T^{1.9215}] = \ln (AE/\phi R) + 3.7721 - 1.9215 \ln E - \frac{0.12039 E}{T} \quad (5.12)$$

where T is the temperature (K), A is the pre-exponential factor, ϕ is the heating rate ($^{\circ}\text{C min}^{-1}$), E is the energy of activation, R is the gas constant, T_s is the DTG peak temperature and θ is $(T-T_s)$.

The kinetic parameters were calculated from the linear plots of the left hand side of the kinetic equations against $1/T$ for all the equations, except the Horowitz-Metzger equation, for which the left hand side was plotted against θ . The values of E and A were calculated from the slope and intercept of the straight lines, respectively.

The entropy of activation was calculated from the equation

$$A = (k T_s/h) \exp (\Delta S/R) \quad (5.13)$$

where k is the Boltzmann constant, h is the Plank's constant and ΔS is the entropy of activation. The heat of reaction ΔH for the

different stages of decomposition was evaluated from the DSC curves by area integration of the peak.

5.2 EXPERIMENTAL

5.2.1 Materials

Poly(cardanyl acrylate) and poly(3-pentadecylphenyl acrylate) were synthesised as described in chapter 3.

5.2.2 Methods

5.2.2.1 Instruments

Thermogravimetric analysis (TGA) was carried out using a Du Pont 951 modular thermogravimetric analyser in conjunction with a Du Pont 2000 thermal analyst system. 12-15 mg of polymer samples are analysed under nitrogen and air purge. The polymer was coated as a thin film on the sample pan. In order to remove any solvent, volatiles present, the sample was heated and maintained in isothermal condition at 50^oC for 30 min. in dry nitrogen atmosphere. Then the gas purge was changed to air and dynamic TGA was performed at a heating rate of 5^oC per min. DSC was recorded using a Mettler TA 3000 system in air at a heating rate of 5^oC per min. from 30^oC to 200^oC.

5.3 RESULTS AND DISCUSSION

The synthesis and characterisation of poly(cardanyl acrylate) PCA was discussed in the previous chapters. It can be seen from figure 4.4 of chapter 4 that the structure of PCA has the characteristic

non-conjugated double bonds of unsaturated fatty acids which are known to undergo autoxidation leading to crosslinked polymer structure [47]. When PCA was exposed to air, the originally sticky polymer was transformed into a transparent film, insoluble and infusible.

5.3.1 DSC Analysis

DSC analysis showed an exotherm (T_{\max}) at 132.1°C which was explained as due to the autoxidation and crosslinking. The enthalpy change and the kinetic constants for the polymerisation reactions were evaluated from the DSC curves using Roger's method as described earlier.

5.3.1.1 Heat and kinetics of polymerisation

The heat and kinetics of autoxidation of poly(cardanyl acrylate) was evaluated from the DSC curve which is shown in Figure 5.1. The peak exothermic temperature $T_{(\text{exp})}$, temperature of onset of cure reaction T_1 , and the temperature of completion of reaction T_2 , were determined from the DSC curve and their values are given in Table 5.1. The activation energy and pre-exponential factor obtained are given in Table 5.2.

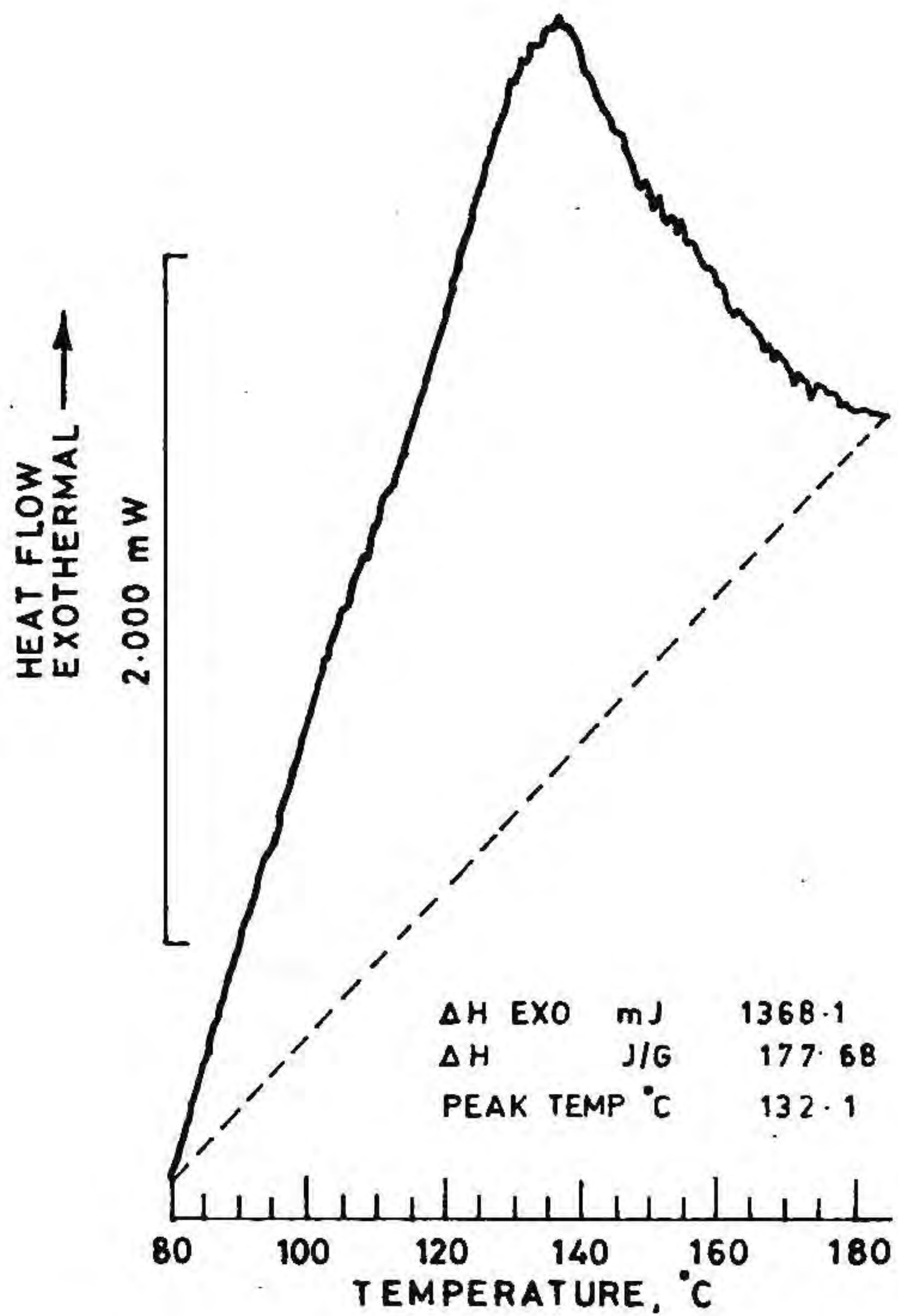


Fig. 5.1: DSC curve for poly(cardanyl acrylate)
(integrated form of Fig. 4.2)

Table 5.1: Exothermic reaction temperature and ΔH of polymerisation from DSC curve of PCA

Sample	T_1 ($^{\circ}\text{C}$)	T_{exo} ($^{\circ}\text{C}$)	T_2 ($^{\circ}\text{C}$)	ΔH (J g^{-1})
PCA	80	132.1	185	177.68

Table 5.2: Kinetic parameters for the polymerisation (oxidative curing) of PCA from DSC analysis

Sample	E (kJ mol^{-1})	A (s^{-1})
PCA	35.21	7.4×10^1

Heat of polymerisation

The area under the DSC curve is a measure of heat of polymerisation, ΔH . The instrument was calibrated using pure indium of $\Delta H = 28.47 \text{ J g}^{-1}$ and $\text{mp} = 156.4^{\circ}\text{C}$. The ΔH values of the samples were determined using the equation

$$\Delta H_s = \Delta H_i \frac{w_i \cdot A_s}{w_s \cdot A_i}$$

where ΔH_s = heat of polymerisation of the sample, ΔH_i = heat of fusion of indium, w_i = weight of indium, w_s = weight of the sample, A_s = area under cure curve of the sample, and A_i = area of indium fusion. The calculated values of ΔH of polymerisation are also given in Table 5.1.

Kinetics of polymerisation

It can be seen from the table 5.2 that the activation energy (E) for the oxidative curing of poly(cardanyl acrylate, PCA is 35 kJ mol^{-1} . This value is quite low in comparison to the E value (60 kJ mol^{-1}) for the thermal crosslinking of acrylates [48]. This can be understood from the low energy needed for autoxidation reaction which is taking place even at ambient conditions [49].

5.3.2 TG Analysis

Further work by TG analysis in air showed an interesting pattern in the TG curve. Conventional TG, except a few polymers[49], in general shows a gradual decrease in percentage weight as temperature goes up. But in the case of PCA, an increase in weight in the temperature range of $80-135^\circ\text{C}$ was observed. This phenomenon is depicted in Figure 5.2(a) where the maximum at 130°C corresponds to maximum absorption of oxygen when the polymer has completely turned into a crosslinked material (separately given in Figure 5.2, $50-160^\circ\text{C}$). This behaviour is totally absent in poly(3-pentadecylphenyl acrylate) (Figure 5.2 b) a saturated analogue of poly(cardanyl acrylate) used as control. This value obtained for PCA coincides with the temperature

Heating rate $5^{\circ}\text{C min}^{-1}$

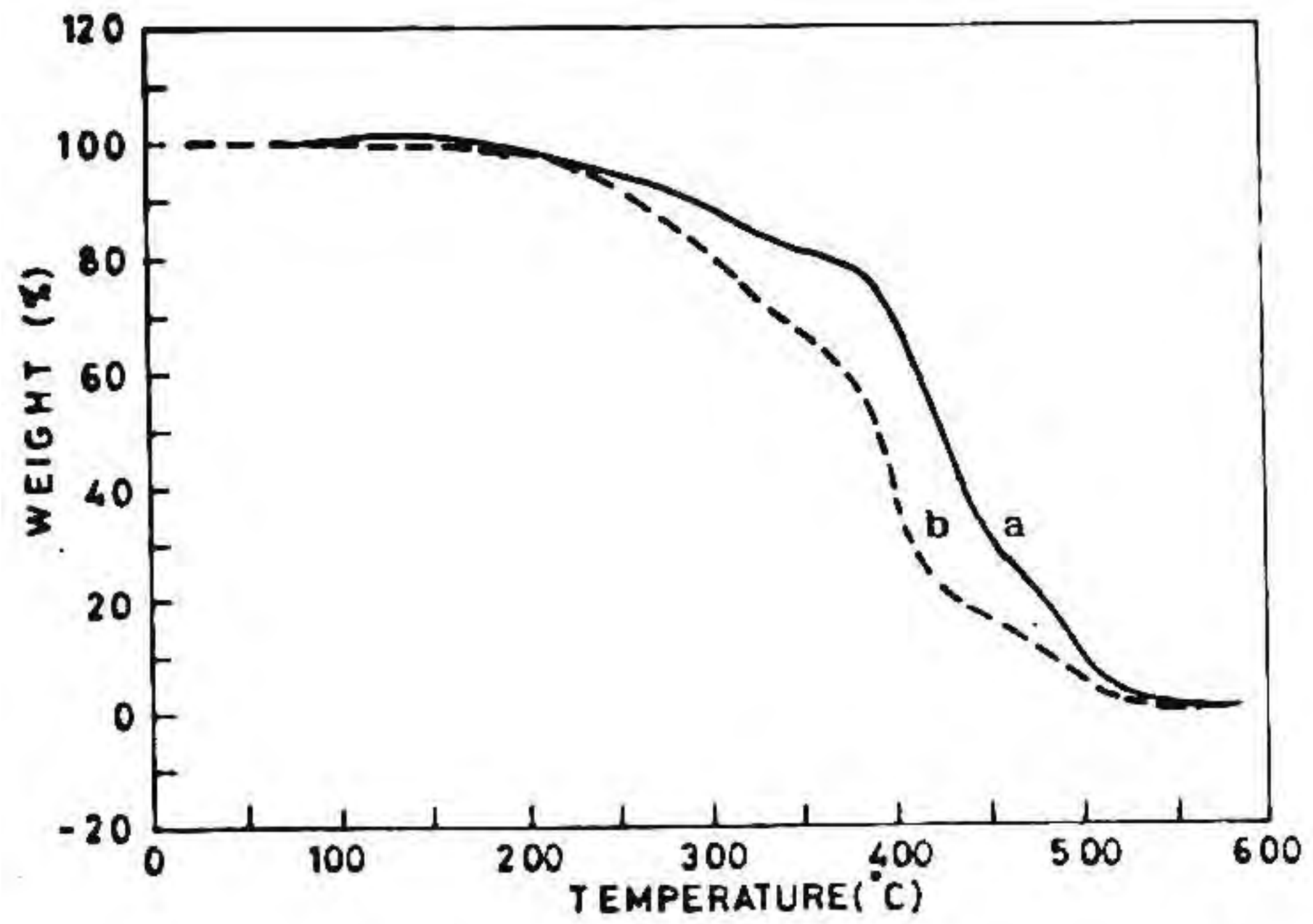


Fig. 5.2: TG curves of (a) poly(cardanyl acrylate), (b) poly(3-pentadecylphenyl acrylate) in oxygen atmosphere

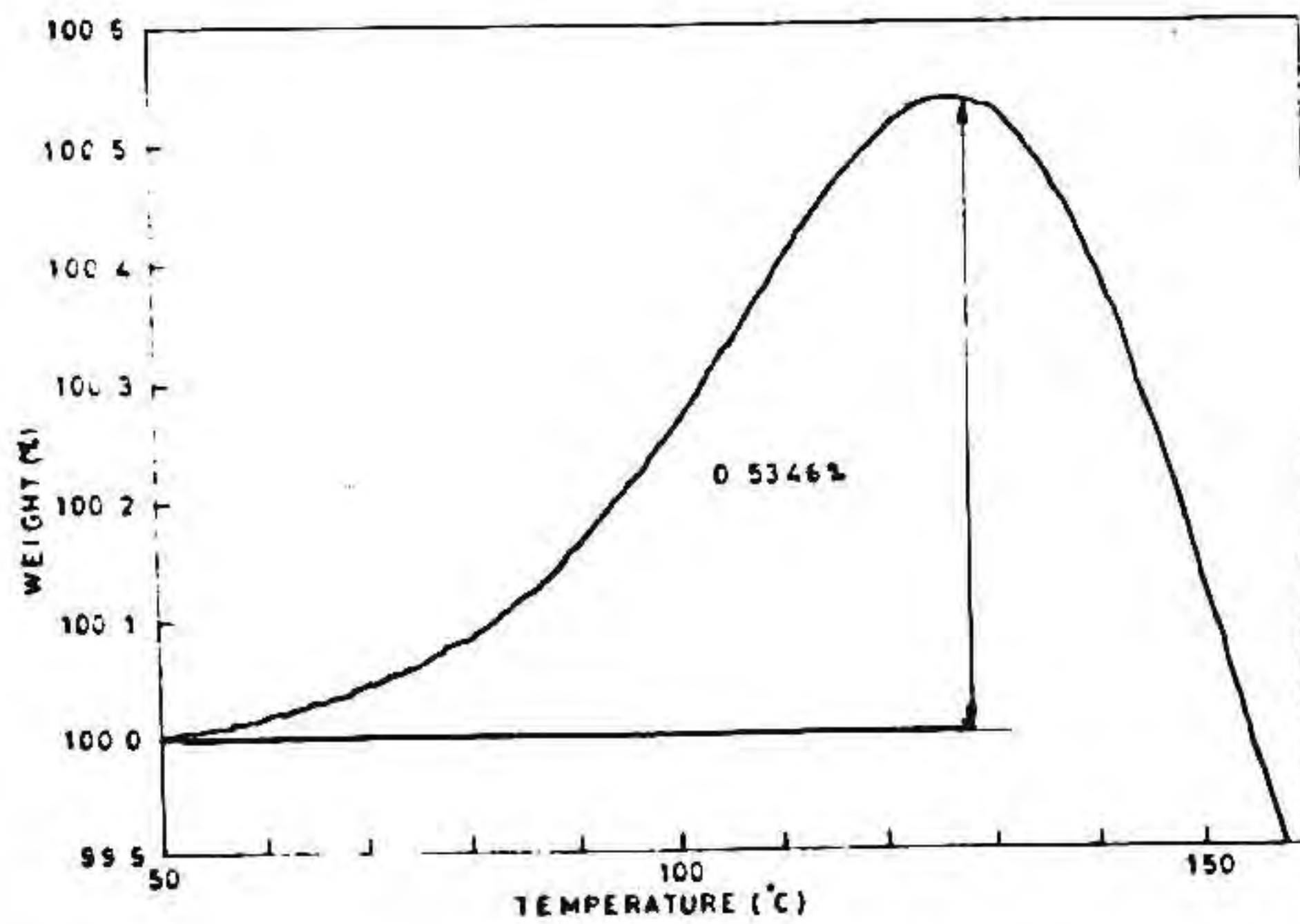


Fig. 5.2: TG curves of magnified portion of $(50-160^{\circ}\text{C})$ of poly(cardanyl acrylate) in oxygen atmosphere

maximum (132.1 C) reported earlier in the DSC pattern of PCA. These observations lend support to the oxygen absorption and crosslinking mechanism proposed.

It is found that the decomposition pattern of PCA and control sample poly(3-pentadecylphenyl acrylate) are similar. The fact that PCA registers a higher thermal stability in air might result from the crosslinking reaction by autoxidation in the early stage.

5.3.2.1 Thermal decomposition kinetics

The thermal stability of the poly(cardanyl acrylate) was evaluated from TG study in nitrogen atmosphere. Figure 5.3 shows the TG curve of the PCA. The temperature of inception T_i , the temperature of maximum decomposition T_s , and the temperature of completion of decomposition reaction T_f , were determined from the TG curves are given in Table 5.3. The percentage char yield at 500°C for PCA is also given in this table.

Kinetic parameters, viz. activation energy E , pre-exponential factor A , and order parameter n , for the thermal decomposition of PCA was evaluated from the TG data. The decomposition of PCA is a single stage reaction and the fractional decomposition α (0.11-0.90) for the respective temperature was calculated from the TG curves (Table 5.3). The order parameter n , and other kinetic parameters were calculated using the method described earlier.

The kinetic parameters for the decomposition of PCA was evaluated using the non-mechanistic equations. The results are listed in Table 5.4.

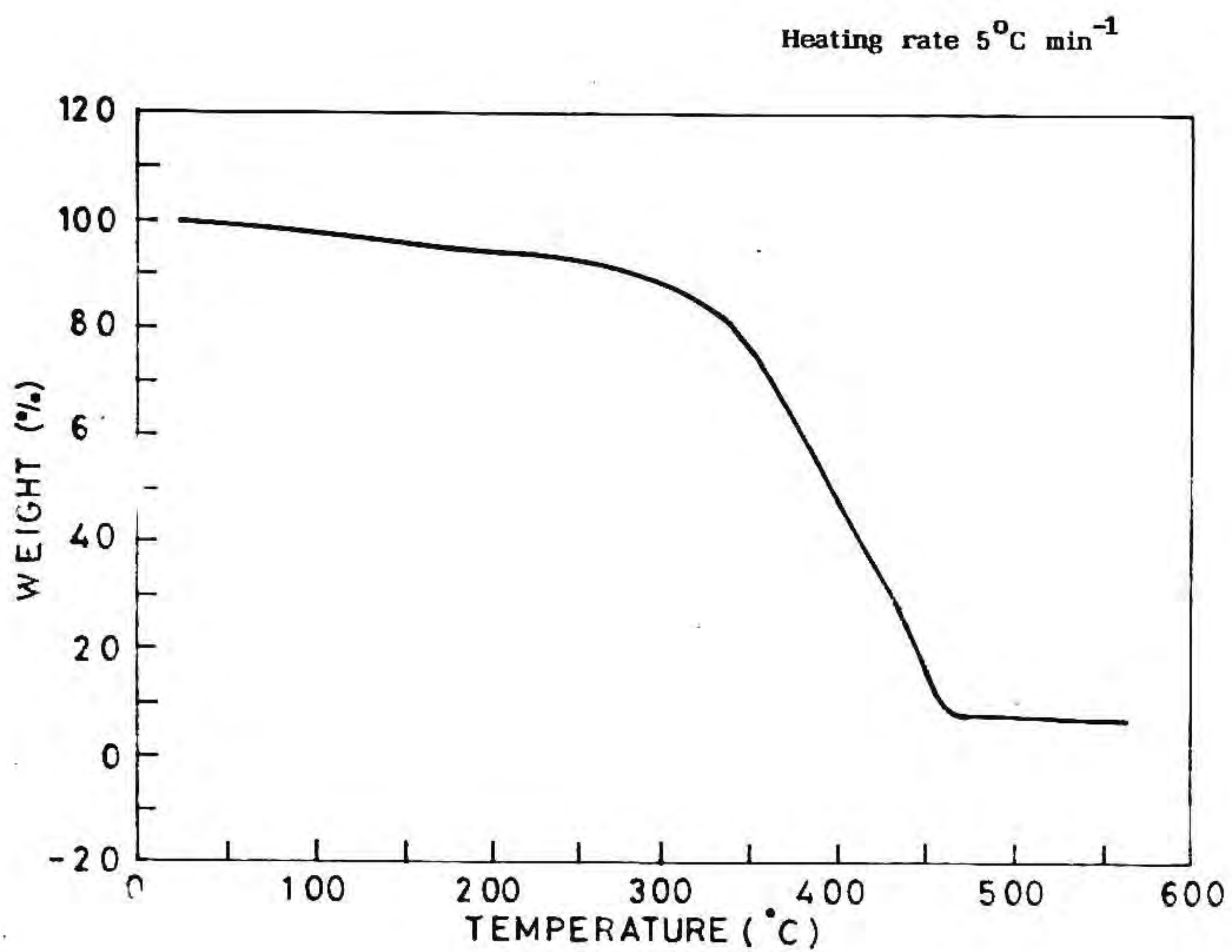


Fig. 5.3: TG curve of poly(cardanyl acrylate) in nitrogen atmosphere

Table 5.3: α and temperature (K) values for the thermal decomposition of poly(cardanyl acrylate)

Heating Rate: 5°C min⁻¹

α	Temperature (K)	
0.1175	573	
0.1301	583	
0.1466	593	
0.1691	603	$T_i = 300^\circ\text{C}$
0.1986	613	$T_s = 440^\circ\text{C}$
0.2356	623	$T_f = 460^\circ\text{C}$
0.2821	633	
0.3353	643	Char yield at 500°C = 7.11%
0.3946	653	
0.4569	663	
0.5190	673	
0.5783	683	
0.6360	693	
0.6966	703	
0.7618	713	
0.8423	723	
0.9036	733	

Table 5.4: Kinetic parameters for the decomposition of poly(cardanyl acrylate) using nonmechanistic equations from TG data

n		0.67
E (kJ mol ⁻¹)	CR	44.65
	MT	47.29
	HM	66.54
	MKN	45.03
A (s ⁻¹)	CR	2.2 x 10 ⁰
	MT	4.3 x 10 ⁰
	HM	1.0 x 10 ²
	MKN	2.1 x 10 ⁰
Δ S (JK ⁻¹ mol ⁻¹)	CR	-245.4
	MT	-239.9
	HM	-213.8
	MKN	-246.0
	CR	0.9983
	MT	0.9989
	HM	0.9978
	MKN	0.9985

CR, Coats-Redfern; MT, Mac Callum-Tanner; HM, Horowitz-Metzger;
MKN, Madhusudanan-Krishnan-Ninan

The correlation coefficients (r) were in the range 0.9978 to 0.9989 indicating nearly perfect fits. It can be seen from the table that the order parameter for the decomposition reaction is a decimal number (0.67). It is known from the literature [50] that this apparent order 'n' does not necessarily have to be an integer but can also be a decimal number.

From the table it can be seen that the kinetic parameters calculated with Horowitz-Metzger equation are higher than the values obtained from the other three equations. This is due to the inherent error involved in the approximation employed in the derivation of the Horowitz-Metzger equation [45]. The negative values of ΔS indicate that the activated complexes for all the stages of decomposition have high ordered structure than the reactant, and the reaction in these cases may be described as "slower than normal" [51].

5.4 CONCLUSION

1. Poly(cardanyl acrylate), PCA was found to absorb oxygen and undergo crosslinking reaction under TGA and DSC experiments.
2.
 - a. The heat of polymerisation for poly(cardanyl acrylate) calculated from DSC curves is 177.68 J g^{-1} , while kinetic constants for the polymerisation reaction are in the range $E = 35 \text{ kJ mol}^{-1}$ and $A = 7.4 \times 10^1 \text{ s}^{-1}$
 - b. Activation energy for decomposition of PCA is in the range of $44\text{-}66 \text{ kJ mol}^{-1}$ and the values of A are in the range $10^0\text{-}10^2 \text{ s}^{-1}$

3. The results obtained in thermal analysis of PCA indicate that TGA and DSC could be used for monitoring the oxygen absorption and crosslinking reaction of polymers which are undergoing autoxidation reaction.

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P a r t B

CHAPTER 6

CATIONIC GRAFT COPOLYMERISATION OF CARDANOL ONTO CELLULOSE *

6.1 INTRODUCTION

The grafting of synthetic polymers to natural polymers from renewable resources offers the potential of preparing newer varieties of engineering materials with specific and improved properties for a wide range of applications [1-3]. Cellulose graft copolymers find a variety of applications in a number of areas as given in the introductory chapter. In view of the numerous applications of cellulosic graft copolymers cited, there has been considerable amount of research and development effort towards the macromolecular engineering of cellulose to produce novel copolymers containing cellulose and grafted poly(vinyl) or any other synthetic polymer [4].

A search through the literature on grafting of vinyl monomers onto cellulose [1-7] indicates that one area that needs further input is the grafting of bio-monomers isolated from plant materials. There has been interest in utilising copolymers of natural and synthetic polymers as completely biodegradable carriers for pharmacons and agricultural chemicals [8]. There exists a variety of bio-monomers having interesting structural features for incorporating speciality properties[9,10]. This prompted us to utilise a regionally available monomer for graft copolymerisation reaction as a substitute for synthetic monomers and

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evaluate the properties. Among the bio-monomers, cardanol [11] can be easily functionalised and polymerised cationically into polymers with specific performance properties such as ion exchange, flame retardant, liquid crystals etc.

This chapter contains the results of the work on grafting of cardanol onto cellulose. Of the various methods presented in the introductory chapter for graft copolymerisation of cellulose, cationic method was selected because, cardanol during initial probing experiments on polymerisation [12,13] did not respond to free radical, radiation, photo-initiation or other methods involving free radical active centre except that of carbocationic active centre (Anionic or redox systems may work but was not experimented with). Plesch [14] proposed that polymeric halides eg. poly (vinyl chloride) (PVC) could be used to generate polymer cations in the presence of Lewis acids such as AlCl_3 , TiCl_4 and that the PVC carbocation could initiate the polymerisation of styrene and other vinyl monomers. Later, Kennedy et al [15] extensively studied cationic graft copolymerisation of various polymers using different initiators and various methods and products. But there are only limited reports on the cationic graft copolymerisation of cellulose. Richards et al [16] proposed a mechanism of carbocation formation on cellulose molecule in presence of Lewis acids and subsequent grafting of the polymer. Rausing et al [17] reported the cationic graft copolymerisation of isobutylene onto cellulose using $\text{BF}_3 \cdot \text{etherate}$ as cationic initiator. As a prelude to studying the cationic polymerisation of cardanol onto cellulose, Pillai et al studied the kinetics of cationic

polymerisation of cardanol using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ [12-13].

On the basis of the above reported studies, the study on grafting of cardanol onto cellulose is important as a substitute to synthetic monomers. The grafting of cardanol onto cellulose is important not only to prepare novel cellulose graft polymers, but also for the preparation of polymers where speciality properties such as flame retardant, ion exchange properties etc. could be introduced by chemical modifications of the hydroxyl group.

6.2 EXPERIMENTAL

6.2.1 Materials

Details of cellulose and cardanol used were given in chapter 2.

Borontrifluoridediethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) : $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (Fluka) was used after purification by distillation under vacuum (3-4 mm Hg) and the fraction at 65°C was collected. (BF_3 content: 48%).

Arzenazo-1 dye : The dye (Fluka) was used as received for the water repellency tests.

Solvents were used of Merck (India) products and was distilled before use.

6.2.2 Methods

6.2.2.1 Synthesis of cellulose graft copolymers

Sheets of Whatman No.41 filter paper (1.5 x 12 cm) were used

for this study. The sheets (five in a batch) immersed in $\text{BF}_3 \cdot \text{Et}_2\text{O}$ placed in screw capped test tubes and allowed to interact for 1-2 h at ambient temperature in a glove box. The paper strips were drained and dried in vacuo, and then immersed in cardanol in a stoppered test tube for another three hours. The paper strips were then washed with acetone and Soxhlet extracted for 24 h. in acetone to remove homopolymer. The degree of grafting (G) was calculated using the formula $G = \frac{A-B}{B} \times 100$ where A is the weight of the grafted sample after extraction and B is the weight of the original sample [18].

6.2.2.2 Hydrolysis of the grafted cellulose

The grafted chain (poly cardanol) was isolated by hydrolysing the graft copolymer with 72% sulphuric acid according to the method of Guzman et al [19].

6.2.2.3 Water repellency

The water repellency of the samples was measured by following methods such as (i) sinking technique [20], (ii) water penetration test [17] and (iii) contact angle measurements [21].

(i) Sinking method:

This method was used to measure the water repellency of a sample like paper and textiles. In this method the time required to sink a material in water was measured as per the following procedure. Sample specimens of 1 cm were floated on water containing 1% wetting

agent at constant temperature. The time required to sink the sample was noted.

(ii) Water penetration test:

Water penetration test [17] involves the measurement of time required to penetrate water through the grafted material and the test was carried out as follows. The edges of the sample of the paper to be tested were protected by dipping in paraffin wax. One side of the sample was then dusted with Arzenazo-1 dye. Sample was allowed to float on water surface, keeping the powdered side of the sample upward. As soon as the water penetrates the paper, its surface will turn red as the dyestuff particles dissolve in water. The time elapsed from the beginning of the test to the moment when the red colour can first be observed is considered as the water penetration time.

(iii) Contact angle measurements:

The change in contact angle of a material with water droplet is a measure of change in the surface property such as hydrophobicity or hydrophilicity [21] and was carried out as follows: Contact angles measured with a horizontal travelling microscope with a cross hair eye piece attached to a goniometer (Spindler and Hoyer, Gottingen, FRG). The grafted filter paper specimen was put on a wooden block as the stage. The stage was illuminated from behind at a sufficient distance to minimize heating of the drop by light source. The drops were sufficiently small (0.3-0.4 mm dia) to avoid gravitational distortion, yet were large enough to measure conveniently. Contact

angle measurements were made quickly after drop formation.

6.2.2.4 Acid resistance test

Acid resistance [19] of the samples tested by using various percentages of sulphuric acid, 72% and 97%. The samples were dipped into sulphuric acid of a known concentration. The time required to complete degradation of cellulose were noted.

6.2.2.5 Instruments

IR spectra were recorded on a Perkin-Elmer Model 882 spectrophotometer. SEM was carried out using a JEOL JSM-35 C instrument with the sample sputtered with gold. TG-DTG analysis of the polymers were carried out using a Du Pont 951 modular thermal analyser system in conjunction with a Du Pont 2000 thermal analyst system. DTA experiments were carried out using Du Pont 901 DTA coupled with Du Pont 2000 thermal analyst system. XRD patterns were recorded using a Philips PW-1710 powder diffractometer using Cu-K α radiation. Further details regarding the instrumentation and computational work are given in chapter 2.

6.3 RESULTS AND DISCUSSION

The synthesis and characterization of cellulose graft copolymers using synthetic monomers and polymers are well studied [1-5]. In general, the grafting is carried out by free radical and radiation induced techniques. This may be one of the first attempts to graft a bio-monomer isolated from a plant material onto cellulose. In the case of cardanol,

grafting was not observed when carried out by free radical or γ -ray irradiation techniques. This was in conformity with the observation that cardanol did not undergo homopolymerisation by these methods. The possible explanation for the unsuccessful grafting reaction by free radical method is due to the radical quenching ability of cardanol [22]. So grafting of cardanol onto cellulose was carried out using a cationic initiator $\text{BF}_3 \cdot \text{etherate}$ as reported by Pillai et al for the homopolymerisation of cardanol [12]. There are a few reports on the cationic graft copolymerisation of vinyl monomers onto cellulose such as grafting of isobutylene, α -methyl styrene etc. [23]. Lewis acids on interaction with cellulose generates cations which are capable of initiating cationic polymerisation reaction and subsequent grafting [34].

The grafting of cardanol onto cellulose was carried out as per the procedure mentioned in the experimental part.

6.3.1 Effect of time on grafting percentage

Figure 6.1 shows the percentage grafting of cardanol with time of contact of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ with the filter paper. There is an induction period upto 20 minutes after which only grafting reaction starts. A maximum percentage of 25 is reached in about 100 minutes, and then no further improvement could be observed.

6.3.2 Effect of concentration of $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Figure 6.2 shows the effect of change of concentration of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The minimum concentration required for the graft copolymerisation was 20% (vol/vol) $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in methylene chloride. The

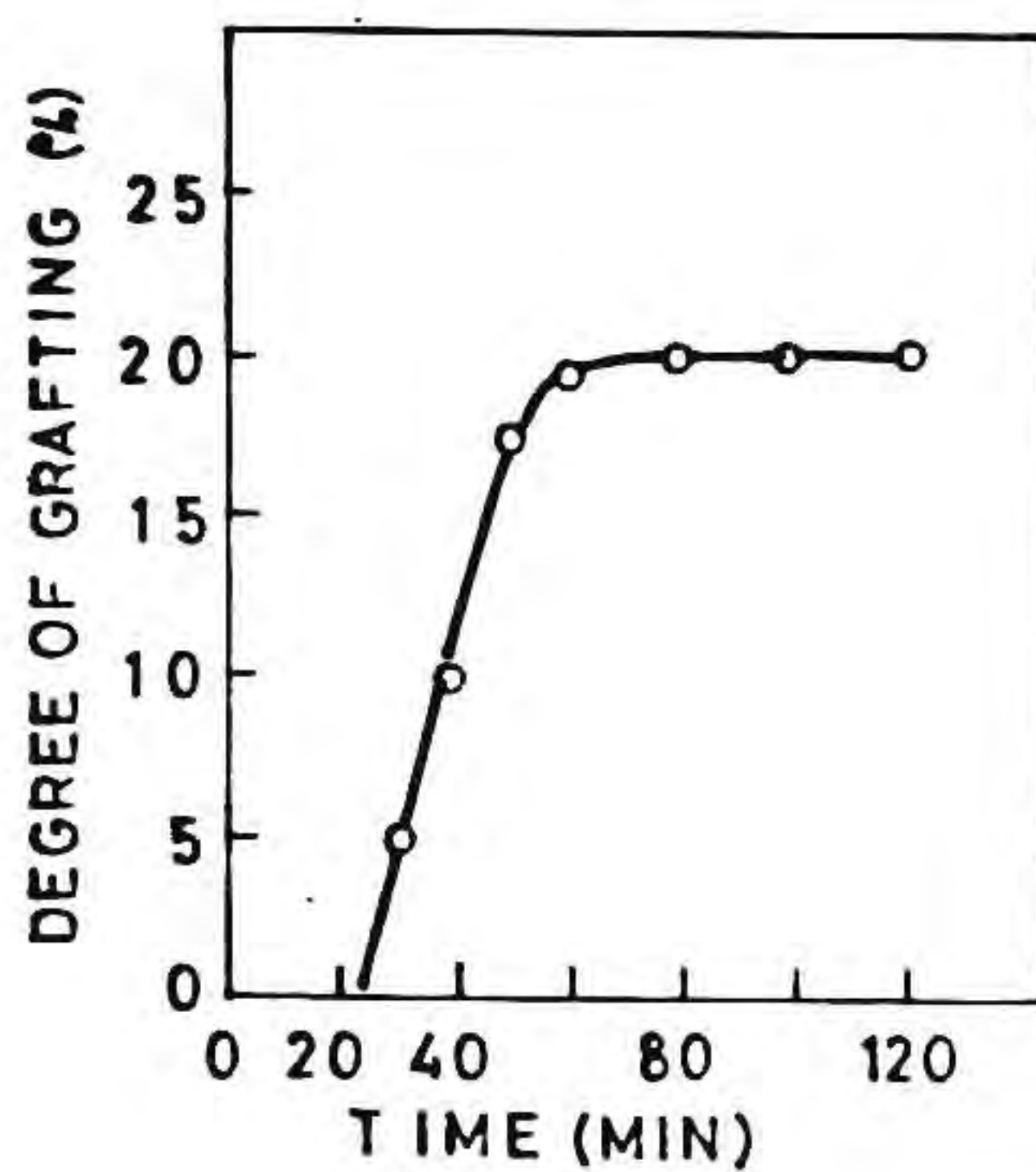


Fig. 6.1: Effect of time on percentage grafting

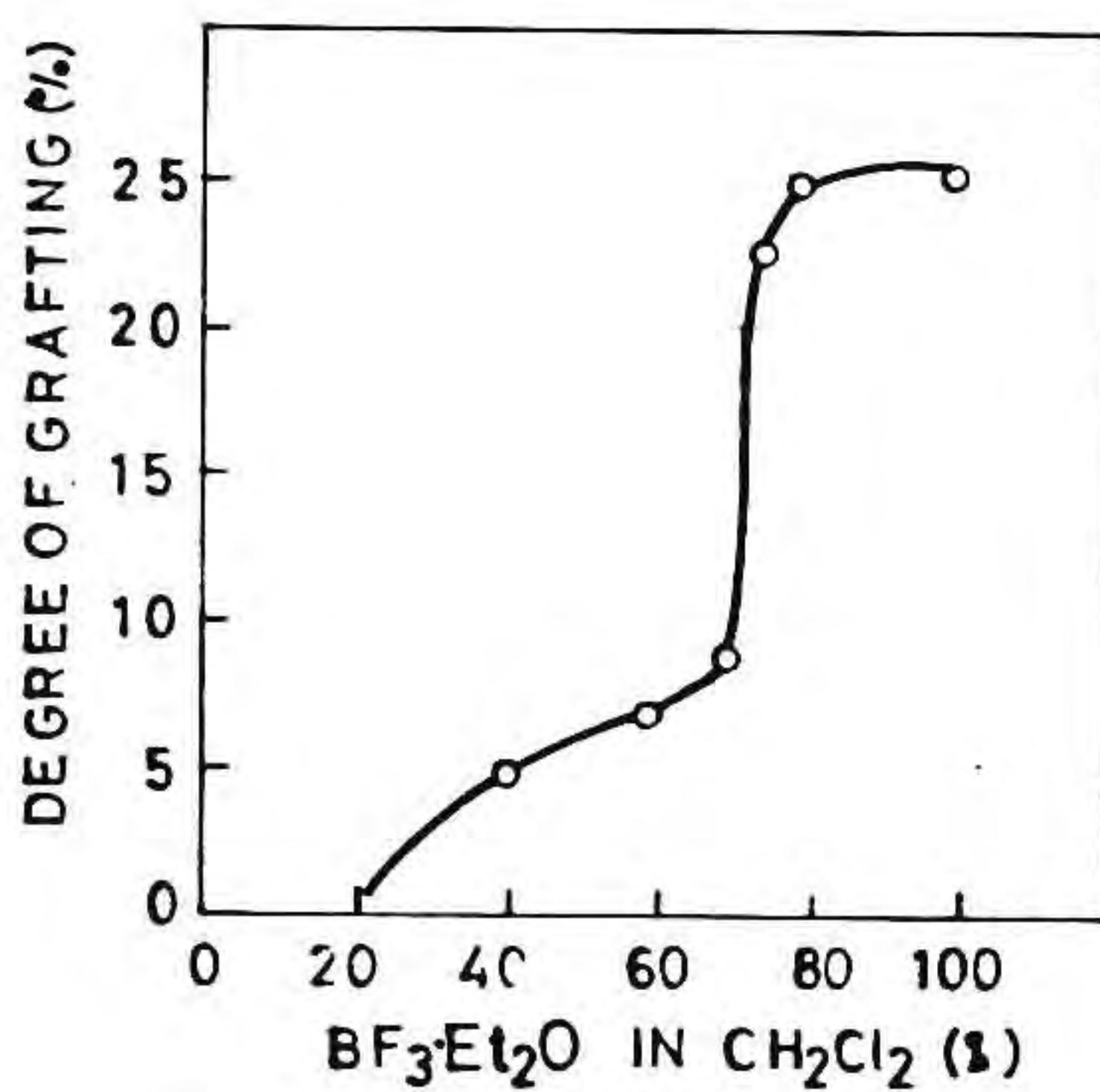


Fig. 6.2: Effect of concentration of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 (vol/vol) on percentage grafting

percentage grafting is only 8-9% upto a concentration of 70% (vol/vol) and then there is a sharp increase in percentage grafting to 25% at 80% (vol/vol) concentration of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in methylene chloride. It is possible that the active ionic species for effecting the grafting needs a critical concentration.

6.3.3 IR results

Figure 6.3 shows the IR spectrum of the original filter paper and grafted paper. The spectrum of grafted one shows additional peaks at 3000 cm^{-1} and 1600 cm^{-1} etc. showing the presence of aromatic structure in the sample (Table 6.1). This indicates an evidence for grafting because aromatic structure can come only from grafted cardanol.

6.3.4 SEM results

Scanning electron micrographs shows that grafted cardanol polymer existing as granules on the surface of cellulose (Figure 6.4c). Whereas with extended period of grafting a neat film could be visible in Figure 6.4d in comparison to the ungrafted samples (Figures 6.4a&b). Similar changes in SEM photograph of the grafted samples have been reported in literature [24].

6.3.5 Thermal decomposition studies

Thermogravimetric analysis (TG) results:

Thermograms of cellulose and cellulose grafted with cardanol are shown in Figure 6.5. Shapes of thermograms of cellulose and

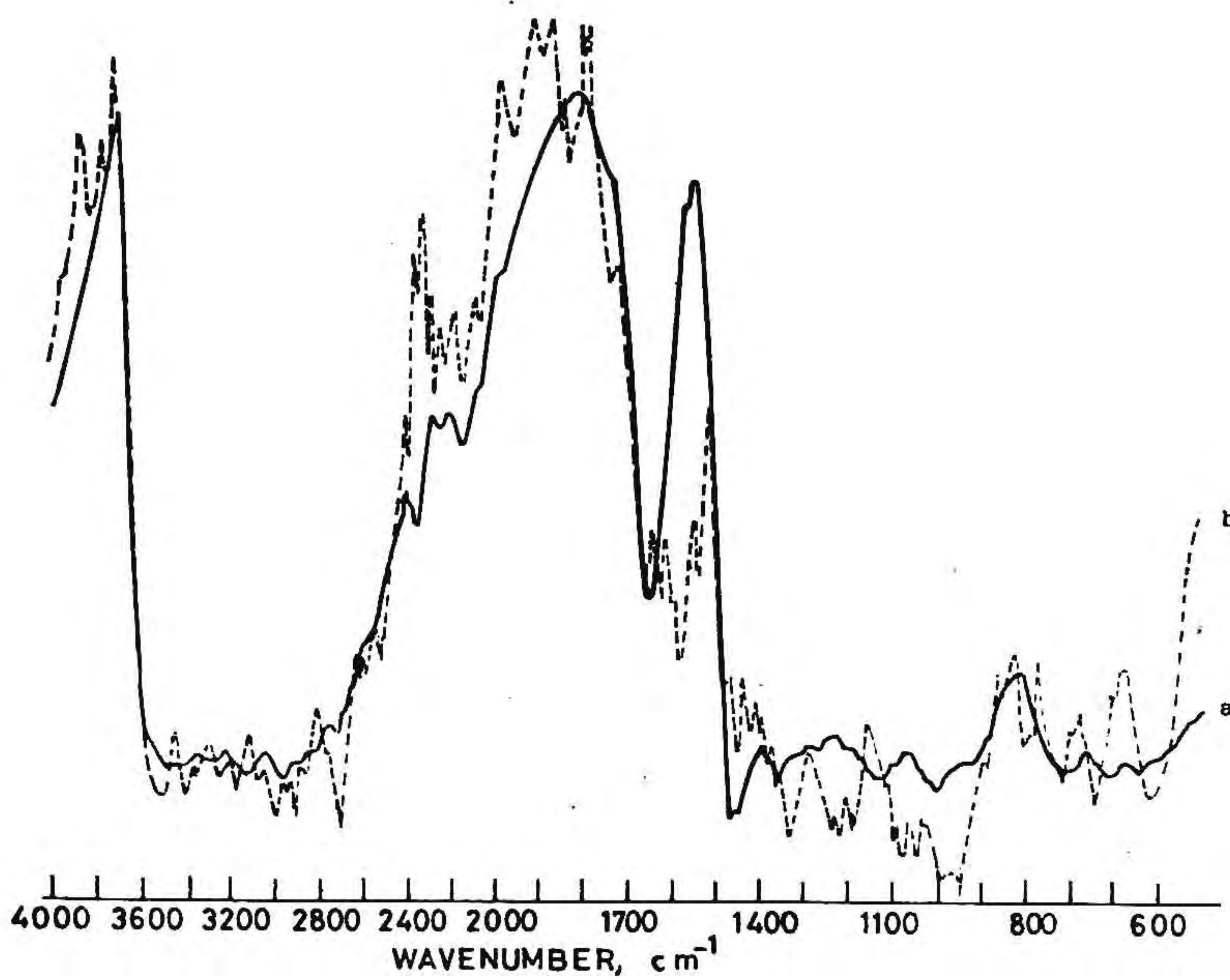


Fig. 6.3: IR spectrum of (a) Whatman No.1 filter paper,
(b) cardanol grafted paper

Table 6.1: IR spectra of cardanol grafted cellulose

Peak (cm^{-1})	Assignment of groups
3300-3600	OH Str
3200	C-H Str
2960	
3020	=C-H Str (vinyl)
3000	C-H Str (aromatic)
2855	-CH ₂ Sym Str
1600	Vinyl and aromatic C-H Str
1635	
1685	
1482	C-O-H def.
1455	
1456	-CH ₂ - bending of aliphatic attached to aromatic
1015	aromatic
1048	

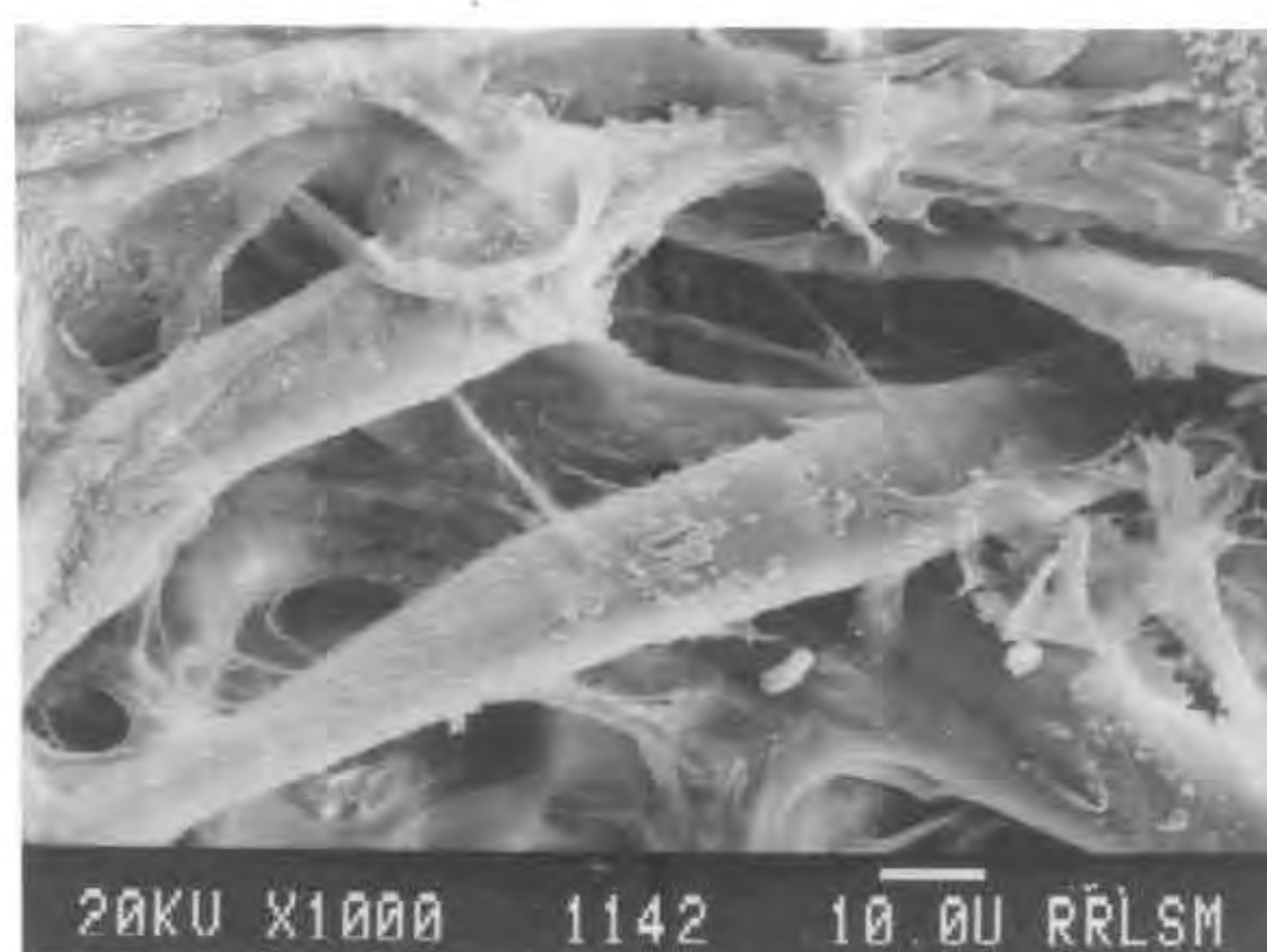


(a)

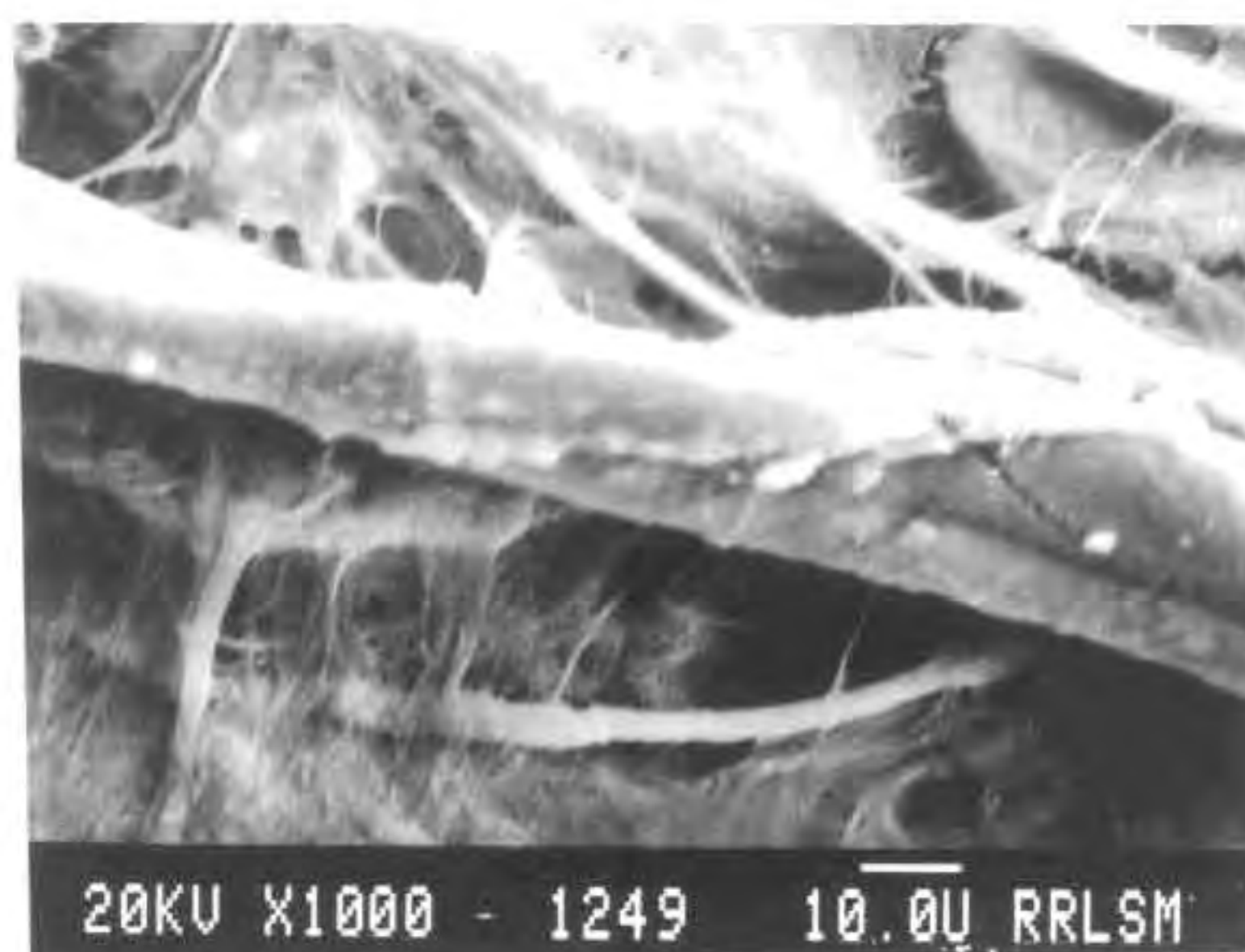


(b)

Fig. 6.4: SEM photographs of (a) untreated paper, (b) $\text{BF}_3 \cdot \text{Et}_2\text{O}$ treated paper



(c)



(d)

Fig. 6.4: SEM photographs of (c) grafted paper 1 h reaction, (d) 2 h reaction

grafted cellulose samples do not differ from each other significantly. However, it can be seen from Table 6.2 that after the initial weight loss, the graft copolymer registers a higher stability than the cellulose control sample. Thus in the control sample, major weight loss of about 80% occurs between 330 and 360^oC, whereas in the grafted samples it occurs between 330-490^oC for a sample with 25% cardanol polymer graft add-on. Thus for a sample with 25% cardanol graft add-on, even upto a temperature of 470^oC, only about 70% loss in weight of the grafted sample takes place. Similar behaviour has been observed in the case of styrene grafted cellulose by Shukla et al [25] and Sharma et al [26]. The graft copolymer has also gives a char residue of 19.5% (weight) at 500^oC in comparison to 4% (weight) of the control sample. The formation of higher char in grafted cellulose might be due to either (1) the presence of phenolic moiety (it is well known that phenolic structure give rise to high char yield on thermal decomposition [27]) or (2) crosslinking of grafted cardanol (the film obtained after the acid hydrolysis of the grafted product was insoluble and infusible). Ramani Narayan et al in a study on grafting of polystyrene onto acetylated wood has reported similar observations and confirms that these observations lend support to formation of a crosslinked graft copolymer [28].

Kinetics of decomposition of cellulose and cardanol grafted cellulose:

The kinetic parameters for the decomposition of cellulose and cardanol grafted cellulose were evaluated (300-380^oC) using the non-mechanistic equations. The results are listed in Table 6.3. The correlation coefficients (r) were in the range 0.9939-0.9967 and 0.9899-0.9922

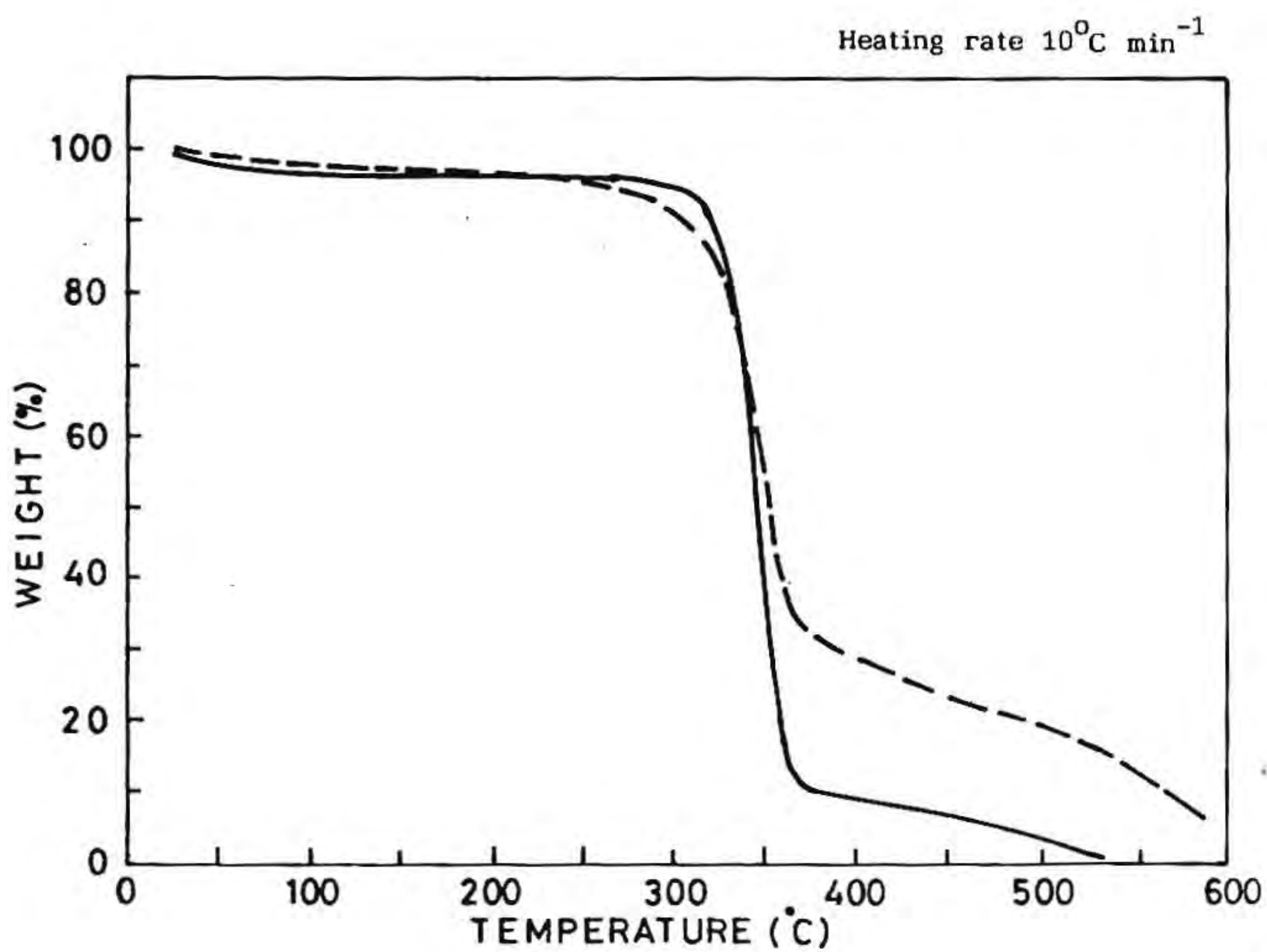


Fig. 6.5: TG-curves of (a) Whatman cellulose, (b) cardanol grafted cellulose

Table 6.2: Temperature of decomposition at different weight losses of cellulose grafted with cardanol polymer

(Heating rate = $10^{\circ}\text{C min}^{-1}$)		
Weight loss %	Temperature of decomposition graft add-on	
	0.00	25.32
10	320	305
20	330	330
30	340	340
40	342	345
50	345	355
60	350	360
70	355	390
80	360	490
90	380	560

indicating nearly perfect fits. It can be seen from Table 6.3 that the order parameter for decomposition of cellulose and grafted cellulose are decimal numbers. It is known from the literature [29-30] that this apparent order n , does not have to be an integer but may also be a decimal number. It can also be seen that the kinetic parameters evaluated with the Horowitz-Metzger equation are always higher than the values from the other three equations. This is due to the inherent error involved in the approximation employed in the derivation of the Horowitz-Metzger equation [31].

Table 6.3 shows that the activation energy of the cardanol grafted sample is lower than that of the control cellulose. Although this could appear inconsistent with TGA results it could be observed from Fig. 6.5 that the initial stages of decomposition of cardanol grafted cellulose is faster than that of cellulose itself. This is true for most of the hydrocarbon grafted cellulose polymer [28] which generally show increased susceptibility to heat. Unlike hydrocarbon polymers, cardanol has a phenolic moiety which as was explained earlier lends increased stability to the grafted polymer. Thus, as could be expected, the ΔS values of the cardanol grafted polymer showed negative values in comparison to that of the control sample (cellulose). The decomposition stages with positive values of ΔS indicate that the activated complex has a less ordered structure compared to the reactant and the reaction in these cases may be described as "faster than normal" [32]. The stages having negative entropy of activation indicate that the activated complex has a more ordered structure than the reactant and the

Table 6.3: Kinetic parameters for the decomposition of cellulose and cardanol polymer grafted cellulose using non-mechanistic equations from TG data

	Cellulose		Grafted cellulose	
n		1.32		1.48
E (kJ mol ⁻¹)	CR	181.25	CR	116.55
	MT	184.23	MT	119.03
	HM	195.32	HM	119.03
	MKN	181.45	MKN	116.82
A (s ⁻¹)	CR	1.36 x 10 ¹³	CR	2.45 x 10 ⁷
	MT	2.42 x 10 ¹³	MT	3.71 x 10 ⁷
	HM	2.05 x 10 ¹⁴	HM	2.79 x 10 ⁸
	MKN	1.42 x 10 ¹³	MKN	2.55 x 10 ⁷
Δ S (JK ⁻¹ mol ⁻¹)	CR	0.51	CH	-109.81
	MT	5.27	MT	-106.06
	HM	23.01	HM	- 89.29
	MKN	0.83	MKN	-109.17
r	CR	0.9959	CR	0.9914
	MT	0.9948	MT	0.9914
	HM	0.9967	HM	0.9922
	MKN	0.9939	MKN	0.9899

CR - Coats-Redfern; MT - MacCallum-Tanner; HM - Horowitz-Metzger;
MKN - Madhusudanan-Krishnan-Ninan

reaction is "slower than normal". This explains the decomposition pattern of the grafted product.

6.3.6 DTA results

Figure 6.6a shows the DTA curves of cellulose and grafted cellulose. In the DTA curve of cellulose, an endotherm was observed at around 150°C due to moisture desorption, followed by an exothermic process starting at about 260°C due to oxidative attack at the carbonyl groups and the C-H bonds. The major endothermic reaction was observed to start at 305°C with a peak at 341°C , which reflects the thermal depolymerisation of cellulose. The DTA curve shown in Figure 6.6b indicates that grafting with cardanol gives an altered DTA curve showing a new endothermic peak at around 360°C . This new endothermic peak was appearing after the major cellulose decomposition endotherm at 341°C , representing the presence of polycardanol copolymer. The endothermic peak around $100\text{--}110^{\circ}\text{C}$ corresponding to moisture absorption seems to be disappearing with increase in cardanol graft add-on due to increased hydrophobicity of the grafted sample as also reported in the case of styrene grafted cellulose [25,26].

6.3.7 Water repellency tests

In sinking technique, the cardanol polymer grafted sample took 1600 seconds to sink in water compared to 10 seconds for the untreated sample indicating excellent water repellent properties.

In comparison, polystyrene or polyacrylate grafted cellulose took 240-720 seconds for sinking of the paper [3] indicating that cardanol

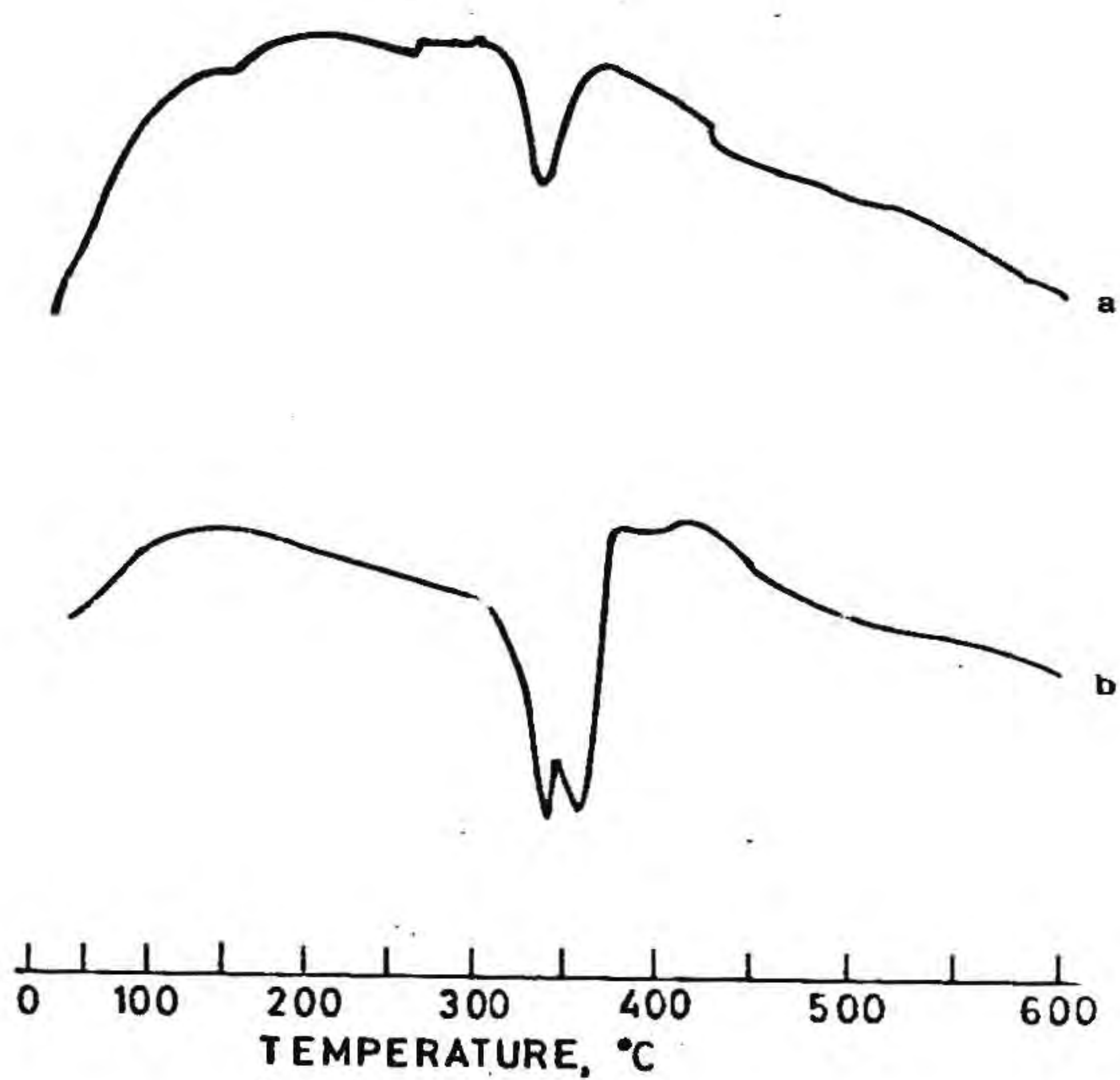


Fig. 6.6: DTA curves of (a) Whatman cellulose, (b) cardanol grafted cellulose

grafted cellulose has water repellency much superior to these systems. This could be understood from the fact that cardanol has a C_{15} hydrocarbon side chain which being hydrophobic in nature increases the water repellency. This could be further illustrated from the water repellency values of n-butyl acrylate having a butyl side chain (720 sec) in comparison to that of polystyrene (240 sec) (Table 6.4).

Table 6.4: Water repellency at about 30% graft add-on of various acrylates or styrene in comparison to cardanol grafted cellulose

Sample	Extent of grafting (%)	Time required to sink (sec)
Untreated cellulose	0	1
Cellulose grafted with n-butyl acrylate	29.4	720
Isobutyl acrylate	29.6	480
Methyl methacrylate	28.9	120
Styrene	30.7	240
Cardanol	25.32	1600

In the water penetration test described earlier, the red Arzenazo-1 dye develops red colour instantaneously in the case of untreated paper, whereas the treated one withstands more than 12 h.

Contact angle measurements are generally used to study the surface properties of materials. Cellulose when grafted with cardanol

polymer increases the hydrophobicity of the polymer. The contact angle of the grafted material gave a value of more than 90° which is in comparison to the contact angle value of polyethylene with water droplet. The hydrophilic nature of cellulose surface was totally changed to hydrophobic in nature which is comparable to a hydrocarbon polymer. This suggests that cardanol grafted cellulose could be of use in applications (for example, oil spillage) where a better hydrophobic material than that of styrene or polyethylene grafted cellulose is required. It was further noted that a membrane of cardanol grafted cellulose could separate a mixture of water and chloroform effectively indicating its possible use in the separation of organic solvents from aqueous environments.

6.3.8 Acid resistance study results

Acid ageing studies [24] of cardanol grafted and ungrafted cellulose were carried out using various strengths of sulphuric acid and the data are tabulated in Table 6.5. The grafted product showed enhanced resistance to deterioration by acid hydrolysis. The poly cardanol (25%) grafted cellulose took 24 h for complete degradation compared to the ungrafted one, which took only 10 min for complete degradation in 72% sulphuric acid. Concentrated sulphuric acid (97%) was also used to conduct the characterisation and the time for degradation are 60 min and 5 min respectively for grafted and untreated cellulose.

Jenkins et al [24] in their study on photo-initiated cationic polymerisation for use in paper preservation have observed that the

Table 6.5: Acid resistance values of cellulose and cardanol grafted cellulose

Sample	% of acid H_2SO_4	Time required to complete degradation
1. Untreated	72	10 min
Grafted	72	24 h
2. Untreated	97	5 min
Grafted	97	60 min

grafted polymer degrades much faster in H_2SO_4 in comparison to cardanol grafted cellulose. The superior resistance of cardanol grafted cellulose might be due to crosslinking of polycardanol during grafting. This is exemplified by the fact that the film obtained after the acid hydrolysis is insoluble and infusible.

The polymer obtained by acid hydrolysis of cardanol grafted cellulose was characterised by solubility studies, IR, XRD and SEM. The solubility of the polymer film in almost all solvents indicating that the grafted product is crosslinked. This was confirmed by the IR spectrum (Figure 6.7) of the polymer, which was similar to a spectrum of the cationically polymerised and crosslinked product obtained using $BF_3 \cdot Et_2O$ as catalyst [12], the characteristic absorption at 3020 cm^{-1} which is due to the side chain unsaturation present in cardanol was absent.

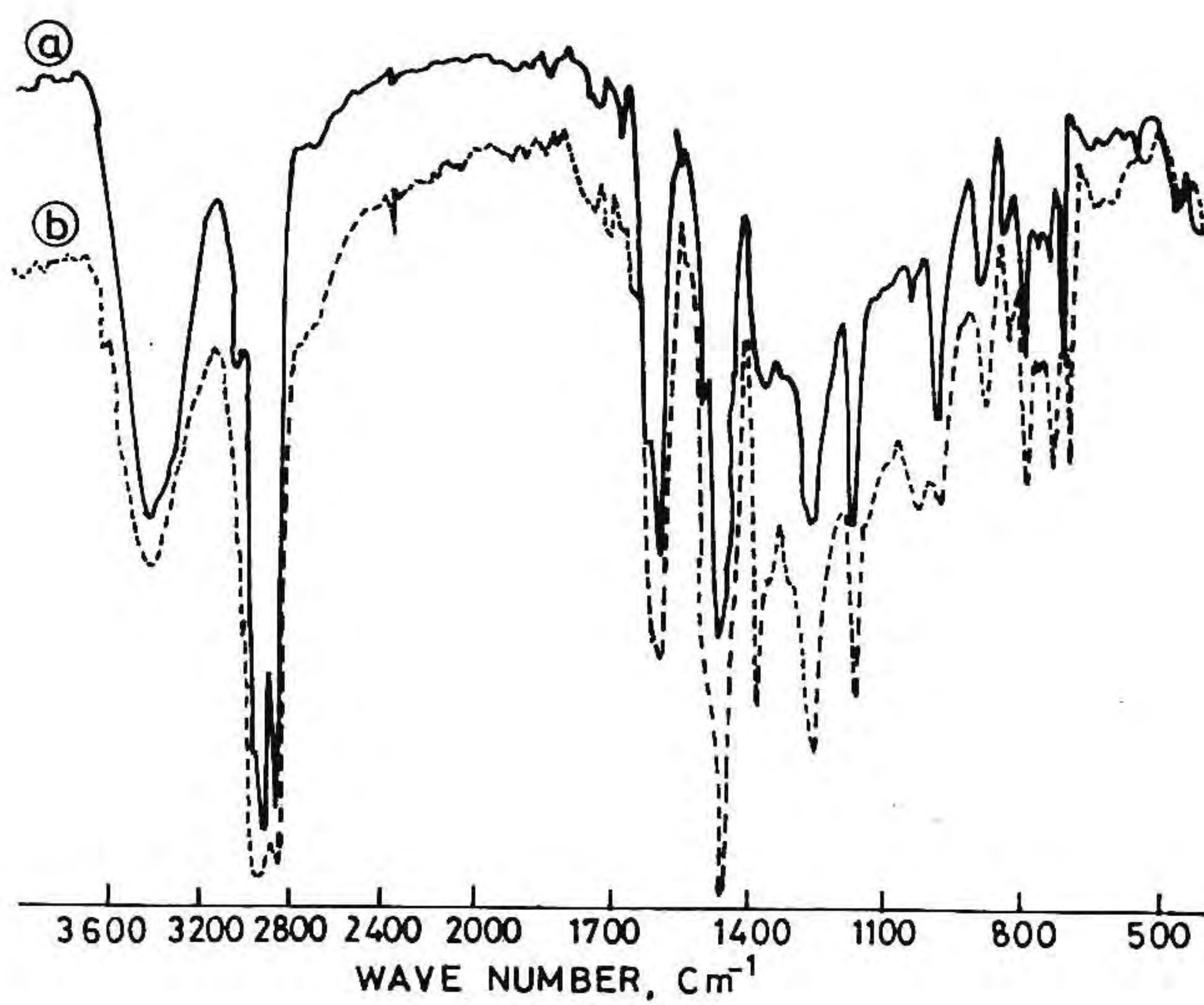


Fig. 6.7: IR spectrum of (a) the film obtained after acid hydrolysis of cardanol grafted paper, (b) crosslinked product of cardanol by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ polymerisation.

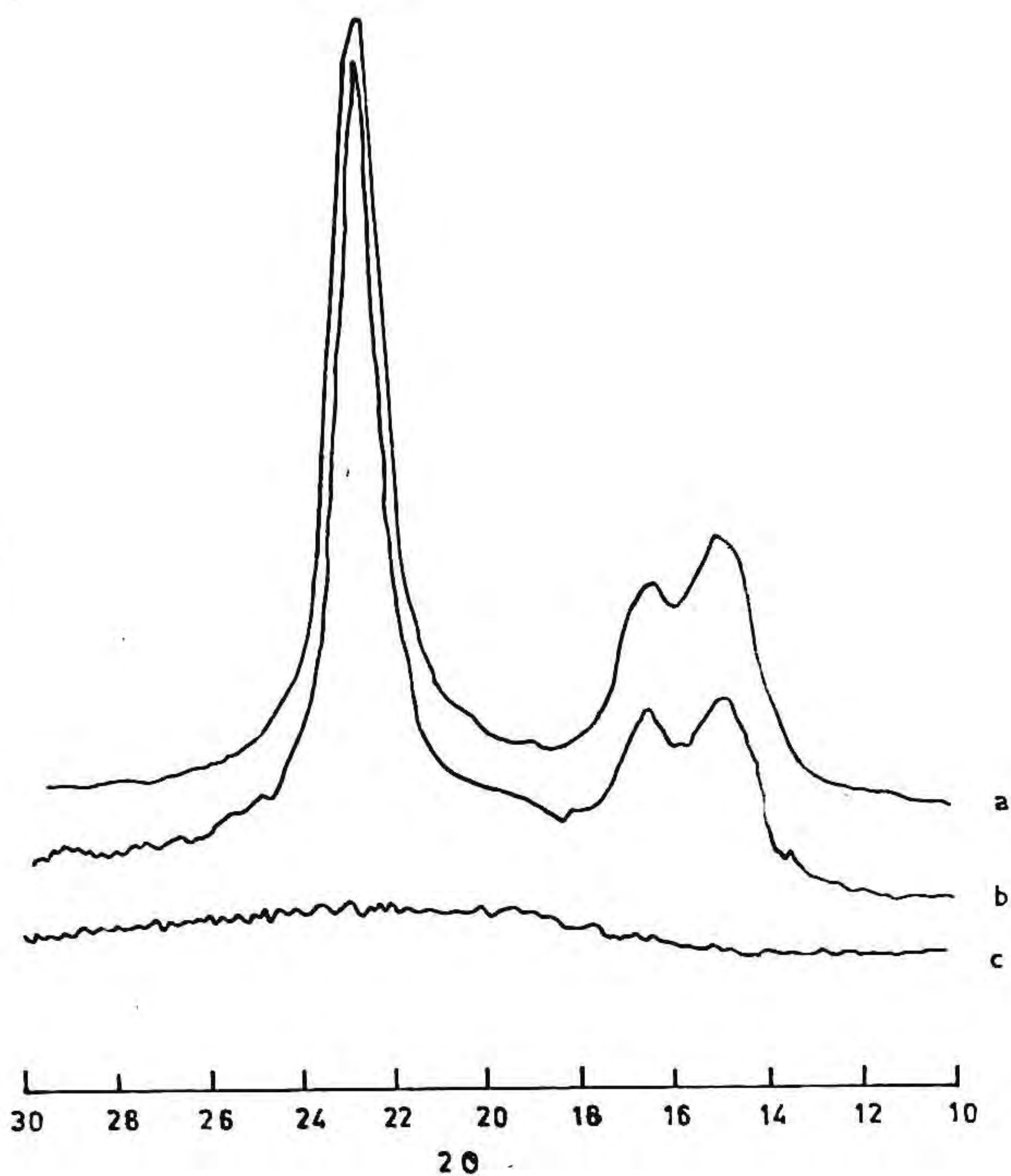


Fig. 6. 8: XRD patterns of (a) Whatman filter paper, (b) cardanol grafted filter paper, (c) film obtained by acid hydrolysis of cardanol grafted paper

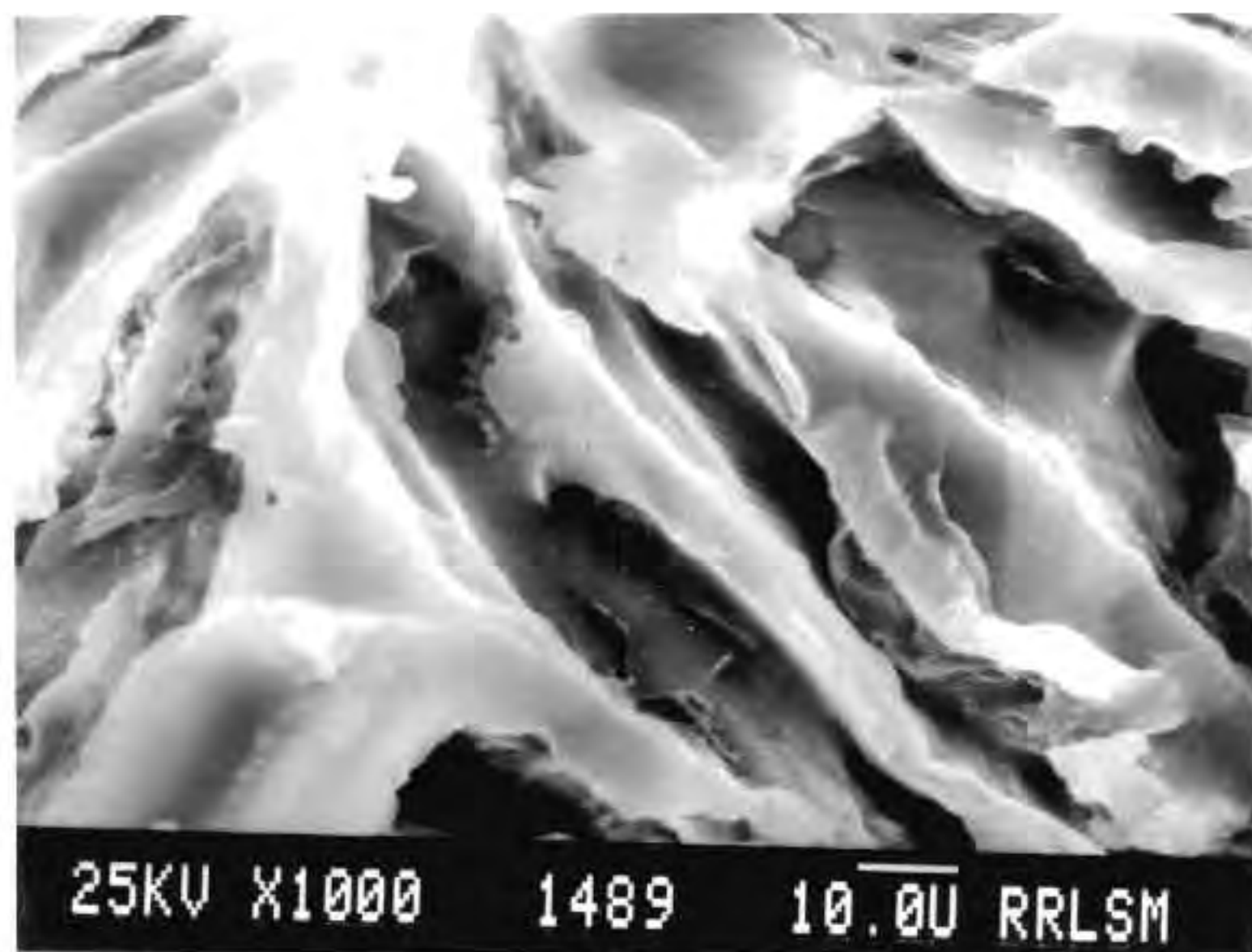
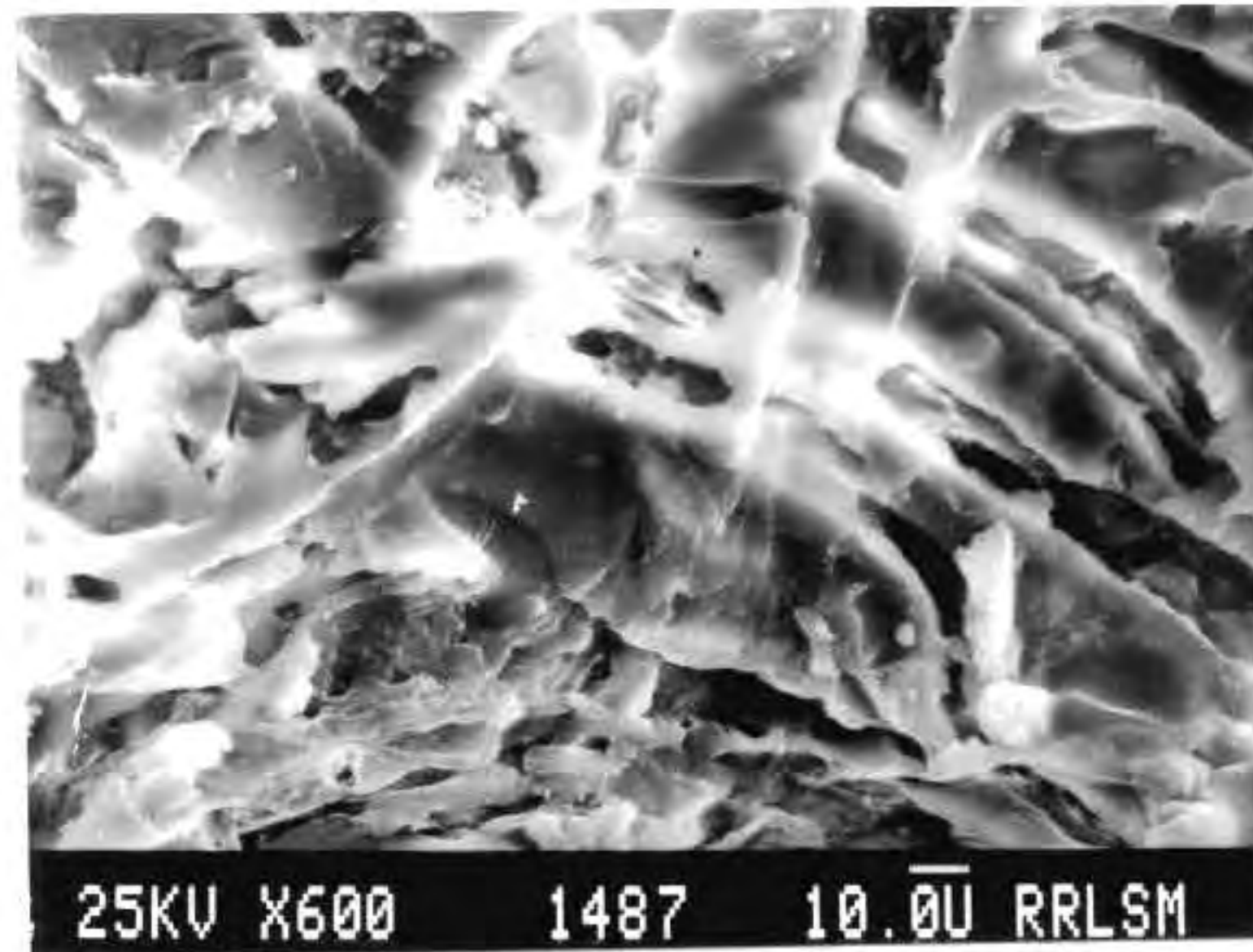


Fig. 6.9: SEM photograph of film obtained by acid hydrolysis of cardanol grafted filter paper

X-ray diffraction patterns of the cardanol grafted cellulose before and after hydrolysis are given in figure 6.8. The disappearance of the crystalline peak of cellulose in Figure 6.8c of the film obtained after acid hydrolysis indicate that cellulose is completely removed by hydrolysis and that the film is totally amorphous in nature. SEM pictures were supporting these observations (Figure 6.9).

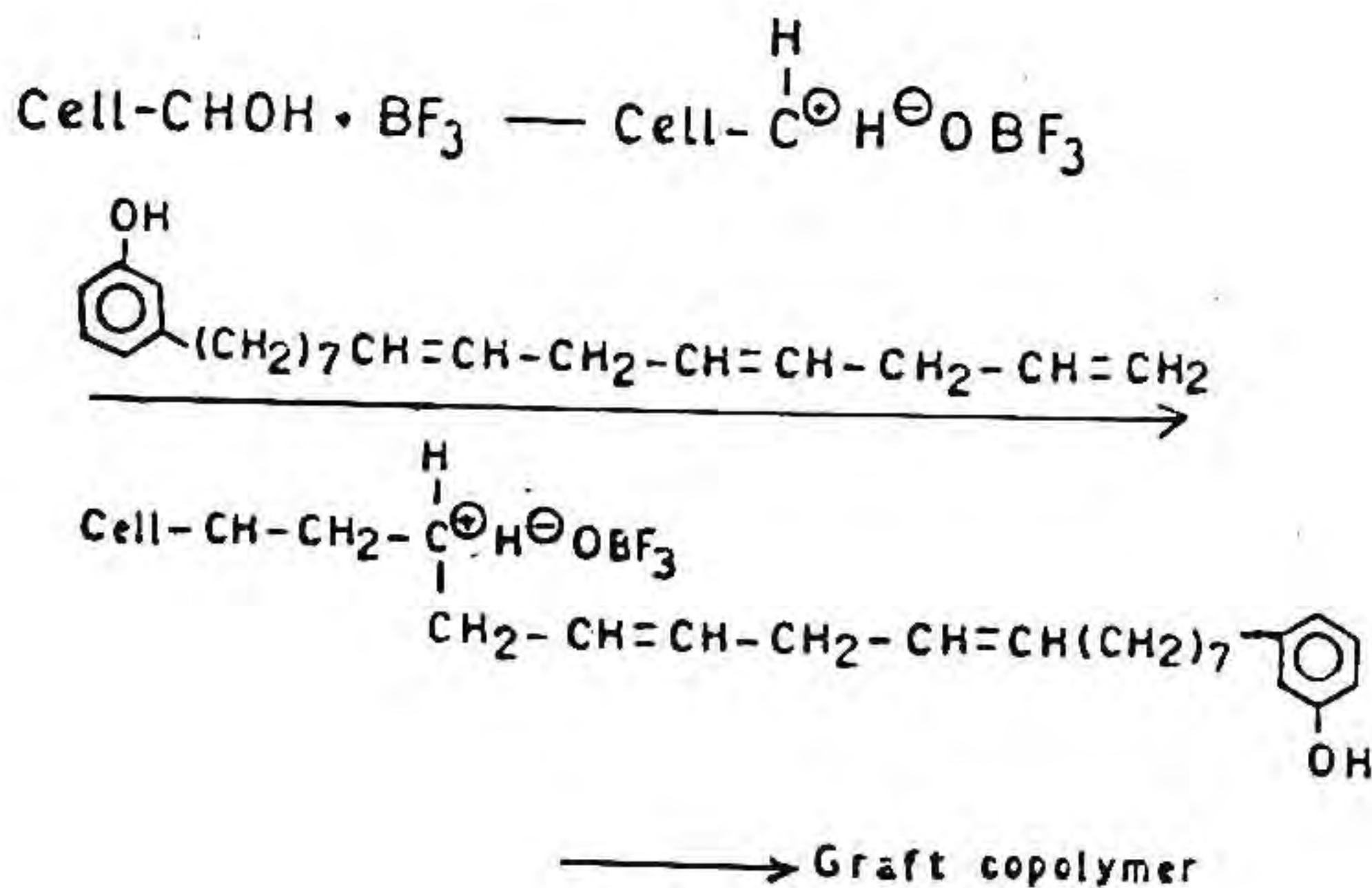
6.3.9 Mechanism of grafting of cardanol onto cellulose using $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Metal halides of the Friedel-Crafts type (eg. BF_3 , TiCl_4 and AlCl_3) are well known to effect polymerisation of a number of vinyl monomers [33]. The polymerisation reaction takes place rapidly at very low temperatures and proceeds through a mechanism involving ions. Mostly the reaction requires the presence of traces of substances, such as water or hydrochloric acid, which acts as co-catalyst. The monomers polymerised by these substances contain electron-releasing substituents, so that the doubly bonded carbon atoms tend to share a pair of electrons with these electron acceptors. This would imply that their mode of action involves carbonium ions.

Lewis acids are effective catalysts for grafting of vinyl monomers onto cellulose [16]. Cellulose absorbs [34] the catalyst which undergoes chemical reaction with the -OH groups present in cellulose to form stable cationic salts. This means that the catalyst must spread very rapidly over the active surface of the cellulose. The addition compound between cellulose and catalyst must act very rapidly. In actual practice the hydroxyl group of the cellulose serves as a

Lewis-base [17]. The presence of pairs of free electrons around the oxygen atoms in the hydroxyl group determine their character as a base. An entire group of well known polymerisation catalysts of ionic type can thus react with the hydroxyl group of the cellulose, the Lewis-base. The resultant Lewis salt still being a catalyst can thus initiate a polymerisation of a suitable monomer such as isobutylene and α -methyl styrene. Boron trifluoride is an effective Lewis acid type catalyst and is shown to be a good cationic initiator for cardanol. Earlier work in this laboratory [12] has shown that BF_3 etherate forms a carbocationic species with cardanol at the unsaturated double bond in the side chain which initiates polymerisation. It is reported that BF_3 etherate forms a complex with cellulose as in Scheme 6.1. This complex with the carbocationic centre can interact with cardanol transferring the cationic active centre to the unsaturated vinyl group of cardanol (the triene component is shown for simplicity). The overall mechanism of grafting of cardanol onto cellulose can be depicted as in Scheme 6.1.

Eventhough cardanol is a mixture of four components varying in the unsaturation in the side chain, Tyman has proposed that the polymerisation of cardanol under acidic conditions might involve the formation of an allylic carbonium ion from the more reactive triene component [11]. However, Tyman did not provide any experimental evidence regarding the involvement of triene component alone. But, the studies on the kinetics of polymerisation of cardanol using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and protonic acids by Pillai et al indicate conversion of all the monoene, diene and triene into the polymer and the complex nature of



Scheme 6.1: Proposed mechanism of grafting of cardanol onto cellulose

the system cautions not to make conjectures on the nature of the mechanism of polymerisation [12]. It appears, therefore, that the graft copolymerisation of cardanol onto cellulose under $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as initiator could be said to carbocationic in nature and might involve all components of cardanol. Further understanding of the system requires data on the rates of the reaction of the individual components.

6.4 CONCLUSIONS

1. Cardanol, a biomonomer obtained from the plant *Anacardium occidentale* L was grafted onto cellulose by a carbocationic method.
2. The grafted product showed excellent water repellency and enhanced acid resistance.

3. The hydrophobicity of cellulosic materials (and thus affinity for oil) could be increased by grafting cardanol instead of styrene or polyethylene for preparing oil absorbents.
4. Cardanol grafted paper could find use in separation of organic solvents from aqueous solutions by using as a membrane. Preliminary experiments gave encouraging results.
5. The phenolic moiety of cardanol in the grafted cellulose can be further modified for appropriate applications.

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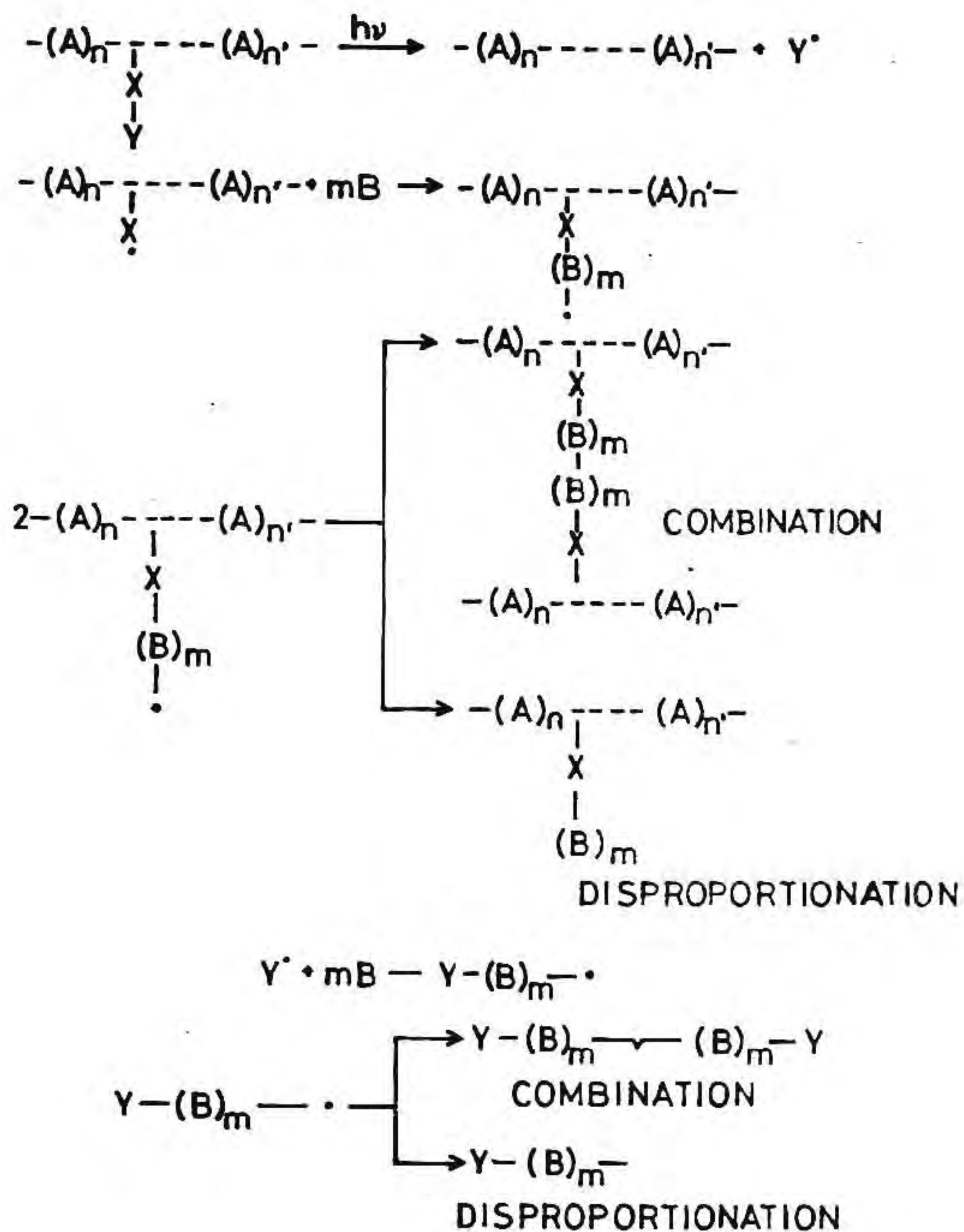
CHAPTER 7

PHOTO-INDUCED GRAFT COPOLYMERISATION OF METHYL METHACRYLATE ONTO CELLULOSE CONTAINING BENZOYL XANTHATE CHROMOPHORE

7.1 INTRODUCTION

The preceding chapters dealt with studies on chemical modifications of a natural monomer, cardanol and a natural polymer, cellulose. The chemical modification of cardanol was effected by modifying the hydroxyl group by acrylate/methacrylate moiety followed by polymerisation whereas the chemical modification of cellulose was achieved by the method of grafting, using cardanol itself as the monomer source. This chapter deals with the graft copolymerisation of a synthetic monomer viz. methyl methacrylate (MMA) onto cellulose by a photo-induced method of grafting using benzoyl xanthate chromophore.

As described in the earlier chapter, graft copolymerisation is one of the widely accepted methods for tailoring the properties of natural polymers such as cellulose and related materials to specific requirements because grafting frequently results in the superposition of properties relating to backbone and side chain polymer. Among the different techniques described in the introductory chapter, photo-induced grafting has the advantage of being applicable at low temperatures, especially at room temperature [1]. Because of the selective absorptivity of certain groups (chromophores), it is possible to produce reactive free radical centers at definite positions in the macromolecules [1,2]. Thus, photo-induced graft copolymerisation has more

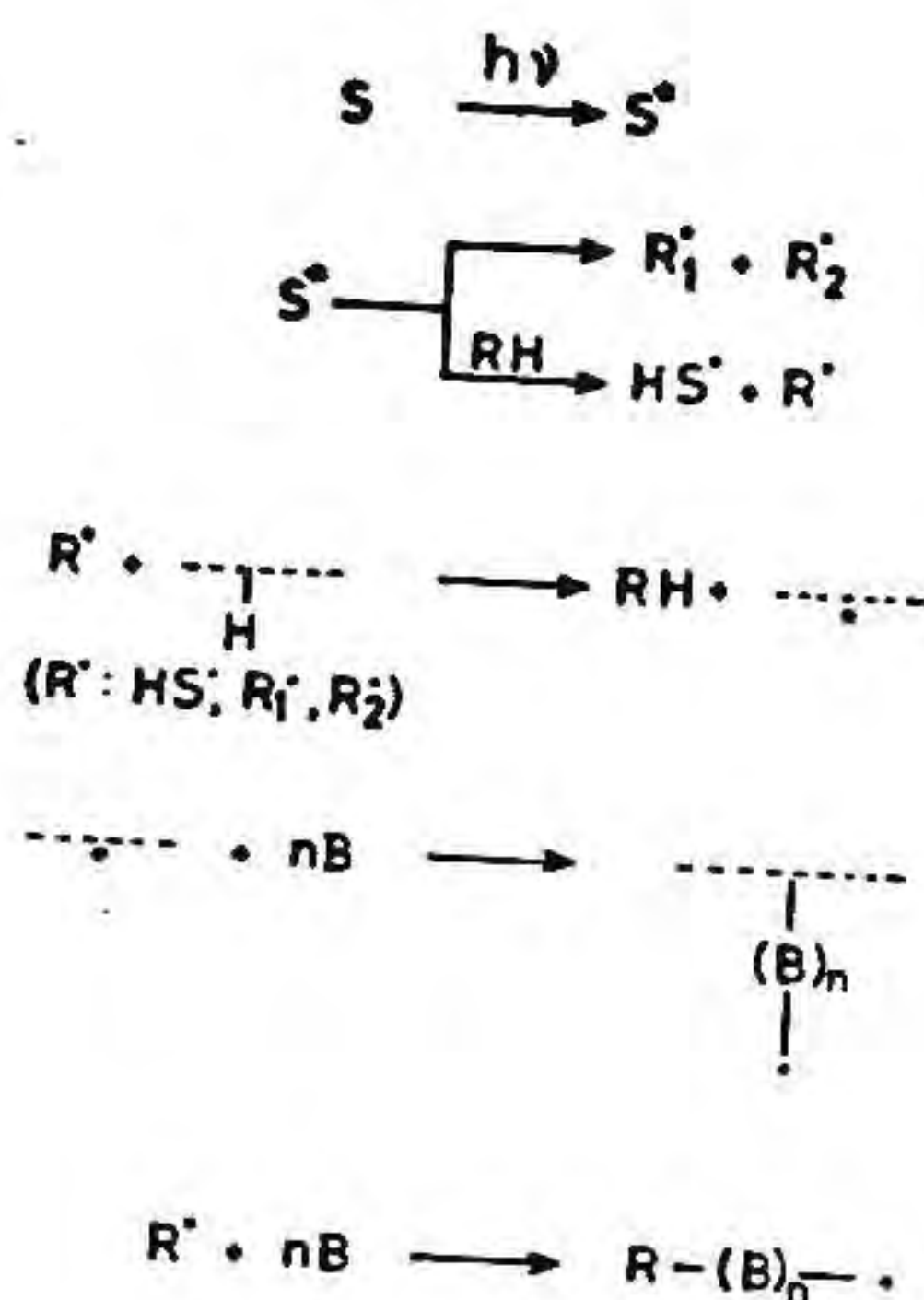


Scheme 7.1: Free radical graft copolymerisation. Initiation by lateral photolabile groups

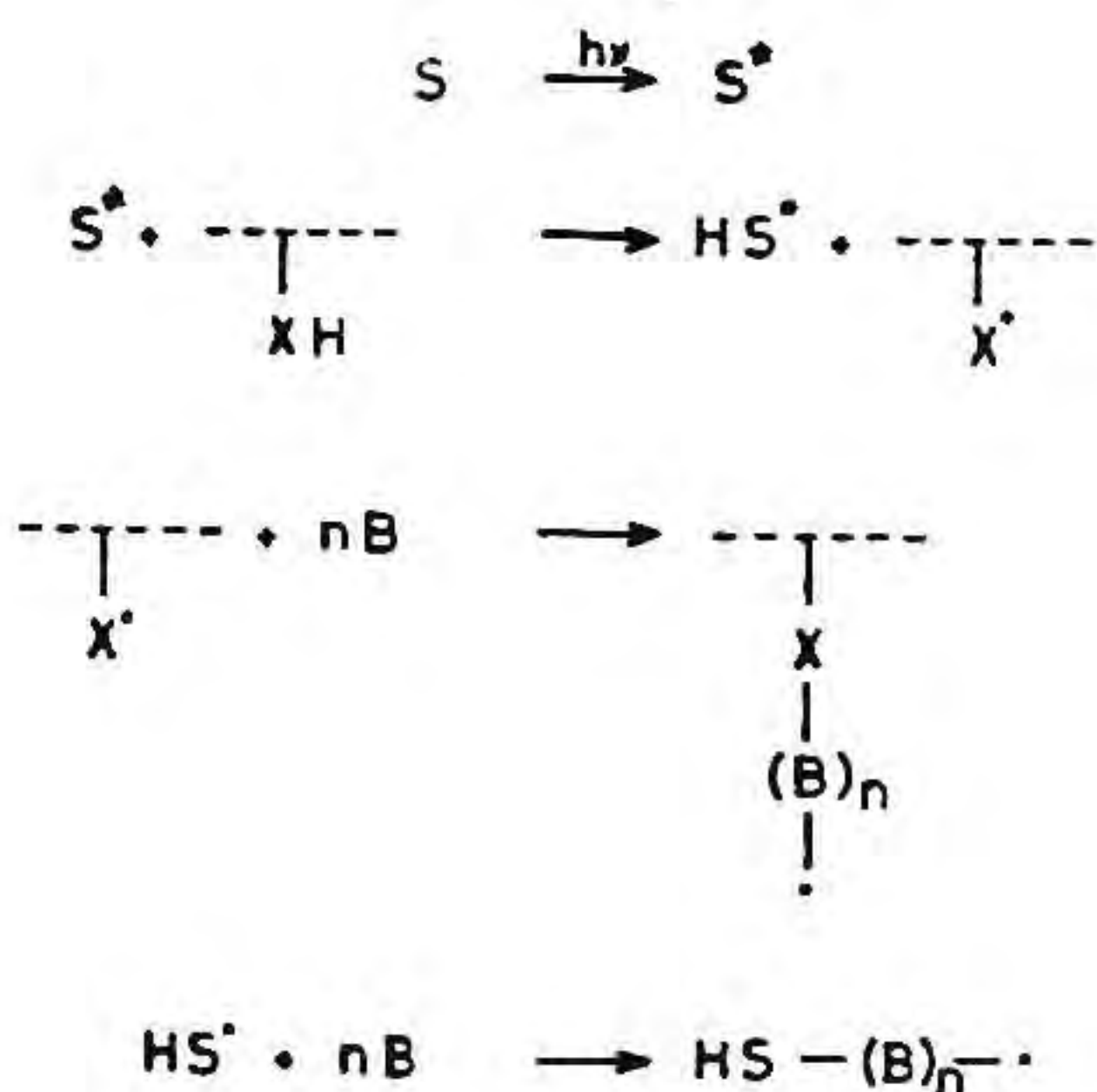
control compared to the thermal methods of grafting. Generally there are two types of photo-induced grafting methods in which radical centers are produced by (a) photolysis of pendant chromophoric groups on the polymer (b) by attack on macromolecules by radicals or electronically excited molecules that are produced by the photolysis of light sensitive molecules [1-3]. Method (a) is illustrated in Scheme 7.1 which shows that apart from graft copolymer, homopolymer also be formed if radical Y generated by the photolysis of side groups X-Y is reactive towards monomer B.

The indirect method (b) is illustrated in Schemes 7.2 and 7.3 for the cases of attack on macromolecules by free radicals and reaction of electronically excited sensitizer molecules S^* with lateral functional groups, respectively. It should be pointed out that this method can be conveniently employed in surface grafting, where solid polymer samples are brought into contact or soaked with a liquid monomer solution prior to irradiation with UV light.

Photo-induced grafting of vinyl monomers onto cellulose and cellulose derivatives namely methyl cellulose, ethyl cellulose, acetyl cellulose, hydroxy ethyl cellulose and carboxy methyl cellulose were studied by Hon et al [4]. Takahashi et al [5,6] have studied the photo-induced graft copolymerisation of cellulose derivatives containing groups such as aldehyde, carboxyl, carboxy methyl, chlorine and nitro groups in the absence of a photosensitizer. In the case of cellulose, free radical centers are generated by chain scission and dehydroxy-methylation reactions. However, the free radicals are generated in



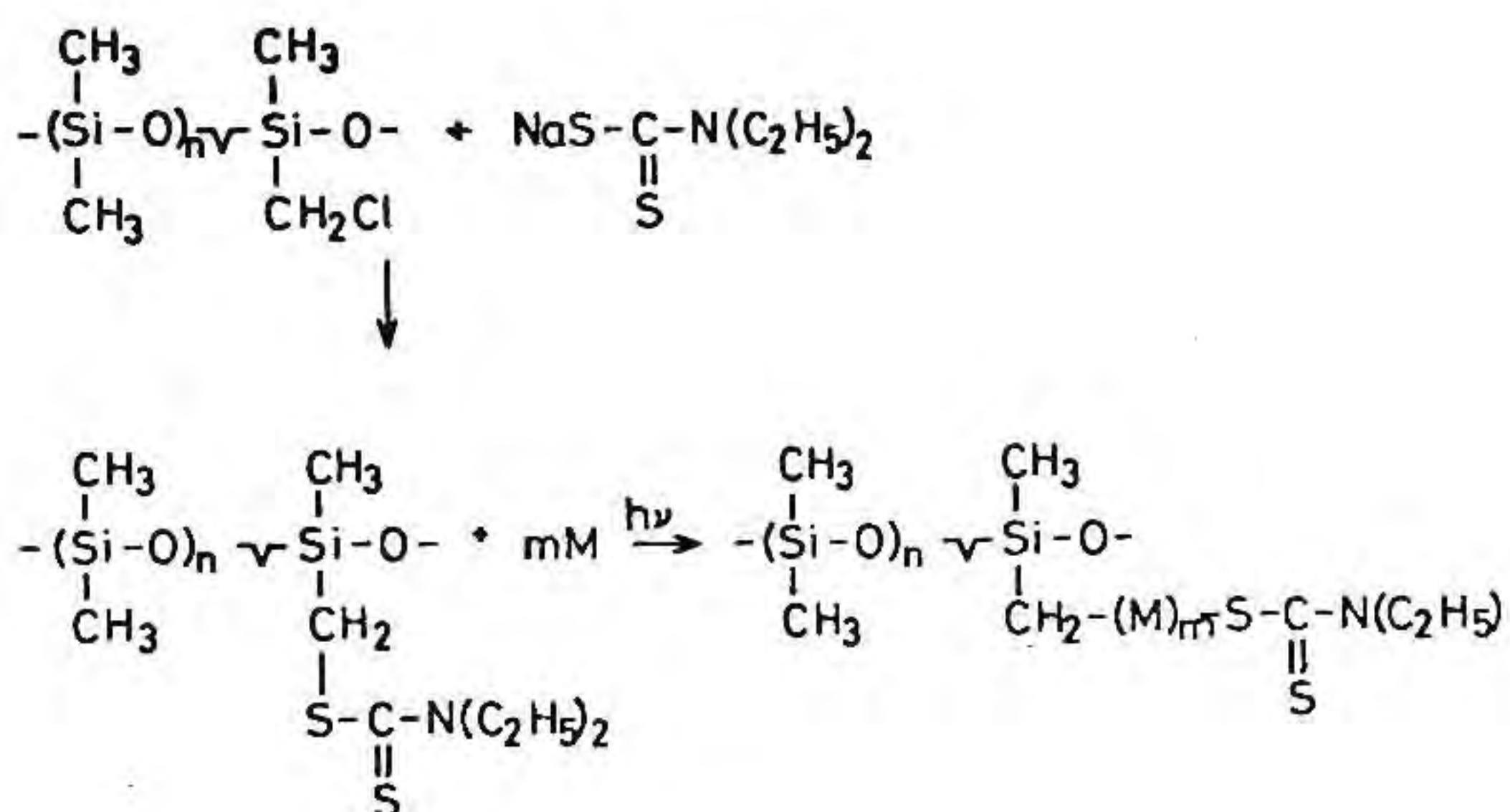
Scheme 7.2: Free radical graft copolymerisation. Initiation by attack on macromolecules by low molecular weight radicals
(Denotations; S = Sensitizer, RH = Solvent or additive)



Scheme 7.3: Free radical graft copolymerisation. Initiation reaction of excited sensitizer molecules with functional groups on the polymer chain

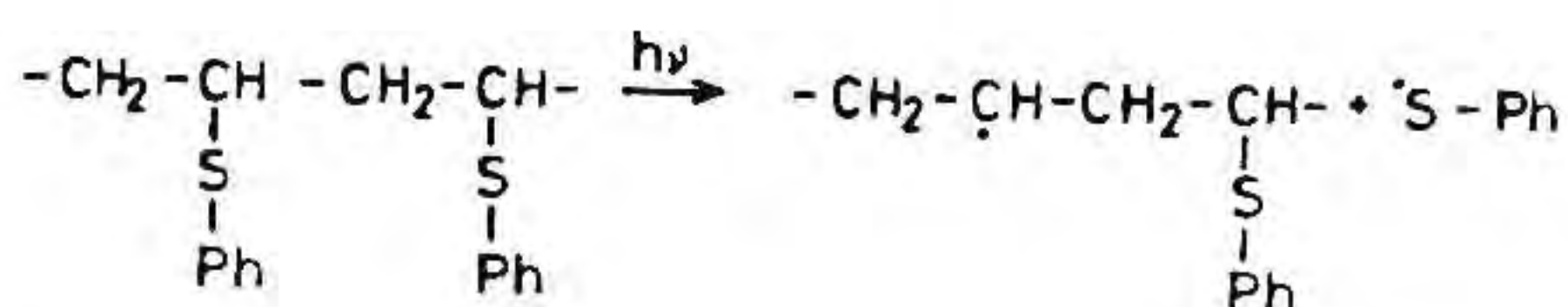
cellulose derivatives by cleavage of substituted side chains. Therefore, grafting reaction of cellulose took place at the polymer backbone and that of cellulose derivatives took place at the substituted side chain. There are number of excellent reviews on photo-induced grafting of cellulose and cellulose derivatives describing these aspects [7,9].

There have been reports on the use of several sulphur containing chromophores for the photo-induced synthesis of block and graft copolymers [1]. Mezger and Cantow synthesised block copolymers containing blocks of cellulose triester and polystyrene, polychloroprene and poly(methyl acrylate) respectively [10,11]. The cellulosic hydroxyl group was permitted to react with 4,4'-dithiobis(phenylisocyanate) resulting in the formation of polymer chains containing -S-S- group. Irradiations of this polymer in the presence of styrene, chloroprene or methyl acrylate with light of $\lambda > 300$ nm led to the formation of block copolymer. Otsu et al have introduced the "iniferter" method [12,13] for the preparation of graft copolymers, with the aid of polymers possessing dithiocarbamate groups. Such polymers are obtained by reacting halogenated linear polymers with sodium dialkyldithiocarbamates. In this regard it is notable that poly(vinyl chloride) [14], partially chloromethylated polystyrene [15] and partially chlorinated polydimethylsiloxane [16] have been converted to the corresponding dithiocarbamate derivatives which on irradiation with UV light in the presence of radically polymerisable monomers, resulted in the formation of graft copolymers. For example, the reaction mechanism for chlorinated dimethylsiloxane is depicted as follows (Scheme 7.4).

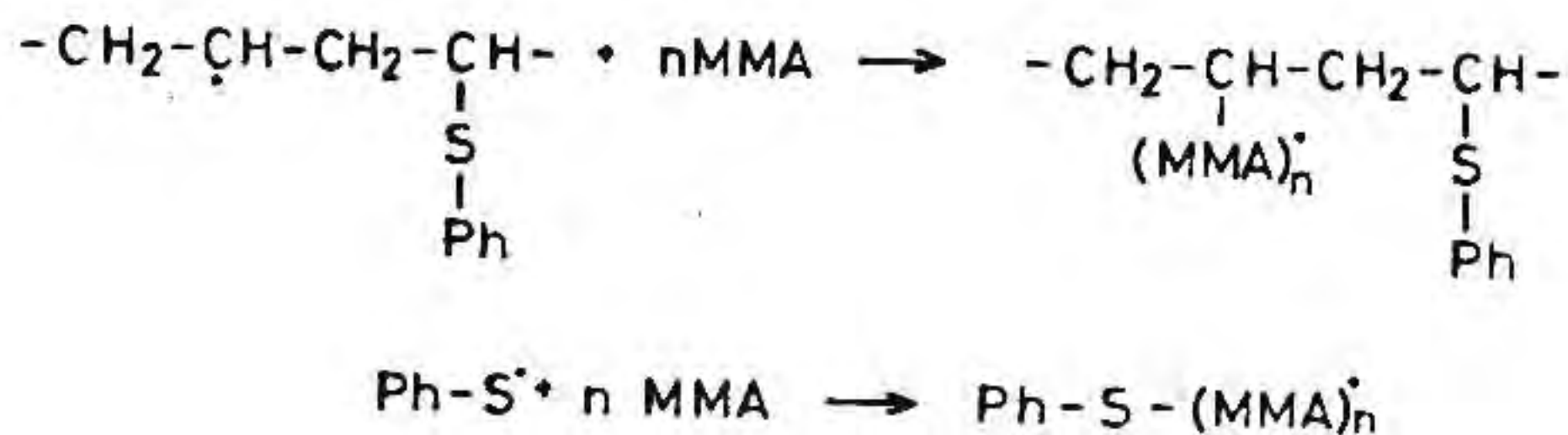


Scheme 7.4: Reaction of sodium diethyldithiocarbamate with partially chlorinated polydimethylsiloxane and grafting of monomer M onto the dithiocarbamated polymer

Methyl methacrylate (MMA) was grafted onto poly(phenyl vinyl sulphide) (PPVS) by Konde et al [17] upon irradiation of a solution of the polymer in the monomer in Pyrex tube with the light of a high pressure mercury lamp. PPVS undergoes photolysis according to reaction shown below:



Scission of the carbon-sulphur bond produces two free radicals, both of which are capable of initiating polymerisations. Therefore, graft copolymers and homopolymers are formed simultaneously:



In a recent report, polystyrene beads containing photolabile xanthate chromophores have been used for the photo-induced grafting of various acrylic and vinylic monomers [18]. A serious limitation of these methods however has been that the initiator moiety absorbs below 300 nm, where most of the monomers also have absorption and thereby enhancing the formation of homopolymers. However, the use of aryl xanthates as photoinitiators overcomes this limitation and has been used for the photocrosslinking and photopolymerisation studies [19]. Recently, crosslinked poly(2-hydroxy ethyl methacrylate) bound S-benzoyl O-ethyl xanthate has been used as a heterogeneous photoinitiator for the photopolymerisation of MMA [20]. Referring to a series of these studies, the photolysis of benzoyl xanthate derivative of cellulose is expected to be useful for the graft copolymerisation of various acrylic monomers. This has been illustrated by the graft copolymerisation of MMA onto S-benzoyl cellulose xanthate. The interest in cellulose is due to the bulk availability of this biodegradable natural polymer which can be easily converted to the corresponding xanthate.

7.2 EXPERIMENTAL

7.2.1 Materials

Cellulose: Sheets of Whatman No.41 filter paper were used as the starting cellulosic material for the preparation of sodium cellulose xanthate.

Methyl methacrylate (MMA): MMA (Fluka Chemicals) was washed with 10% aqueous sodium hydroxide, dried over anhydrous sodium sulphate and distilled under reduced pressure.

Solvents: Solvents used were purified by distillation.

7.2.2 Methods

7.2.2.1 Preparation of sodium cellulose xanthate [21]

Chopped filter paper (Whatman No.41, 10 g) and aqueous sodium hydroxide solution (18%, 100 mL) were mechanically stirred for 2 h, followed by the addition of carbon disulphide (10 mL). The reaction mixture was stirred for an additional 3 h and the contents were poured into excess of methanol. The precipitated sodium cellulose xanthate was washed with cold methanol and dried under vacuum.

IR (KBr) 1220 cm^{-1} (C=S)

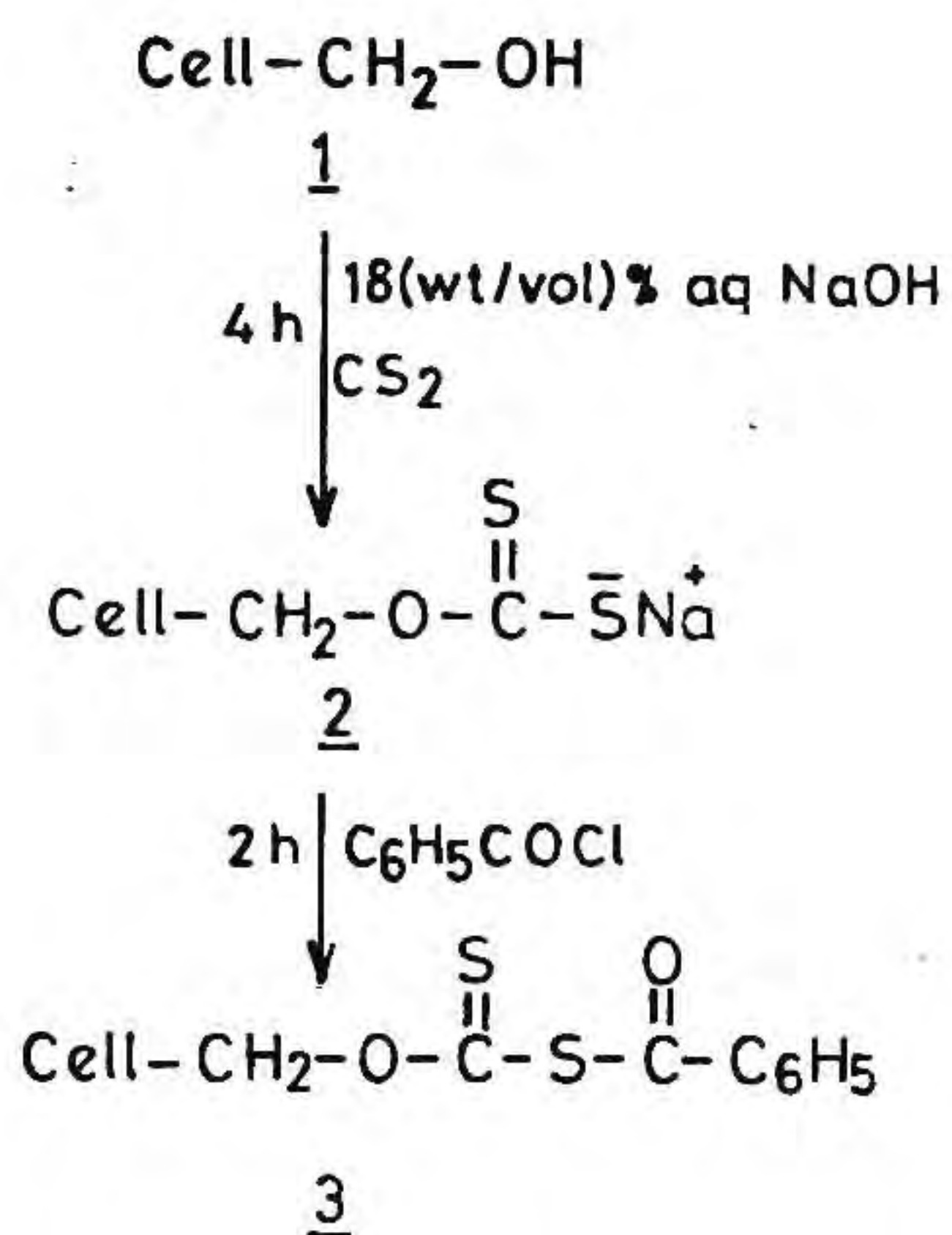
7.2.2.2 Preparation of S-benzoyl cellulose xanthate (3)

To a solution of benzoyl chloride (5 mL) in dichloromethane (20 mL) sodium cellulose xanthate (2 g) was slowly added with constant stirring. The stirring was continued for an additional period of 2 h and the bright yellow S-benzoyl cellulose xanthate formed was filtered, washed with dichloromethane, water and acetone and dried under vacuum (Scheme 7.5).

IR (KBr): 1720 (C=O) , 1220 (C=S) and $1050\text{ cm}^{-1}\text{ (C-O)}$

7.2.2.3 Photografting: Irradiation set-up

Photografting experiments were carried out on an Oriel optical illuminator with a 500 W super high pressure mercury lamp (USHIO USH 508 SA). Light of 400 nm wavelength was selected using 345 nm long pass and 400 nm band pass filters and focussed through a slit of 2 cm in



Scheme 7.5: Preparation of S-benzoyl cellulose xanthate

diameter. All irradiations were done at $30 \pm 1^{\circ}\text{C}$, using constant temperature bath. The light intensity was maintained constant throughout the grafting experiments.

7.2.2.4 Photografting of MMA: General procedure

A mixture of S-benzoyl cellulose xanthate (1 g) and MMA (2 mL) was suspended in a pyrex vessel containing 50 mL of distilled water. The reaction mixture was degassed for 10 min with pure argon and irradiated for known periods of time. The grafted polymer was collected by filtration, dried and extracted with chloroform for 12 h, using a Soxhlet apparatus. After extraction, the grafted cellulose was collected and dried in a vacuum oven at 60°C . The homopolymer of MMA was obtained by pouring the concentrated chloroform extract in excess of methanol. The percentage grafting (G) and graft efficiency (GE) were calculated from the change in weight of cellulose on grafting and weight of homopolymer [22].

7.2.2.5 Instruments

IR spectra were recorded on a Perkin-Elmer Model 882 spectrophotometer. Number-average (\bar{M}_n) and weight average (\bar{M}_w) molecular weights were determined using GPC (Hewlett-Packard 1081 B HPLC equipped with RI detector). Scanning electron micrographs of the polymers were taken on a JEOL-JSM 35 C instrument with the sample sputtered with gold. Thermogravimetric analysis was carried out using a Du Pont 951 modular thermogravimetric analyser in conjunction with a Du Pont 2000 thermal analyst system. X-ray diffraction patterns were obtained from a Philips PW-1710 powder diffractometer using Cu-K_{α} radiation.

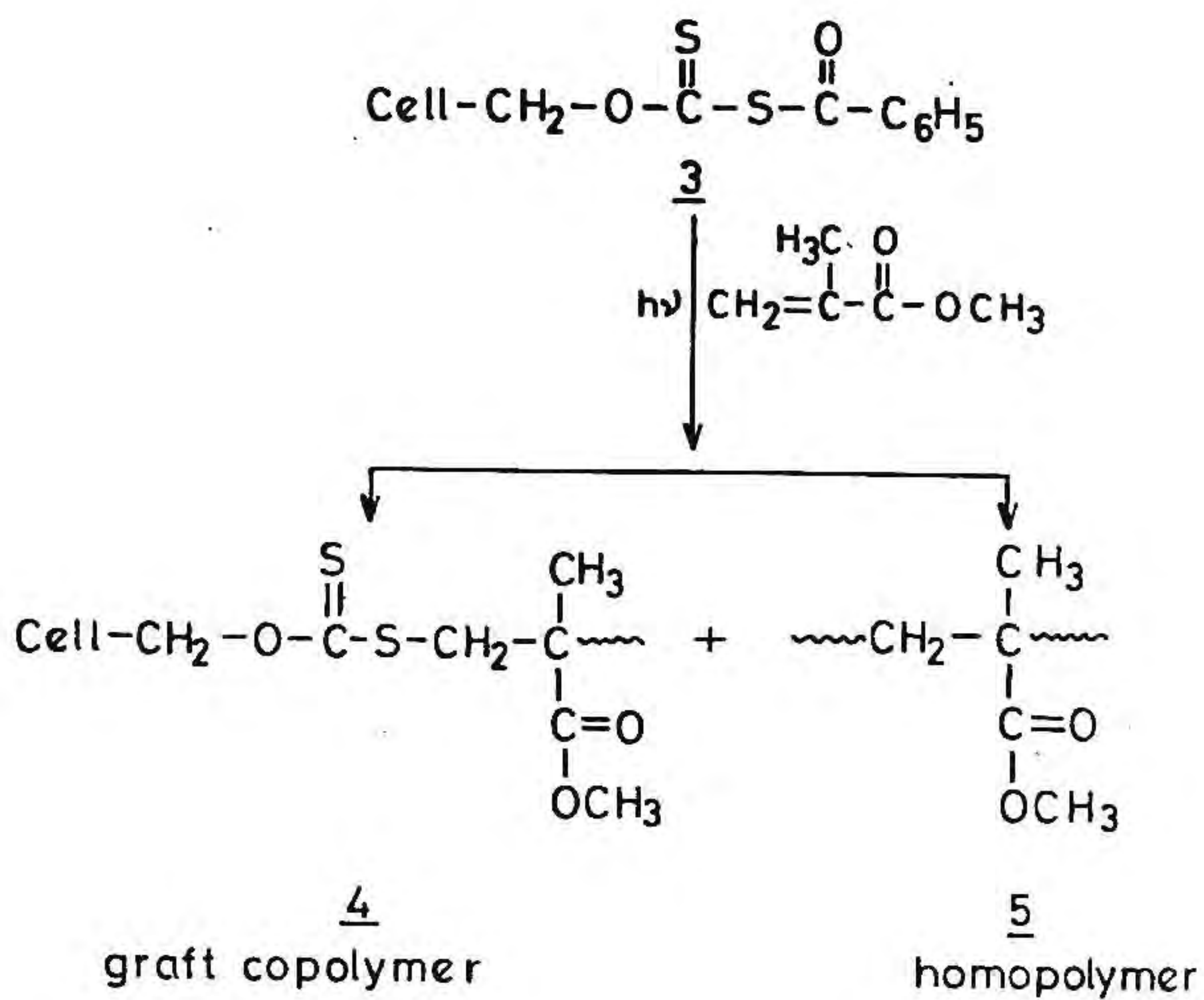
Further details regarding the instrumentation are given in chapter 2.

7.3 RESULTS AND DISCUSSION

7.3.1 Photografting of MMA onto S-benzoyl cellulose xanthate

Photografting of MMA onto cellulose xanthate was carried out in different solvents under identical conditions (Scheme 7.6). Among the different solvents used, water and methanol gave maximum efficiency for grafting. As mentioned in the experimental section, instead of adding the monomer directly into the suspension of cellulose xanthate (3) in water or methanol, a presoaking procedure was adopted. This procedure has a profound effect on efficiency of grafting as compared to the direct addition of the monomer. Since methanol and water are non-solvents for MMA, high local concentration and intimate contact of the monomer with the photoinitiator moiety of the cellulose matrix are achieved. This must have enhanced the efficiency of photoinitiation and subsequent termination of the growing PMMA chains by the thiocarbonyl thiyl radicals of the cellulose, which in turn improve the efficiency of grafting.

Table 7.1 presents the results of the graft copolymerisation of MMA in water at different time intervals. Figure 7.1 shows the relationship between the graft efficiency and the irradiation time. The graft efficiency was found to increase to a certain extent and then gradually decrease with increased irradiation time. This could be due to competition between grafting and homopolymerisation. At initial stages, the rate of grafting reaction is high due to the high rate of



Scheme 7.6: Photografting of PMMA onto S-benzoyl cellulose xanthate

Table 7.1: Results of the photo-induced graft copolymerisation of MMA onto cellulose S-benzoyl xanthate

Time of irradiation (min)	% Grafting	Grafting efficiency (%)	Molecular weight of the hydrolysed PMMA	
			(\bar{M}_n)	(\bar{M}_w)
15	50	55	8993	18533
30	72	60	14062	21717
45	85	82	14231	22071
60	120	75.6	14576	22339
45 (Methanol)	115	80	14323	22172

Wt. of cellulose S-benzoyl xanthate = 1 g

Wt. of methyl methacrylate = 2 mL (1.872 g)

Solvent: water or methanol = 40 mL

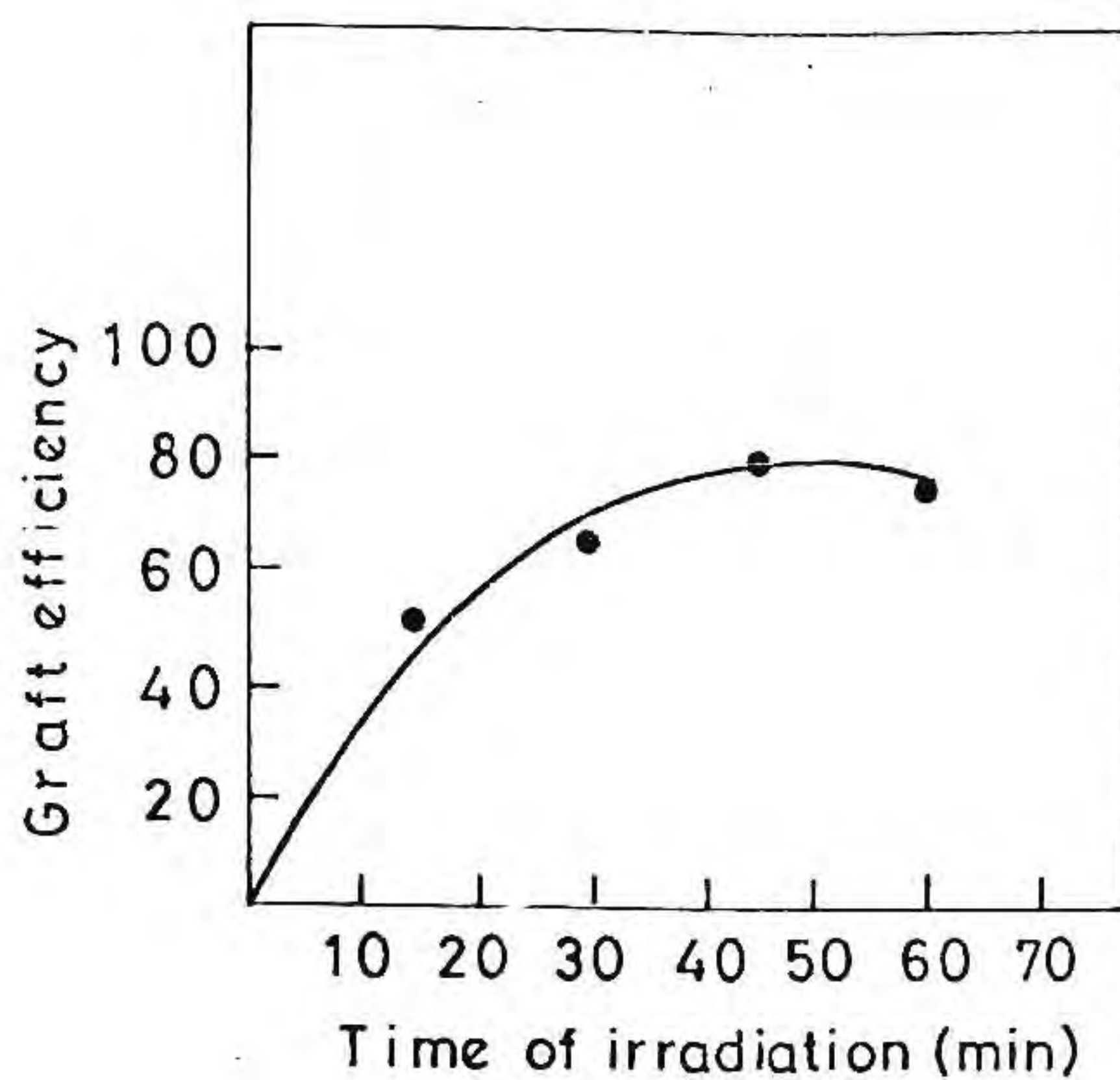


Fig. 7.1: Relationship between the graft efficiency and the time of irradiation

formation of free radicals onto cellulose by UV irradiation. On prolonged irradiation, the free radical concentration in the solution increases thus favouring the homopolymerisation reaction.

7.3.2 Isolation of grafted chain and measurement of molecular weight

The grafted chain (poly MMA) was isolated by hydrolysing the grafted copolymer with 72% sulphuric acid and purified by reprecipitation [23]. The purified sample was used for molecular weight measurements using GPC. The GPC analysis of the grafted PMMA chains did not show any significant change in their molecular weights (Table 7.1). This observation suggests that the irradiation time does not have much influence on the molecular weights of the grafted PMMA chains. The data were in agreement with an earlier study on the photopolymerisation of MMA using aroyl xanthate initiator [19].

7.3.3 Evidence for grafting MMA onto S-benzoyl cellulose xanthate

The photo-induced grafting of MMA onto cellulose xanthate (3) was confirmed by several analytical techniques.

The IR spectrum (Figure 7.2) of the grafted cellulose showed the presence of characteristic absorptions of PMMA at 1735 cm^{-1} . The PMMA chains were isolated from the grafted cellulose and compared with standard samples of PMMA. The IR spectra are found to be identical in both the cases.

Further confirmation on the grafting of MMA onto the cellulose xanthate (3) was obtained from comparative studies of the scanning electron microscope (SEM) pictures of the ungrafted and grafted cellulose.

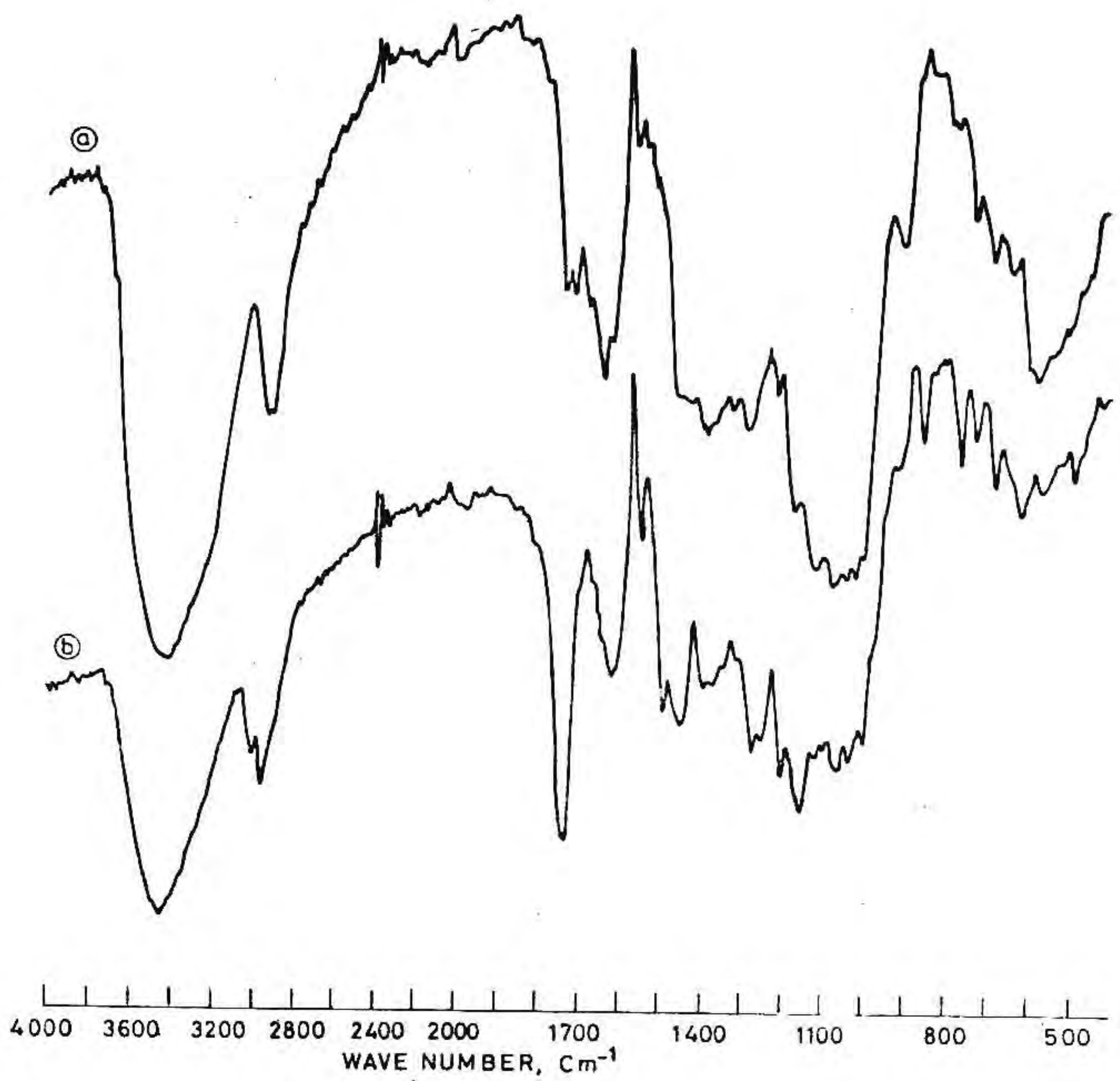
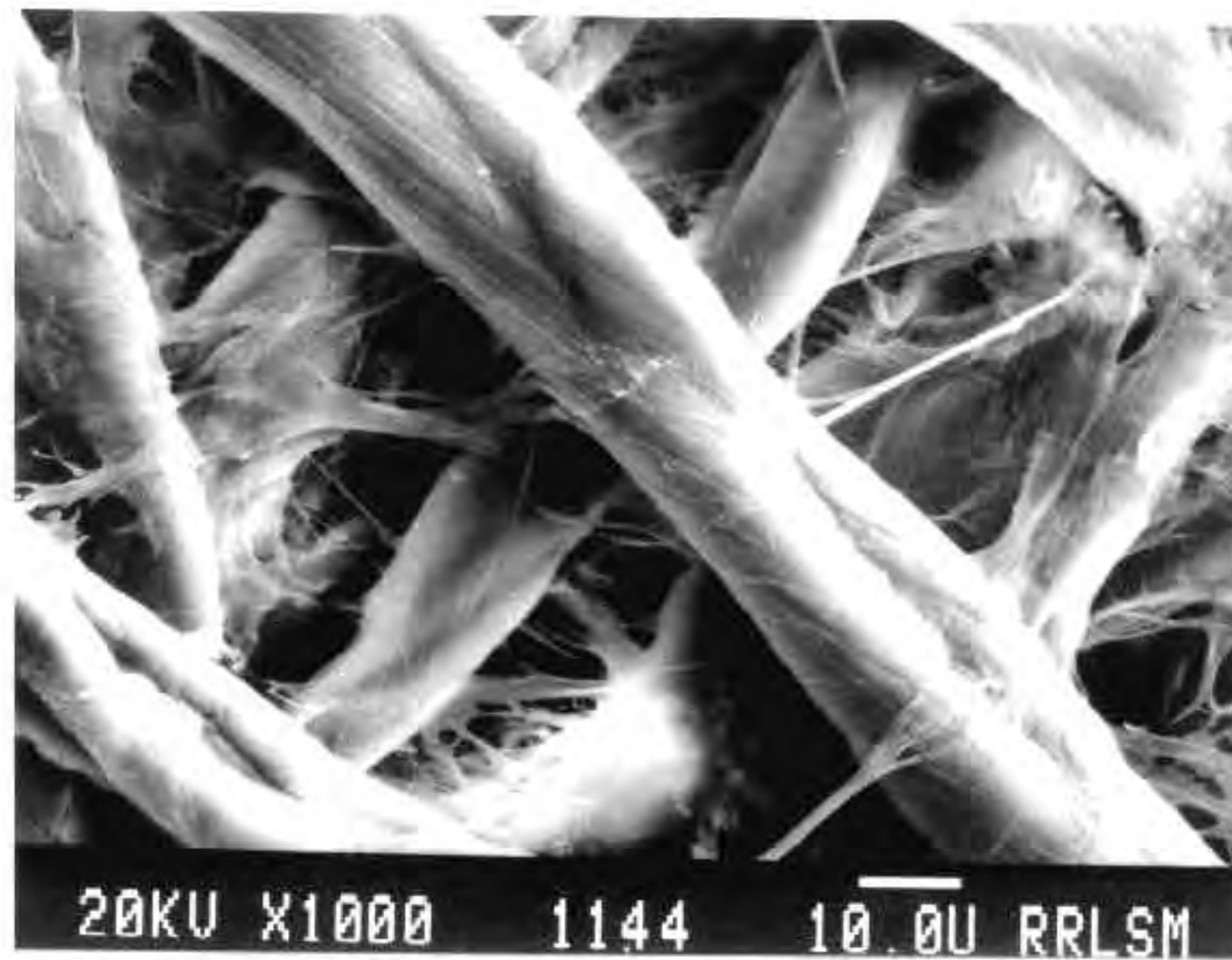
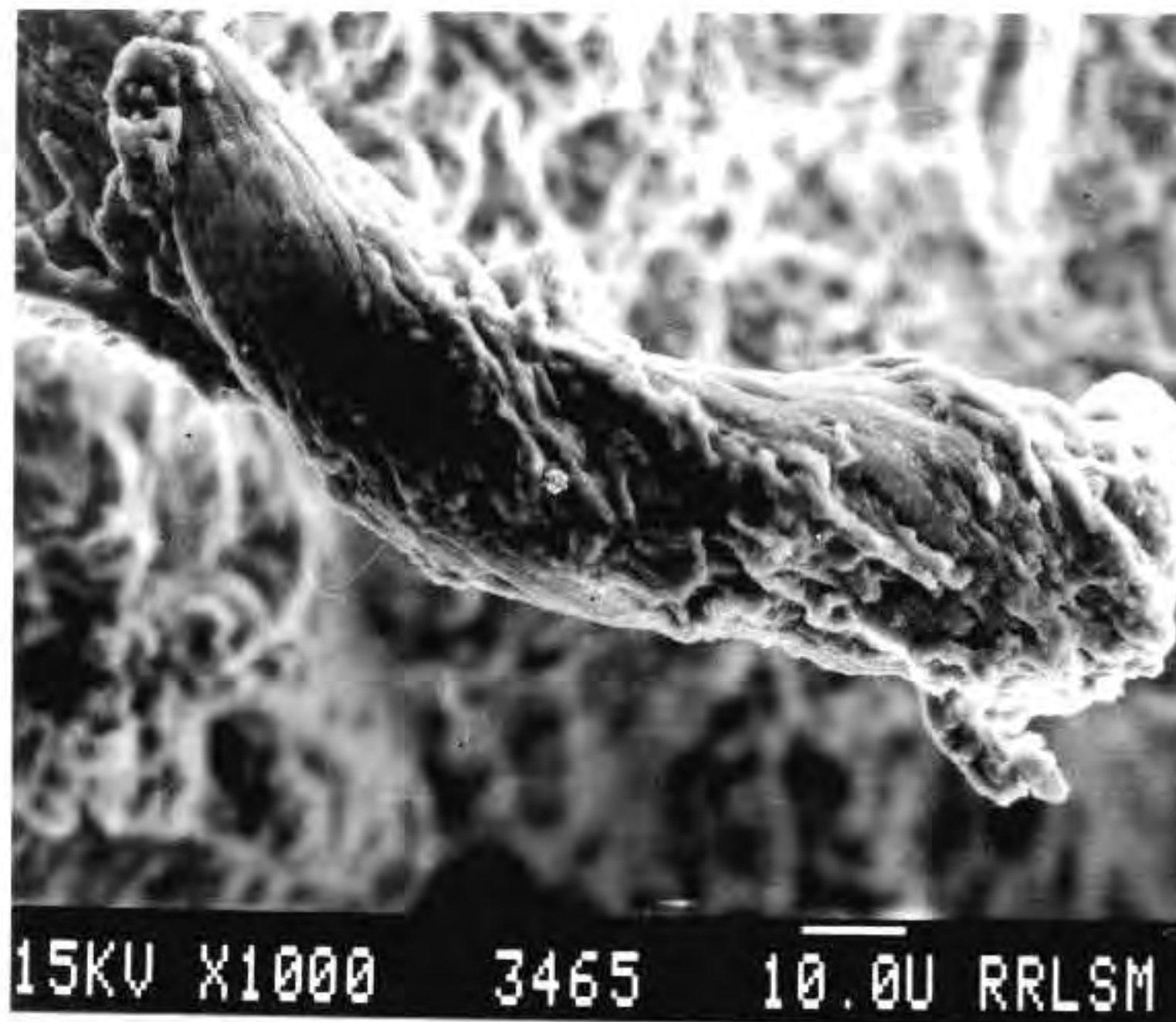


Fig. 7.2: IR spectrum of (a) S-benzoylcellulose xanthate,
(b) PMMA grafted cellulose xanthate



(a)



(b)

Fig. 7.3: SEM photograph of (a) untreated cellulose, (b) PMMA grafted cellulose xanthate

The SEM picture of the ungrafted cellulose at magnification X1000 is shown in Figure 7.3a which indicates a nearly smooth fibre surface. Figure 7.3b is the SEM picture of the MMA grafted cellulose at magnification X1000. This picture clearly shows that the space between the fibers has been filled in the case of grafted fibers. In order to check whether it is due to occlusion by PMMA homopolymer, SEM was taken after exposing the grafted fiber to chloroform extraction for 24 h and found to be the same.

Further evidence for the grafting of MMA was obtained from thermogravimetric analysis (TGA) of the ungrafted and grafted cellulose. Figure 7.4 shows that the initial decomposition temperature T_i of the former is lower (240°C) than that of the latter (296°C) (120% grafting). This enhancement in T_i with the increase in the percentage grafting supports the grafting of MMA onto cellulose xanthate [24].

In Figure 7.5, the x-ray diffraction (XRD) patterns of ungrafted and PMMA grafted cellulose are compared with that of pure PMMA. From the XRD patterns, it is clear that the peak corresponding to PMMA ($2\theta = 10$ to 18°) increases with increase in the percentage grafting.

7.4 MECHANISM OF PHOTOGRAFTING

Aroyl xanthates are known to undergo homolytic scission [24] of the $\text{C}(=\text{O})-\text{S}$ bond, generating benzoyl and thiocarbonyl thiyl radicals.

It is expected that S-benzoyl cellulose xanthate also undergoes an analogous photocleavage generating the thiocarbonyl thiyl radicals on the cellulose and benzoyl radicals in solution. It is well known that the sulphur centered radical is much less reactive [25] than the

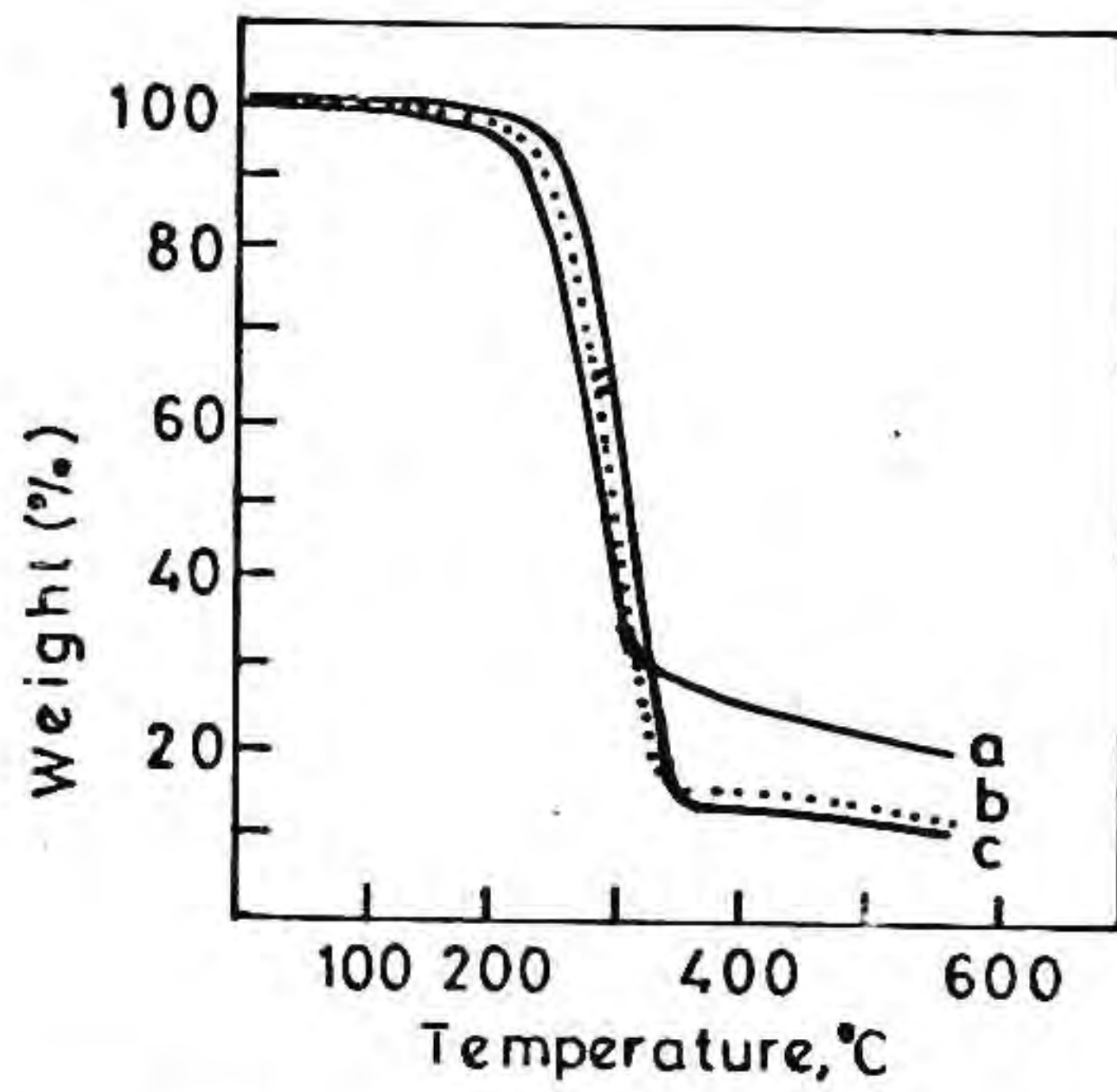


Fig. 7.4: TG-curves of (a) S-benzoyl cellulose xanthate, (b) 50% PMMA grafted, (c) 120% PMMA grafted

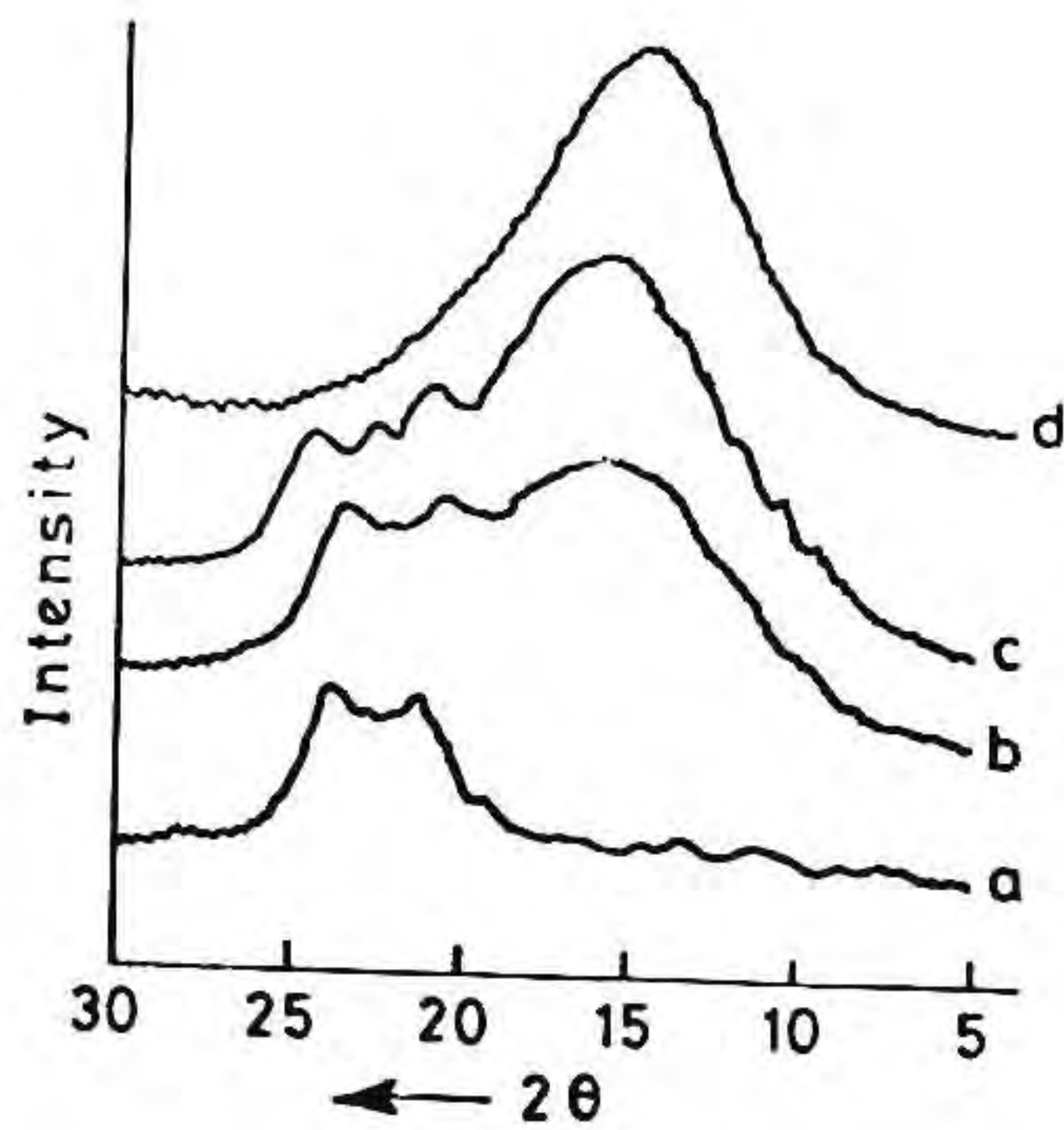
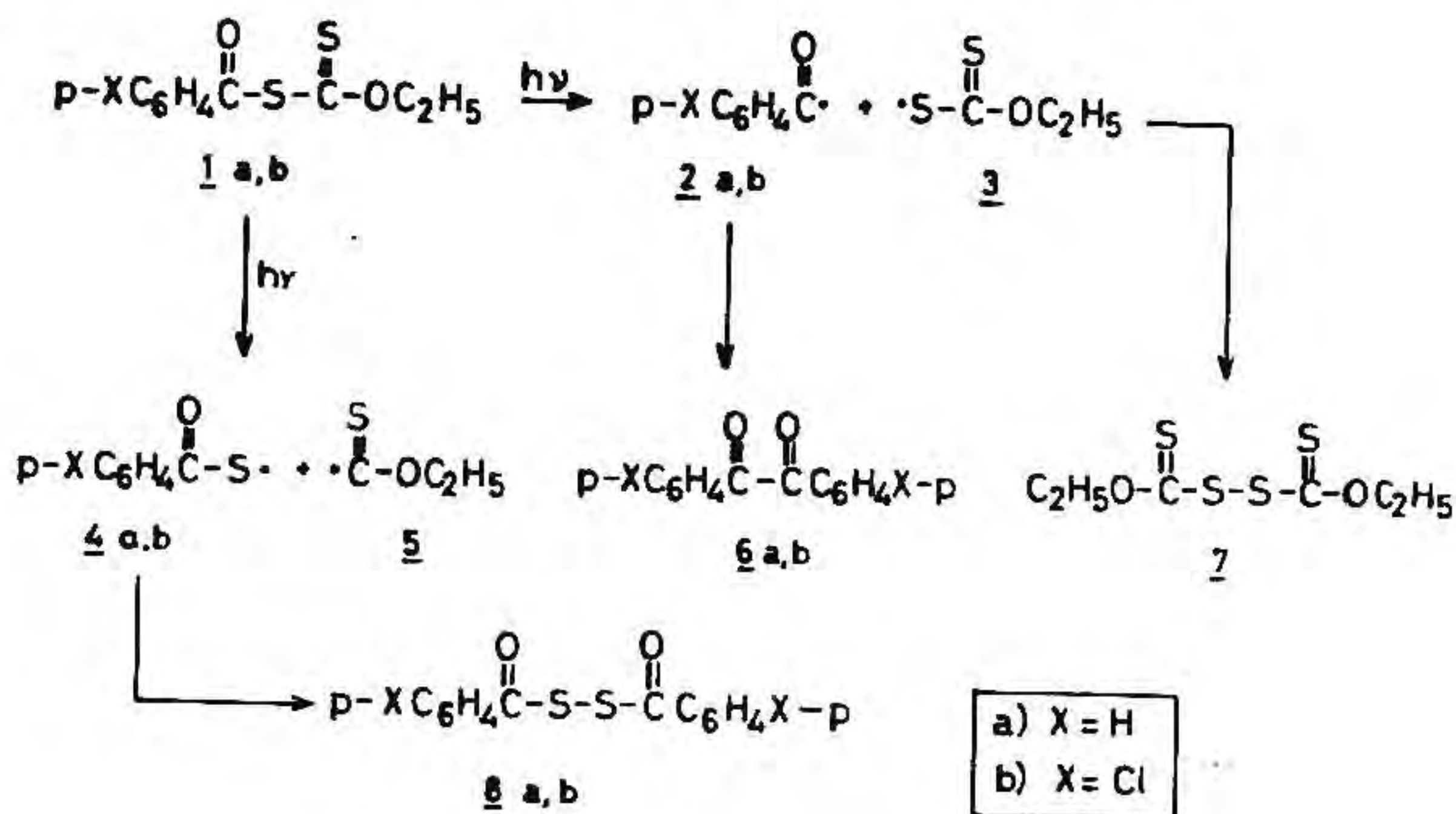


Fig. 7.5: XRD patterns of (a) S-benzoyl cellulose xanthate, (b) 50% PMMA grafted, (c) 120% PMMA grafted, (d) PMMA homopolymer

carbon centered radical towards olefinic monomers. Consequently, monomer molecules preferably add to carbon centered rather than to sulphur centered radicals, thus extending the polymer chain, whereas sulphur centered thiocarbonyl thiyl radicals present on cellulose act as terminators and eventually leading to the grafting of MMA.



Scheme 7.7: Photodissociation of aroyl xanthates

7.5 CONCLUSIONS

In the present study, we have observed that methyl methacrylate can be grafted photochemically onto cellulose using photo-active S-benzoyl xanthate group. The xanthate chromophoric group introduced in cellulose, are capable of producing benzoyl radicals and thiocarbonyl thiyl radicals on UV irradiation which initiate graft polymerisation. This could be of use as an efficient method of grafting of acrylic monomers onto cellulose by a photochemical method for the preparation of cellulose graft copolymers.

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SUMMARY AND OUTLOOK

Chemical modification of natural monomers and polymers offers vast scope for production of speciality polymers. This is evident from the large number of scientific publications emerging in this field. Cardanol, a bio-monomer and cellulose, a natural polymer, are interesting because, they have the required structural features for imparting desired properties. Thus free radically polymerisable monomers, cardanyl acrylate/methacrylate were synthesised from cardanol through the hydroxyl group. These monomers on suspension polymerisation gave crosslinked beads in the absence of crosslinking agents. Solution polymerisation resulted in a soluble, low molecular weight polymer contrary to the crosslinked polymers by bulk/suspension polymerisation. The soluble polymer obtained in solution polymerisation undergoes autooxidation and crosslinking at ambient conditions through the unconjugated unsaturated side chain present. The polymers synthesised were characterised by molecular weight measurements, spectral methods, microscopy and thermal analysis. The kinetics of cure reaction and kinetics of thermal decomposition of the polymers were also evaluated.

Cardanol with its long side chain is expected to generate significant property improvements when grafted onto cellulose. Cardanol was thus cationically grafted onto cellulose using BF_3 .etherate as initiator. The grafted product was characterized by water repellency tests, spectral methods, microscopic techniques and thermal analysis. The

grafted product showed superior properties in water repellency and acid resistance compared with other synthetic polymer grafted cellulose. Further studies on grafting on cellulose showed that S-benzoyl cellulose xanthate is photocleavable and MMA was grafted onto cellulose by a photo-induced method. This method of grafting through the photocleavable xanthate group is new and can be extended to other vinyl monomers.

The present study shows that:

- a. Poly(cardanyl acrylate) and poly(cardanyl methacrylate) can be used as,
 - i. Crosslinked beads in polymer supported reactions
 - ii. Self-crosslinkable polymer in speciality coatings
- b. Cardanol grafted cellulose can find application as:
 - i. Water repellent papers and textiles
 - ii. For the preparation of organic solvents/oil absorbing materials
- c. A new method has been proposed for photo-induced grafting of vinyl monomers onto cellulose

It is shown in this thesis that high performance materials with improved properties could be produced by appropriate chemical modifications of a natural monomer, cardanol and a natural polymer, cellulose. Further, this is an indication that natural monomers/polymers could definitely form alternate sources for polymers with high performance properties.