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STUDIES IN POLYSULFIDES

(a) SYNTHESIS OF THIOL MONOMERS AND POLYMERS THEREFROM

(b) SYNTHESIS OF ORGANOTHIOSILICON COMPOUNDS FOR EVALUATION IN POLY (VINYL CHLORIDE)

A Thesis Submitted to the
University of Poona
for the degree of
DOCTOR OF PHILOSOPHY
in Chemistry

by

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To

MY PARENTS

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PART-I

GENERAL INTRODUCTION

The chemistry of organic sulfur compounds centres around thiols (also called mercaptans), whose discovery, in 1834, has been accredited to Zeise. This important discovery has been aptly described to have opened up a whole new section in organic chemistry and not just a series of new organic compounds. With the rapid advances of science and technology steadily opening new avenues the past few decades have witnessed the splendid growth of thiols from the cocoon of scientific curiosity to an important and indispensable class of compounds reaching the previously inaccessible areas. A large number of thiols have been synthesized since their academic inception and the addition of new ones to the ever-growing repertoire of sulfur compounds seems to be endless.

The special interest that attaches to the study of the behaviour of thiols is felt more and more strongly in biochemical research and in industry. And this acme of interest and activity is all the more fascinating, but not surprising either, realising the ability of these compounds to enter reactions beyond the reach of their oxygen analogues creating entirely new and useful structures. And this is evident from the ever-growing multifaceted applications thiols are finding.

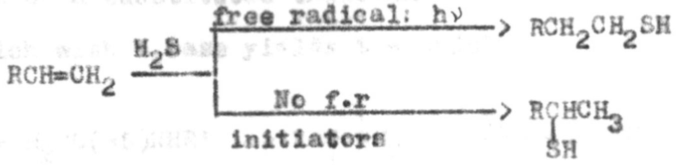
Many aspects of thiol chemistry and early work have been well reviewed by Malisoff et al[1].

Methods of Preparation of thiols

Consequent to the tremendous development in the chemistry of thiols, new reagents and methods are constantly being worked out in the direction of the synthesis of thiol compounds. Some of the important methods are briefly described below:

1. Addition of Hydrogen Sulfide to Olefins[2,3]

Hydrogen sulfide addition to olefins has been an industrially important method for thiol-synthesis. Hydrogen sulfide addition to terminal olefins in presence of free radical initiators, or when photochemically induced yields the anti-Markownikoff product (i.e. terminal thiol) while in the absence of these, the reverse is true.



Radical addition of H_2S to olefins is a very general reaction applicable to terminal, internal or cycloolefins. Ultraviolet radiation of λ2537 Å is generally used. UV radiation of λ around 3000 Å is also employed in conjunction with sensitizers[4]. γ-radiation[5,6] and X-rays[7] have also been used to effect the addition.

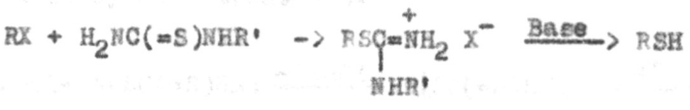
Ionic addition of H_2S to olefins has been effected with many protic[8] and Lewis acid catalysts[9]. Korshunov et al[10] have found alkylaluminium chlorides to be effective catalysts for the addition. Ionic additions to α,β-unsaturated carbonyl compounds and nitriles are generally catalyzed by alkali hydroxides and amines[11,12]. However, the sulfide formed by a typical thiol-olefin addition reaction is the normal by-product in all these reactions.

2. By the Reaction of alkyl halides with various reagents

Alkyl halides have been reacted with many compounds for the preparation of thiols. The reagents and the schematic representation of reactions are shown below:

(i) Using Thiourea

This is perhaps the widely used laboratory method for the preparation of thiols. An alkyl halide reacts with thiourea or a substituted thiourea[13] to form an isothiuronium salt which with a base yields the thiol.



$$RX + H_2NC(=S)NHR' \rightarrow RS\underset{NHR'}{\underset{|}{C}}=\overset{+}{N}H_2\ X^- \xrightarrow{\text{Base}} RSH$$

Kamada[14] has reported the synthesis, by this method, of 1,8-bis(thiomethyl) naphthelene in 72% yield from the corresponding bischloro compound. Klayman et al[13], using acetyl thiourea, have synthesized many alkyl and aryl thiols, and this synthetic route may prove useful in the preparation of water and alkali-sensitive thiols.

(ii) Alkali Metal Hydrosulfides

This is a good method for the preparation of thiols from alkyl halides. Sodium hydrosulfide and, less commonly potassium hydrosulfide, or alkaline hydrosulfides[15] are used for this reaction.

$$R{-}X + NaSH \rightarrow RSH + NaX$$

Takikawa et al[16] have observed good yields in the liquid ammonia medium. The metal hydrosulfide reaction is most useful for primary halides and the reaction is very difficult for tertiary halides because elimination reaction predominates. Sulfides, formed by the reaction of the halide with thiol, are the major by-products.

(iii) Sodium Trithiocarbonate

Martin et al[13] reported a convenient synthetic method for dithiols from alkyl dihalides and sodium trithiocarbonate followed by acid treatment.

$$Cl{-}R{-}Cl + 2NaSC(=S)SNa \xrightarrow{-2NaCl} R[SC(=S)SNa]_2 \xrightarrow{H^+} HS{-}R{-}SH$$

Very good yields are obtained.

(iv) Reaction with Sodium Polysulfide followed by Reduction

Alkyl dihalides react with sodium polysulfide to form alkyl polysulfide which can be reduced to yield the dithiols.

Eliel et al[18] have synthesized a series of high molecular weight aliphatic dithiols by the reaction of alkyl dihalides with sodium disulfide followed by reduction with lithium aluminium hydride.

$$X\text{-}(CH_2)_nX \xrightarrow[\text{DMF}]{Na_2S.9H_2O} \overline{S(CH_2)_nS} \xrightarrow{2H} HS(CH_2)_n\ SH$$

The main advantage of this method is the maximum stereochemical control that can be achieved with good yields.

3. <u>By the Hydrolysis of Thiol Esters</u>

Synthesis of thiols by the hydrolysis of thiol-esters, -RCOSR'- is a method of high general utility particularly useful in making olefin-based thiols.

Addition of thiols, e.g. thiolacetic acid CH_3COSH, is similar to the addition of hydrogen sulfide to olefins described earlier. Under free radical conditions or photochemical radiation, thiol acids add to olefins to give anti-Markownikoff products, which are readily hydrolyzed by aqueous base[19] or ammonia[20] to yield the thiol.

$$RCH{=}CH_2 + CH_3COSH \xrightarrow[h\nu]{\text{f.r or}} RCH_2CH_2SCOCH_3$$

$$RCH_2CH_2SCOCH_3 \begin{array}{l} \xrightarrow{NaOH} RCH_2CH_2SH + NaOAc \\ \xrightarrow{NH_3} RCH_2CH_2SH + NH_2Ac \end{array}$$

By this method Guthrie et al[19,21] have synthesized high molecular weight polythiols having as many as 6-7 thiol groups per molecule.

4. From Polyhydroxy Compounds and Mercapto Acids

The acid-catalyzed esterification of hydroxy compounds with mercapto acids to yield thiol terminated compounds is a popular and industrially important method. The reaction involved can be shown, e.g.

$$HO\text{-}R\text{-}CH + 2SHCHR'COOH \rightarrow R(OCOCHR'SH)_2$$

The use of a variety of simple and polyhydroxy compounds, good yield and absence of by-products highlight the wide utility of this method. Some of the hydroxy compounds which have been used are glycerol, pentaerythritol, polyalkylene diols and polyalkylene triols[22,23].

5. Synthesis of Thiols by Reduction of Disulfides and other Sulfur Compounds

Disulfides, RSSR, on reduction give thiol compounds

$$RSSR \xrightarrow{2H} 2RSH$$

A myriad of reducing agents have been used to effect the reduction, e.g. zinc-acid, tin-acid, sodium borohydride[24] and lithium aluminium hydride[25]. Recently, Woods and Klayman[26] have found sodium hydrogen selenide to be an efficient reducing agent for good yields of thiols. The reactions involved are:

$$RSSR + 2HSeNa\ (excess) \rightarrow 2RSH + Se^{0} + H_2Se$$

$$RSSR + HSe^{-} \xrightarrow{H^{+}} 2RSH + Se^{0}$$

Borgogno et al[27] have used formamidinic acid to effect disulfide-reduction under phase-transfer conditions.

Thiols have also been occassionally synthesized by the reduction of:

(a) Thiocyanates[28,29]

$$RSCN \xrightarrow[Zn-HCl/ACOH]{Na-NH_3\ or} RSH$$

(b) <u>Xanthates</u>

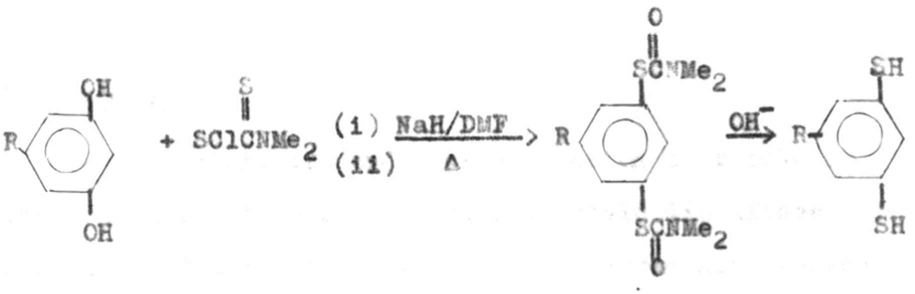
$$EtOCSSK + Rx \xrightarrow{NH_2} RSH + EtOCSNH_2$$

This method is particularly useful for water-soluble halides.

6. Aromatic Dithiols

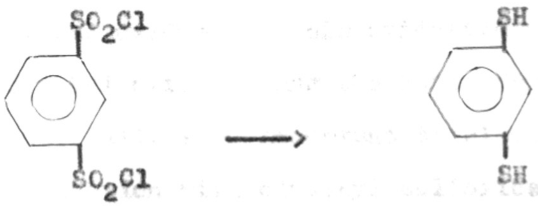
(i) From Resorcinols

A method for the synthesis of aromatic dithiols has been developed starting from aromatic dihydroxy compounds and dimethylamino thiocarbonyl chloride[30]. The method essentially consists of the formation of O-aryl-N-dimethyl carbamate, thermal rearrangement to the corresponding S-aryl analogue followed by hydrolysis to yield the thiol.



(ii) From Sulfonyl Chlorides

Another important method for the synthesis of aromatic dithiols involves the reduction of bis(sulfonyl chlorides) by zinc-acid[31] or phosphorous and iodine[32].



Aromatic dithiols are important intermediates for pharmaceuticals, bactericides and insecticides.

Reactions of Thiols

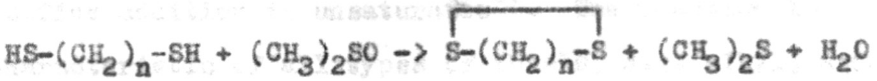
Thiols react with a variety of organic and inorganic compounds involving the thiol group. Although some of the reactions are similar to that of their oxygen analogues there are certain decided differences related to the (a) higher acidities of thiols, (b) ease with which thiols undergo oxidation and (c) the ability of thiols to enter free-radical reaction with ease. Some of the important reactions of thiols are briefly described below:

1. Oxidation

A characteristic and facile reaction of thiols is their capacity to easy oxidation to yield disulfides. The oxidation of a thiol to disulfide by oxygen goes rapidly in presence of base. Metals (iron and copper), metal chelates and amines also catalyze this reaction.

$$2RSH + \tfrac{1}{2}O_2 \rightarrow RSSR + H_2O$$

A variety of other mild oxidizing agents are also used, e.g. metal oxides[33]. This oxidative coupling in presence of metal oxides forms the basis for the curing of some industrially very important thiol containing liquid polymers. Oxidation with dimethyl sulfoxide has been used for the synthesis of cyclic disulfides[34].



$$HS\text{-}(CH_2)_n\text{-}SH + (CH_3)_2SO \rightarrow \overbrace{S\text{-}(CH_2)_n\text{-}S} + (CH_3)_2S + H_2O$$

Lowe[35] reports the complete oxidation of thiols and disulfides to the corresponding sulfonic acids by DMSO containing hydrogen halide as the catalyst.

Oxidation with iodine forms the basis for the analytical determination of thiols by iodimetry.

$$2RSH + I_2 \rightarrow RSSR + 2HI$$

2. Reaction with Halogens under Controlled Conditions

Halogens, particularly chlorine, react with thiols under controlled conditions to give sulfenyl halides

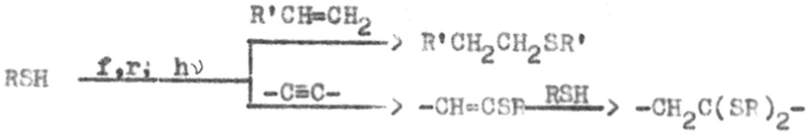
$$RSH + Cl_2 \rightarrow RSCl + HCl$$

(However, sulfenyl chlorides are usually prepared by the chlorination of disulfides). Roos[36] reported the synthesis of the bis(sulfenyl chloride) of 1,2,4,5-tetrachloro-p-xylene dithiol, an useful crosslinking agent for natural rubber.

3. Addition to Olefins and Acetylenes[2]

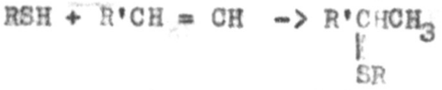
Thiols add, generally with ease, to olefins and acetylenes either by free radical or ionic mechanisms to form sulfides, and this addition resembles the hydrogen sulfide addition to unsaturates[37]. The reaction is characteristic of all types of thiols, e.g. alkyl, aromatic and heterocyclic thiols.

Radical addition of a thiol in presence of the usual free radical initiators, e.g. oxygen, peroxides, azoinitiators or photochemical radiation yields the anti-Markownikoff product. Under the radical conditions thiols yield vinyl sulfides with acetylenes and further addition forms the diadduct[37,38].



$$RSH \xrightarrow{f.r.;\ h\nu} \begin{cases} \xrightarrow{R'CH{=}CH_2} R'CH_2CH_2SR' \\ \xrightarrow{-C{\equiv}C-} -CH{=}CSR \xrightarrow{RSH} -CH_2C(SR)_2- \end{cases}$$

Addition of thiols to unsaturates can also occur by ionic mechanism promoted by acid or sulfur. Metal halides and basic compounds catalyze thiol addition to α,β-unsaturated carbonyl compounds and nitriles[37,39,40]. The ionic additions:



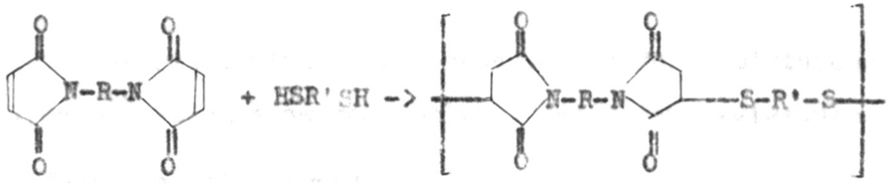
$$RSH + R'CH = CH \rightarrow R'\underset{SR}{C}HCH_3$$

generally give products resulting from normal Markownikoff addition.

4. Addition to Activated Double Bonds

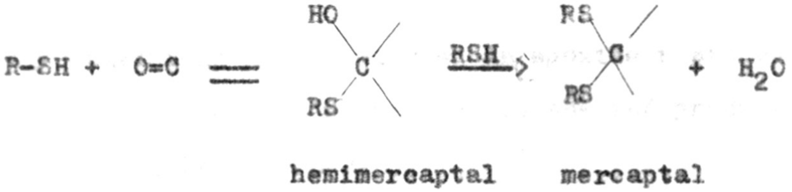
Thiols readily add to activated double bonds, e.g. maleimides and N-substituted maleimides in presence of tertiary amine catalysts to form imidothioethers, e.g.

These reactions are very general. Bisthiols react with bismaleimides to form polyimidothioether polymers[41], a recent class of addition type thermoplastic polymers

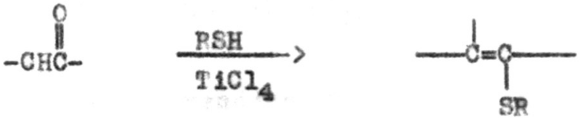


5. Reaction With Carbonyl Compounds

Thiols, similar to their oxygen analogues, undergo acid catalyzed addition to carbonyl compounds (aldehydes and ketones).

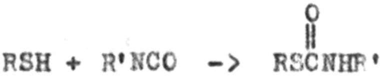


However, the formation of vinyl sulfides from thiols and ketones in presence of titanium tetrachloride catalyst has also been reported by Mukaiyama et al[42].



6. Reaction with Isocyanates

Thiols, like their oxygen analogues, react with isocyanates to form thiourethanes[43] and tin or titanium Lewis acids are known to catalyze this reaction[44].



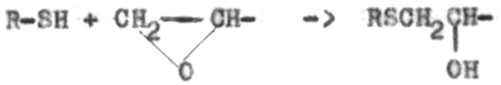
$$RSH + R'NCO \rightarrow RS\overset{\overset{O}{\|}}{C}NHR'$$

Polythiols react with polyisocyanates to form polythiourethane polymers[45] which show good solvent and water resistance.

7. Reaction with Epoxides

Thiols readily react with epoxide compounds to form

2-hydroxy thioethers[46], and basic compounds catalyze this addition.



Many polythiols have been used as epoxide resin curing agents to impart specific properties to the end product. (see Chapter II, Ref. 72-80).

8. Reaction with Elemental Sulfur

Thiols react with elemental sulfur to form stable organic polysulfides.

$$2RSH + nS \rightarrow RS_{(n+1)}R + H_2S$$

This reaction renders it possible to synthesize organic polysulfides in a convenient way[47,48]. This is one reaction the oxygen analogues find it difficult to enter into. Sodium polysulfides also react with thiols to form polysulfides.

9. Formation of Mercaptides

Metal salts of thiols are called mercaptides. Thiols react with many metallic cations to form the mercaptides, a majority of which are insoluble in water.

$$RSH + M^{+} \rightarrow RSM + H^{+}$$

$$2RSH + M^{2+} \rightarrow (RS)_2M + 2H^{+}$$

One of the important applications of this reaction is in the 'sweetening of petroleum distillates'. This process involves the formation of lead mercaptide followed by further reaction to form lead sulfide and organic disulfide. This is the very widely known 'Doctor Test'.

Uses of Thiols

The reactivity of thiols, their ability to take part in a wide variety of reactions and the breathtaking advances in the synthesis of complex organic molecules have made thiols an attractive class of compounds, and enormously important intermediates for various biochemical and industrially important applications. Thiols have come to occupy an important and unique position in the study of polymer synthesis and protection. A brief account of the important applications of thiols with particular reference to the study of polymers is presented below.

1. As Chain Transfer Agents in the Polymerization of Unsaturates

Aliphatic thiols are extensively used in the polymerization of unsaturated monomers to control the polymerization (and molecular weight) and to give products with required processing characteristics and properties. Thiols are indispensable in the manufacture of industrially important rubbers based on acrylonitrile, styrene, butadiene[49-51], ethylene[52], styrene-butadiene graft copolymers[53] and neoprene rubber[54]. Rogozinski et al[55] have used mercapto-acid esters of polyols as chain transfer agents in the polymerization of vinyl chloride.

2. As Thermal Stabilizers for Synthetic Polymers

The role of thiols and their various derivatives assumes paramount importance in the thermal stabilization of synthetic polymers. Thiols have been used in the stabilization of vinyl chloride polymers[56], polyamide fibres[61] and polyoxyphenylenes[62], to name a few. The discoloration prevention efficacy of organotin derivatives of thiols in PVC remains supreme and unsurpassed among a host of thermal stabilizers for PVC[3].

3. As Antioxidants

The antioxidant properties of thiols and their derivatives have been attributed to their ability for peroxide decomposition. This is one of the most important applications of thiols in polymer stabilization. Some of the synthetic polymers for which thiol-antioxidants have been used are polyolefins, vinyl chloride polymers[63] and polyoxymethylenes[64]. Thiols have been used as important intermediates in the synthesis of other antioxidants for synthetic polymers. Recently, Nakamura et al[65] have described the use of thiol-s-triazine compounds as antioxidants for epichlorohydrin rubber.

4. As Vulcanizing Agents and Vulcanization Accelerators

Polythiols have also been employed in the vulcanization of elastomers, e.g. in the thermal vulcanisation of epihalohydrin elastomers[66], in the radiation-vulcanization of polydiene[67] and chlorobutyl elastomers[68]. Roos[36] has reported the use of mono, di- and tri-sulfenyl chlorides (prepared by the chlorination of thiols) as vulcanizing agents for natural rubber. 2-Mercapto benzothiazole and derivatives constitute a very well known and important class of rubber vulcanization accelerators[69].

5. In Epoxy Resin Curing

Polythiols are among the important curing agents for epoxy resins. Some of the polythiols used are mercaptoacid esters of polyols, thiol-terminated polysulfide liquid polymers, cycloaliphatic and heterocyclic polythiols. Many new polythiols have been used to cure epoxy resins at room temperature to give products with reduced water absorption as well as desired hardness (Ref. 72-80 in Chapter II).

6. For Shrink-proofing and Crease-resistant Finishings of Woollen and Cotton Fibres

Poly(thioglycolates) and poly(3-mercapto propionates) find wide applications in the title process and the process for Keratin-containing fibres is extensive and industrially widely used. Some of the thiols used are thioglycolates of glycerol, trimethylol propane, pentaerythritol, polyalkylene diols and triols[70] etc.

7. In Biological Research[71]

Mercaptan containing compounds and polymers, for example, poly(vinyl mercaptan), poly(p-mercapto-styrene) are becoming very important as model compounds in the understanding of reactivity of enzymes containing sulphydryl groups. Mercaptan containing polymers are useful for sequestering heavy metal ions.

Apart from the above mentioned uses, thiols also find important uses in such widely different and important fields as in photography, cosmetics, hairwaving preparations etc. Thiols can perform a vital role in the synthesis of mildewcides, bactericides, bacteriostats, pharmaceuticals, biocides, preservatives, slimicides, disinfectants, anti-dandruff agents, surfactants and in a wide range of syntheses. Biodegradability is another thiol plus; because the presence of the sulfur atom has been shown to enhance the biodegradability of the biocide.

A brief introductory survey on the synthetic methods, some interesting and important reactions and the enormous importance of thiols in the field of polymers and other areas has been made above. The ensuing work in the following chapters deals with:-

- The synthesis of thiols, particularly thioglycolates, and their utilization in the synthesis of new polymers. The thiols synthesized were the poly(thioglycolates) of polyols such as ethylene glycol, polyethyleneglycols-200, 400, 600, castor oil, trimethylol propane (Chapter-I).

- Some of these poly(thioglycolates) and a thiol-terminated polysulfide liquid polymer (prepared from an organic dihalide) were employed to synthesize new aminofunctional compounds which were used as curing agents for a liquid epoxy resin (Chapter-II).
- New polythiourethane polymers were synthesized by reaction of some of the poly(thioglycolates) with aromatic diisocyanates, and properties of these polymers were studied (Chapter-III).
- New polyimidothioether polymers and copolymers were synthesized by reaction of poly(thioglycolates) with aromatic bismaleimides, and the resulting products characterized (Chapter-IV).
- Castor oil tris(thioglycolate), which showed an inherent propensity to form solid film on exposure to air, was cured with lead peroxide and p-quinone dioxime using various fillers, and the mechanical properties of cured products were determined (Chapter-V).

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CHAPTER-I

SYNTHESIS OF POLY(THIOGLYCOLATES)

INTRODUCTION

Poly(thioglycolates), the esters of polyhydroxy compounds with thioglycolic acid, are a class of thiol compounds of high industrial importance. These poly (thioglycolates) find a variety of important applications in the synthesis of polymers, in the synthesis of various derivatives highly useful as protecting materials for synthetic polymers against degradative influences, in hair waving compositions, in shrink proofing and crease-resistant finishings for wool and cotton fibres etc. (see General Introduction).

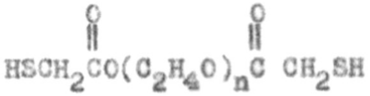
The synthesis of thioglycolate compounds can be accomplished by the usual acid-catalyzed esterification technique, p-toluene sulfonic acid being the widely used catalyst. Vaidya[1] has also employed cation-exchange resin - Amberlite - for the thioglycolate synthesis with good yields. Hayakawa and Toyota[2] have reported the synthesis of mercaptan-containing organic esters from the corresponding halo-esters and alkali or alkaline earth hydrosulfide. The esterification reactions are performed in neutral aromatic hydrocarbon solvents, but chlorinated solvents like tetrachloroethylene have also been used.

PRESENT INVESTIGATION AND RESULTS

In the present study, thioglycolate esters of ethylene glycol, diethylene glycol, polyethylene glycols-200, 400 and 600, trimethylol propane and castor oil were synthesized. Toluene or xylene was used as solvent and p-toluene-sulfonic acid as the catalyst. The synthesis of thioglycolates is briefly described below.

i) Thioglycolate of Glycols

A toluene or xylene solution of the glycol (0.10 mole), thioglycolic acid (0.25 mole) and p-toluene sulfonic acid was refluxed to remove water azeotropically. After all the water was removed, the reaction mixture was washed with hot water, dried and the solvent was removed under reduced pressure. Glycol bis(thioglycolates) have the general structure:



$$HSCH_2\overset{O}{\overset{\|}{C}}O(C_2H_4O)_n\overset{O}{\overset{\|}{C}}\ CH_2SH$$

where n = 1, for ethyleneglycol
n = 4, for PEG-200
n = 9, for PEG-400 and
n =13, for PEG-600

The NMR spectrum of ethylene glycol bis(thioglycolate) is shown in Fig.1.1.

ii) Tris(thioglycolate) of Castor oil

This was prepared by adding thioglycolic acid (0.35 mole)

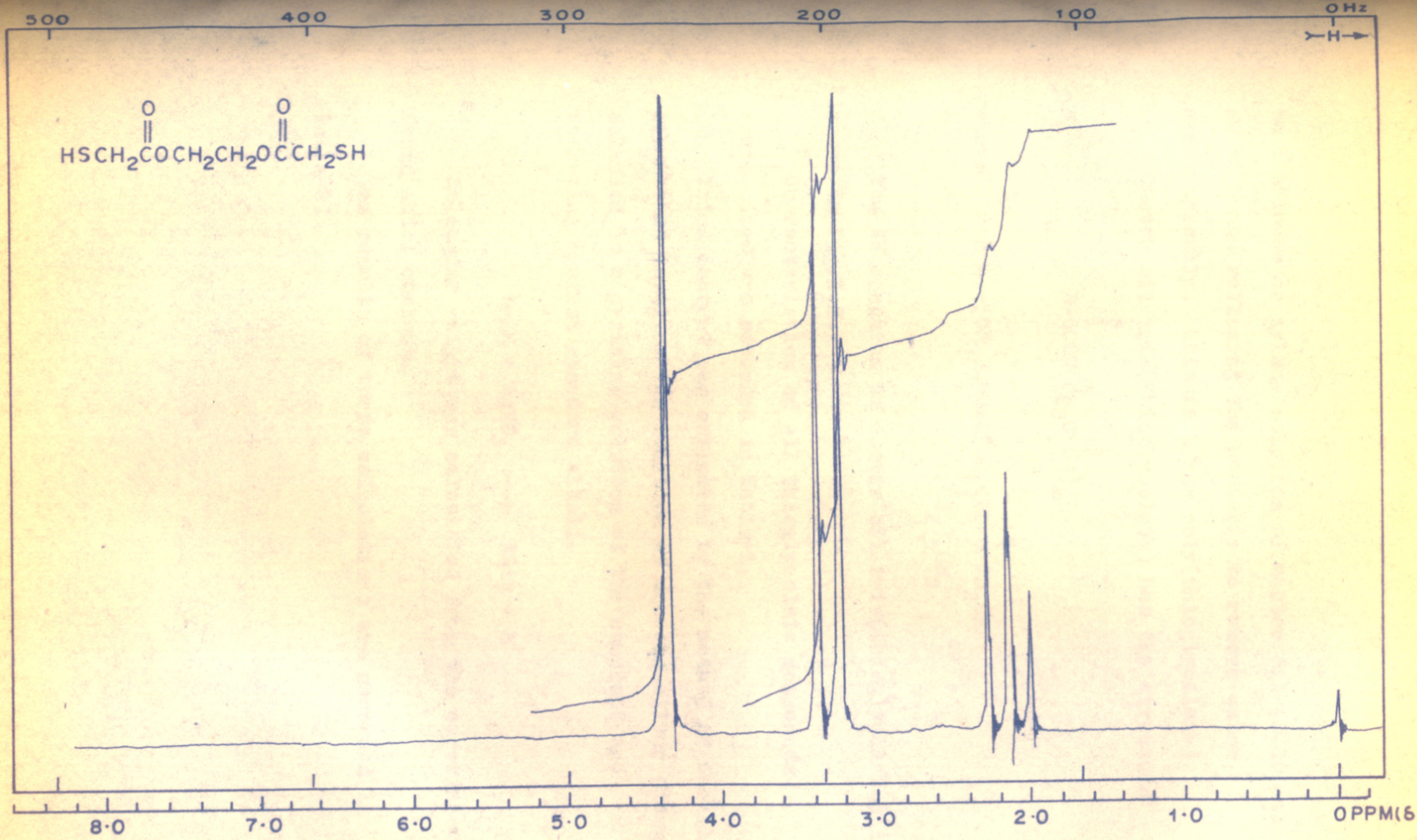
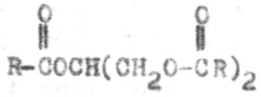


FIG. 1.1 NMR SPECTRUM OF ETHYLENEGLYCOL BIS (THIOGLYCOLATE)

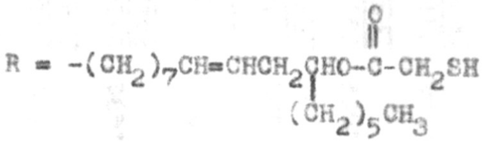
to a toluene or xylene solution of castor oil (0.10 mole) at 90°C and refluxing the contents to remove water azeotropically. This is a new poly(thioglycolate).

Castor oil tris(thioglycolate) has the structure:



$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}OCH(CH_2O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}R)_2$$

where



$$R = -(CH_2)_7CH{=}CHCH_2\underset{\underset{\displaystyle (CH_2)_5CH_3}{|}}{C}HO\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2SH$$

The IR spectrum of castor oil tris(thioglycolate) is shown in Fig.1.2.

Characteristics of all thioglycolate compounds synthesized are recorded in Table-1.

Thiol content was estimated by the method of Saville[3]. The method involves the addition of aqueous silver nitrate solution to a pyridine solution of the compound and titrating against standard alkali.

$$R\text{-}SH + AgNO_3 \longrightarrow RSAg + H^+$$

Molecular weight was calculated from the experimentally found thiol content.

The results of these calculations are recorded in Table-2.

Table-1: Physical Properties of Poly(thioglycolates) and Elemental Analysis Data

No.	Compound	Yield %	Boiling point °C/mm of Hg	d	n_D		Analysis		
							C,%	H,%	S,%
1.	Ethyleneglycol bis(thioglycolate)	89	148/3	1.33	1.514	Calcd	34.28	4.76	30.4
						Found	34.81	5.14	29.9
2.	Diethyleneglycol bis(thioglycolate)*	85	197/3	-	1.505	Calcd	37.79	5.51	25.19
						Found	37.6	5.84	25.31
3.	Polyethyleneglycol-200 bis(thioglycolate)*	86	-	1.26	1.494	Calcd	42.1	6.49	18.71
						Found	42.07	7.01	18.8
4.	Polyethyleneglycol-400 bis (thioglycolate)*	81	-	1.227	1.492	Calcd	46.92	7.4	11.39
						Found	47.13	7.72	11.6
5.	Polyethyleneglycol-600 bis (thioglycolate)*	65	-	1.2265	1.489	Calcd	48.7	7.05	8.6
						Found	48.93	7.43	8.89
6.	Trimethylolpropane mono(thioglycolate)**	87	150/1.5	-	1.502	Calcd	46.15	7.69	15.36
						Found	46.33	7.41	16.1
7.	Trimethylolpropane bis(thioglycolate)**	75	-		1.506	Calcd	42.56	8.65	22.69
						Found	42.63	8.74	23.15
8.	Trimethylolpropane tris(thioglycolate)	90	253 /6	1.55	1.518	Calcd	40.46	5.610	26.96
						Found	40.65	5.74	26.86
9.	Castor oil tris(thioglycolate)**	95	-	-	1.489	Calcd	65.51	9.53	8.33
						Found	66.63	9.79	9.62

* Compound known but physical constants not reported

** New compounds

Table-2: Thiol Content and Molecular Weight Data of Thioglycolates Prepared

Sl. No.	Thioglycolate	Molecular formula	-SH content in %		Molecular Weight	
			Calcd.	Found	Calcd.	Found
1.	Ethyleneglycol bis (thioglycolate)	$C_6H_{10}O_4S_2$	31.49	31.61	210	209.1
2.	Diethyleneglycol bis (thioglycolate)	$C_8H_{14}O_5S_2$	26.03	26.12	254	253.1
3.	Polyethyleneglycol-200 bis(thioglycolate)	$C_{12}H_{22}O_7S_2$	19.00	19.18	342	344.8
4.	Polyethyleneglycol-400 bis(thioglycolate)	$C_{22}H_{42}O_{12}S_2$	11.77	11.90	562	555.6
5.	Polyethyleneglycol-600 bis(thioglycolate)	$C_{30}H_{58}O_{16}S_2$	8.85	8.90	738	745.1
6.	Trimethylolpropane mono thioglycolate	$C_8H_{16}O_4S$	15.87	15.88	208	208.2
7.	Trimethylolpropane bis (thioglycolate)	$C_{10}H_{18}O_5S_2$	23.32	23.27	282	283.4
8.	Trimethylolpropane tris (thioglycolate)	$C_{12}H_{20}O_6S_3$	27.9	28.03	356	353.8
9.	Castor oil tris (thioglycolate)	$C_{63}H_{110}O_{12}S_3$	8.595	8.475	1154	1170

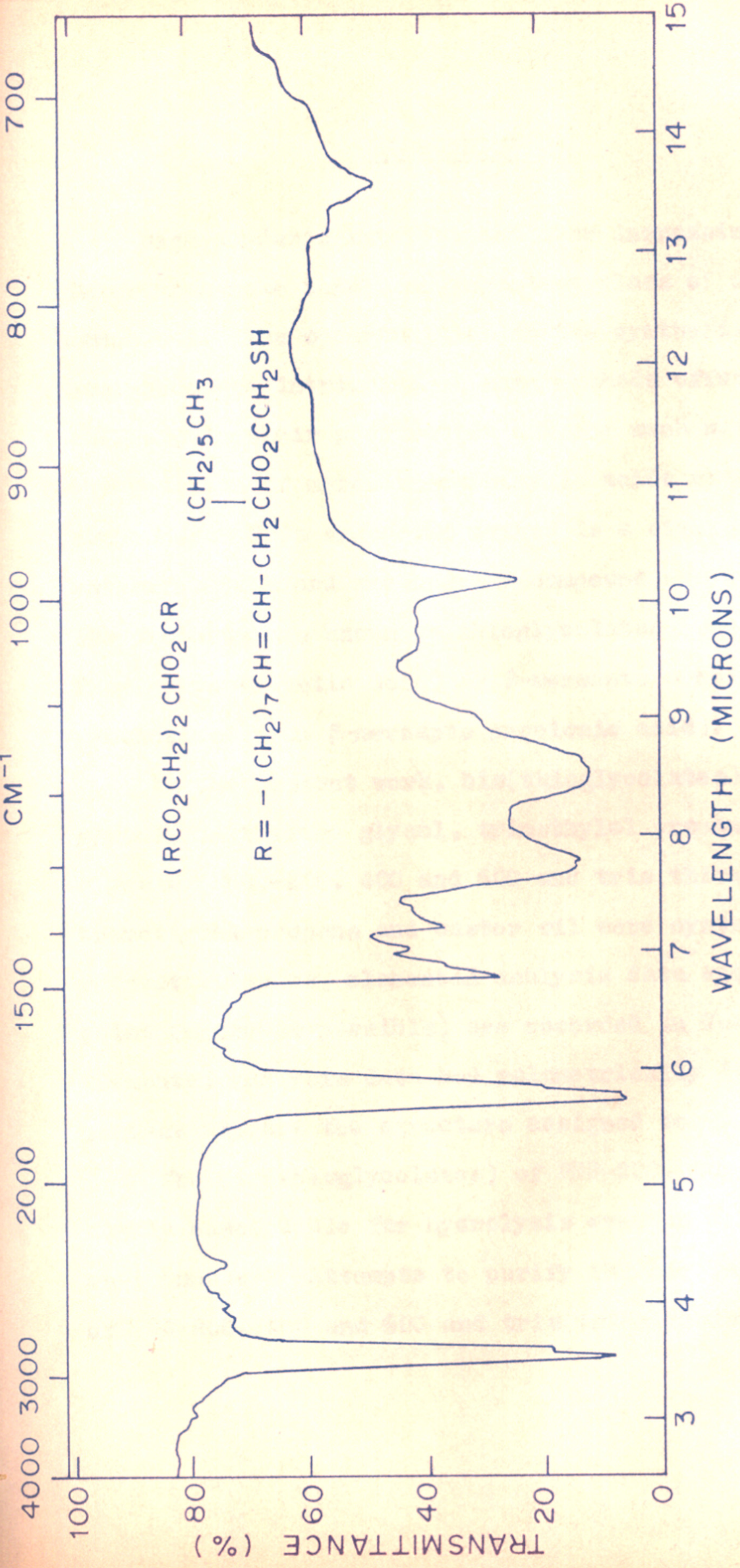


FIG. 1·2 IR SPECTRUM OF CASTOROIL TRIS(THIOGLYCOLATE)

DISCUSSION

High academic interest and ever-increasing commercial importance make thiols an important class of organic compounds. The opportunities in the synthesis of these compounds are intriguing as some methods offer more latitude in their preparation and one such method involves the reaction of mercapto-carboxylic acids with hydroxy compounds. This synthetic method is a simple acid-catalyzed esterification and any hydroxy compound can be employed. The products are known as thioglycolates (when synthesized from mercaptoacetic acid) or β-mercapto propionates (when synthesized from β-mercapto propionic acid).

In the present work, bis(thioglycolates) of ethylene glycol, diethylene glycol, trimethylol propane, polyethylene glycols (PEG)-200, 400 and 600 and tris(thioglycolates) of trimethylol propane and castor oil were synthesized. Their refractive index, elemental analysis data and boiling point (wherever possible) are recorded in Table-1. The elemental analysis data and volumetrically found -SH content support the structure assigned to them.

The bis(thioglycolates) of PEG-200, 400 and 600 were highly susceptible for hydrolysis even in mild basic environments. Attempts to purify the bis(thioglycolates) of PEG-200, 400 and 600 and tris(thioglycolate) of castor oil by distillation under reduced pressure were thwarted by the formation of dark and viscous products during the process.

Thiol compounds generally show a medium intensity band at 2530-2900 cm^{-1} in the infrared region, characteristic of -SH functionality[5]. All poly(thioglycolates) [except castor oil tris(thioglycolate)] show at this band. The band at 1730-1750 cm^{-1} is of C=O in ester group. Bands in the region 1180-1300 cm^{-1} are due to C-O and it is difficult to distinguish the ester C-O and ether C-O bands. The NMR spectrum of ethylene glycol bis(thioglycolate) is shown in Fig.1.1. The thiol group appears as a triplet centered at 2.2δ. The CH_2 of the thiomethyl group is found as a doublet centered at 3.35 δ.

The infrared spectrum of castor oil tris(thioglycolate), however, was of interest (Fig. 1.2). This compound shows a propensity to form clear, brittle film, insoluble in usual organic solvents, on exposure to air or even on storage. Castor oil, which is the triglyceride of ricinoleic acid, contains three double bonds of complete <u>cis</u>-configuration. IR spectrum of pure castor oil has a broad band at 740 cm^{-1} ($\sim$ 13.6 μ) characteristic of <u>cis</u>-double bonds[5,6]. On esterification, however, the 740 cm^{-1} band decreases in intensity and a sharp band of medium intensity appears at 980 cm^{-1} (10.2 μ). This 10.2 μ band is characteristic of the double bond with '*trans*'- configuration and thus it may be concluded that esterification of castor oil with mercaptoacetic acid involves cis-trans isomerization. It is beyond doubt that castor oil tris(thioglycolate) contains a considerable amount of the ester with trans-double bond configuration. However, the relative amounts of *cis*- and *trans*-compounds could not be determined.

EXPERIMENTAL

Materials

Polyethylene glycols-200, 400 and 600 (NOCIL, India) thioglycolic acid (80%) (Veb-Labor Chemie Apolda, Germany) were used.

Preparation of bis(thioglycolates)

A. Ethylene glycol bis(thioglycolate)

A toluene (or xylene) (150 ml) solution of ethylene glycol (6.2 g, 0.10 mole), thioglycolic acid (23.0g, 0.25 mole) and p-toluene sulphonic acid (1-1.5% w/w of the glycol) was refluxed in a three necked flask equipped with a mechanical stirrer, a thermowell and a Dean-Stark arrangement for the azeotropic removal of water. After all the water had been removed, the contents of the flask were cooled, washed with hot water and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the compound was purified by distillation in vacuum.

Bis(thioglycolates) of other glycols, listed in Table-1 were prepared in a similar way.

Physical properties of all glycol bis(thioglycolates) are listed in Table-1.

For ethyleneglycol bis(thioglycolate): IR 1735($-\overset{\overset{O}{\|}}{C}$), 2515 cm^{-1}(-SH).

NMR(CCl_4): δ 2.2(t, SH), 3.35 (d, $\underline{CH_2}SH$), 4.4 (s, $OC\underline{H_2}C\underline{H_2}O$)

B. Preparation of Castor oil tris(thioglycolate)

A toluene (or xylene) (400 ml) solution of castor oil (93.2 g, 0.1 mole) was heated in a 3-necked flask equipped as above to a temperature of 85-90°C, and thioglycolic acid (32.0 g, 0.35 mole) was added followed by p-toluene sulphonic acid (1.5% w/w of castor oil). The contents of the flask were refluxed to remove water azeotropically. After all the water had been removed, refluxing was continued for further 19 hours. The reaction mixture was cooled, washed with hot water, dried over anhydrous sodium sulphate and the solvent was distilled off under reduced pressure.

Physical properties of castor oil tris(thioglycolate) are shown in Table-1.

IR of castor oil tris(thioglycolate): 1730 cm^{-1}(C=O), 970 cm^{-1}(C=C trans).

Analytical Method

Estimation of Thiol Content[3] and Determination of Molecular Weight therefrom

A weighed amount of the sample was dissolved in pyridine (15 ml) and 5% aqueous silver nitrate solution (5 ml) was pipetted out into the flask. The flask was stoppered and kept aside for 5 minutes. At the end of this period, distilled water (100 ml) was added into the flask and the content was titrated against standard sodium hydroxide solution using phenolphthalein indicator.

Calculation

$$\% \text{ SH} = \frac{V.N.(33.06)}{1000\ W} \times 100$$

where V = volume of NaOH for sample
N = normality of NaOH solution
W = weight of the sample in grams

NOTE: In these titrations, blank correction is not necessary because a simple mixture of silver nitrate and pyridine was found to be sensitive to even one drop of NaOH solution.

Molecular Weight[4]

The molecular weight was calculated from the end group analysis of -SH groups, using the relation:

$$M = 100.\ Z.\ E/e$$

where Z = Number of end groups per molecule
E = Molecular weight of the end group
e = Experimentally found content of the end group in percent.

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CHAPTER-II

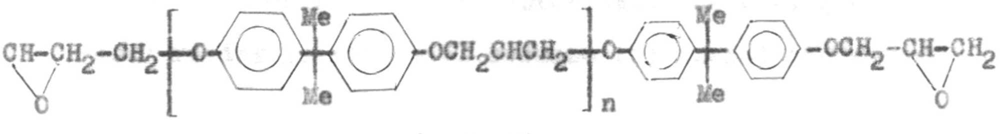
AMINOFUNCTIONAL COMPOUNDS IN THE CURING OF ARALDITE-LY 553, A COMMERCIAL EPOXY RESIN

INTRODUCTION

Ever since their significant commercial debut following the pioneering work of Castan[1] and Greenlee[2] hardly three decades ago, epoxy resins have steadily and rapidly come to occupy an unique place of their own among the thermosetting resins. The rate of publication of technical literature and of a multitude of patents, for which epoxy resins have been an enviable and instant target, remains unparalleled in the thermosetting resin field. This ever-increasing global interest in epoxy resins originates mainly from a large number of unusually valuable properties which can be engineered to a multitude of diversified applications, an extremely wide variety of reactions that can be used for curing and the high versatility of the products that result.

Commercial epoxy resins are characterised by the presence of two or more 1,2-epoxide (α-epoxide) groups per molecule capable of being converted to thermoset form with a crosslinking agent.

The epoxy resins first commercially developed and still dominating are those based on 2,2'-bis(4-hydroxyphenyl) propane (bisphenol-A) and epichlorohydrin. These resins can be represented, in general, as:



(n=0-12)

A large number of other diphenols are also used in the synthesis of epichlorohydrin-based epoxy resins[3,4] e.g. resorcinol, substituted bisphenol-A, polyphenols (phenol-formaldehyde novolacs), tetraphenol ethane, and poly (oxyalkylene) glycols etc. Amano and Nakata[5] have reported new polyepoxides based on polyhalobiphenyl alkylene ethers.

Another class of epoxy resins in vogue are the epoxidized-polyolefins (epoxidized byperacids). The interest in these resins originates mainly from the simplicity of the process and an innumerable number of olefins, both cyclic and polymeric, which can be used. Recently, Matsumura et al[6] have used epoxidized poly(4,1-phenylene oxides) for heat resistant epoxy resin compositions.

The chemistry of α-epoxides has been reviewed by Winstein and Henderson[7] and the chemistry and technology of epoxy resins by Lee and Neville[4,8], Potter[9], Bruins[10], and May and Tanaka[11].

Curing of Epoxy Resins

'Curing' (or hardening) in epoxy resin technology describes the process of conversion of the liquid (or thermoplastic) epoxy resin to solid, infusible, crosslinked thermoset structure. This transformation is accomplished by the addition of a chemically reactive agent (the curing agent or hardner). The transformation or curing of epoxy resins is essential because the useful properties of epoxy resins appear only after curing. Depending on the curing agent and curing conditions, it is possible to obtain products having high electrical insulation properties, good thermal resistance, mechanical properties ranging from extreme flexibility to high strength, a wide but useful range of electrical, thermal and mechanical properties, solvent resistance and a host of other useful properties.

Curing of an epoxy resin can take place by the reaction of epoxy groups themselves (polymerization) or by the reaction of the epoxy group with active hydrogen-containing compounds (polyaddition). A distinguishing feature of the epoxy resin curing is that most of the curing reactions are ionic. A brief account of the epoxy curing by (A) polyaddition, and (B) polymerization reactions is presented below.

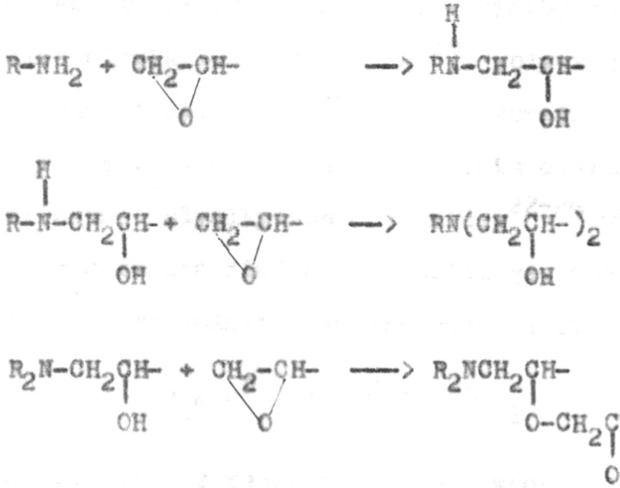
(A) Polyaddition Reactions

Polyaddition is the most widely used reaction for epoxy curing in which the crosslinking occurs by chain extension. This is achieved by the reaction of epoxy groups with active hydrogen compounds. Commonly used active hydrogen compounds are polyamines and their derivatives, polyacids and anhydrides, polymercaptans and polyphenols (phenol formaldehyde novolacs). The most widely used of these are the polyamines.

1. Polyamines

These are the most important and widely used epoxy resin-curing agents which function by chain extension. A polyamine, to be effective as a crosslinking agent, should contain at least three active hydrogens on primary or secondary nitrogens. The amine is incorporated into the structure of the crosslinked polymer and will become part of the backbone.

The reaction of an amine with an epoxide group may be represented as[12,13]:

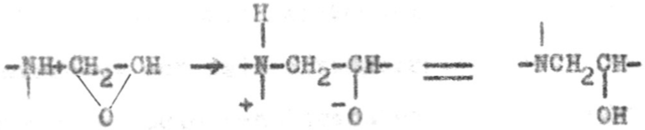


(1)

(2)

(3)

Anderson[14] found that some strongly basic aliphatic polyamines caused a substantial amount of etherification reaction and that aromatic amines do not promote etherification reaction (3) because of substantial steric hindrance in the tertiary amine formed. Sidyakin[15], by I.R spectroscopy and Sojka and Moniz[16], by C-13 NMR spectroscopic studies, showed that the reaction of an amine with the epoxide group involves the formation of a Zwitter ion intermediate which is in equilibrium with the aminoalcohol formed:



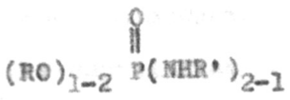
The recent work of Badran et al[17] also supports the above mechanism.

Polyamines may be aliphatic or aromatic. Among the former class simple polyamines (e.g. diethylenetriamine)[11] , long chain polyalkylene polyamines[18], polyether polyamines[19] polyether glycol polyamines[20] and unsaturated polyamines[21] are widely used. A new addition to this class of amines is the siloxane polyalkylene polyamines[22-24] which increase surface hardness and find use in moldings, coatings and adhesives. These amines have the general structure:

$$H_2N\ R^3\ [SiR'R^2O]_n\ R^3NH_2$$

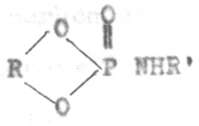
Aromatic amines react with epoxy groups at a slow rate than the aliphatic amines. Currently the most widely used aromatic polyamines are m-phenylenediamine, 4,4'-diamino diphenylmethane, 4,4'-diaminodiphenyl sulfone and xylene diamines. Aromatic amines, although require elevated curing temperatures, provide good solvent resistance and high heat distortion temperatures to cured systems. Aromatic polyamines, synthesised by the reaction of 1-10 moles of aromatic diamine with 1 mole of divinyl sulfone (or diaminodiphenyl sulfone) have been found to give better thermal properties to cured systems[25,26]. Sobel et al[27] and Kwiatowski et al[28] describe a flame-retardant and self-extinguishing epoxy resin composition cured by nuclear-halogenated aromatic ether polyamines, while polychlorinated xylylene diamines impart good flexibility and elasticity[29]. Epoxy resins containing encapsulated m-phenylenediamine[30] (prepared by an interphase stepwise copolymerization with hexamethylene diisocyanate) had a 4 month storage stability at room temperature. Amine blends, either alone[31] or emulsified[32] have been used for regulation of pot life. Metal chloride complex[33] or organometallic compounds[34] combination with aromatic polyamines have also been used to improve adhesion to steel and to give electrical insulation properties.

Amines based on phosphorus compounds are used in flame-retardant and self-extinguishing epoxy resin compositions. Hindersinn[35] describes the use of phosphoramidates of the following two general types:



$(RO)_{1-2}\overset{O}{\overset{\|}{P}}(NHR')_{2-1}$

and



Aminocyclotriphosphazines have also been used to impart good mechanical properties to epoxy resin compositions[36].

Heterocyclic amines and cycloaliphatic polyamine curing agents used include N-aminoethyl piperazine, 2-aminobenzimidazole[37] etc. 4,4'-di(aminocyclohexyl) methane[38], menthane diamine etc. Blends of cycloaliphatic amines with metal perchlorates have been used for room temperature epoxy-hardening[39].

Modified Polyamines

Since the most commonly available polyamines are toxic, irritating or carbonate readily in air, their derivatives have been prepared by adducting or reacting polyamines with many monomeric and polymeric coupling agents having functional groups reactive towards the amino group. Reduced physiological effects[40], ease of handling, convenient mixing ratios with epoxy resins and regulation of pot life, and good shelf life highlight some of the principal advantages of these modified polyamines.

Examples of modified polyamines are cyanoethylated polyamines[41], oxyethylated polyamines[40], halohydrinether-polyamine adducts[42], glycidyl ether-polyamine adducts[43-45], polyamine-aldehyde[46,47] and polyamine-thiourea condensates[48,49] polyamine-urea adducts containing carbon disulfide[50] and polyamine-caprolactam reaction products[51,52].

Polyamines have also been reacted with a variety of polymers to obtain polyamine-polymer derivatives. The polymers (or polyfunctional compounds) used include polyisocyanates[53], chlorosulfonated polyethylene[54], polycarbonates[55], polybutadienes[56], polyurethanes[57], mercaptan terminated polymers[58-61], phenol-formaldehyde reaction products[62], polyepisulfides[63] and oligomeric acrylic resins containing reactive pendant groups[64].

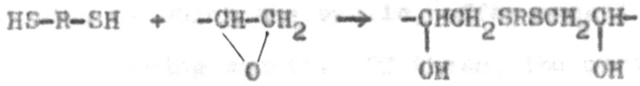
2. Polyamides

Polyamides are used as epoxy hardeners to achieve such special properties as lower toxicity, lower exotherm in large castings, more latitude in stoichiometry, improved flexibility, good water resistance and longer pot life. Generally, the cure of epoxide resins with polyamides is dependent on the reactions with secondary amine and terminal amino groups. Currently, extensively used polyamides are the polyamidoamines resulting from the reaction of polymeric fatty acids and polyamines[65-67]. Unsaturated polyamides have also been used in adhesive epoxy-resin formulations[68].

Modified polyamides[11] are also used, like modified polyamines, in epoxy curing, e.g. polyamide adducts with epoxides[69], acrylonitrile or caprolactam[70]. Polyamide-polyamine blends containing metal oxides find important uses in epoxy curing for increased adhesion strength with improved resistance to low and high temperatures[71].

3. Polymercaptans

Polymercaptans undergo polyaddition reactions with epoxides (in presence of basic catalysts).



$$\mathrm{HS{-}R{-}SH} + \underset{\diagdown O \diagup}{\mathrm{{-}CH{-}CH_2}} \longrightarrow \mathrm{{-}\underset{OH}{C}HCH_2SRSCH_2\underset{OH}{C}H{-}}$$

In epoxy resin technology, the most widely used polymercaptans are the mercaptan-terminated polysulfide polymers[72]. Other polymercaptan curing agents used include mercapto carboxylic acids and their esters[73,74], polyetherthiols[75], reaction products of hydrogen sulfide with diglycidyl ethers[76] etc. Cycloaliphatic polythiols[77-79] are finding increasing uses in the curing of epoxy resins for preparation of enamels, paints, potting compositions, casting laminates and adhesives. Doss[80] describes the use of tolylene bis(polymercapto propyl thiocarbamates) for improving the adhesive strength of epoxy resins to metals.

4. Anhydrides

Next to aminofunctional compounds, anhydrides are the most widely used epoxy-curing agents. In general, anhydrides provide long pot life and low exotherm and yield products with superior thermal and mechanical resistance. They are used principally in laminating formulations and to a limited extent, in high temperature adhesive formulations.

Anhydrides react with epoxy resins both in presence and absence of catalysts (acidic or basic)[81,82].

A variety of commercially available acid anhydrides, majority of which are cyclic, offer excellent properties as epoxy curing agents. Of these, the most widely used are methyl bicyclo [2.2.1]-heptene-2,3-dicarboxylic anhydride, hexachloro bicyclo [2.2.1]-heptene-2,3-dicarboxylic anhydride, hexahydrophthalic anhydride and dodecyl-succinic anhydride. A variety of di- and poly anhydrides have been claimed in the literature for epoxy curing[11]. Majority of these are the Diels-Alder adducts of maleic anhydride with vinyl compounds[83,84]. Other polyanhydrides used in epoxy curing include aromatic ether or thioether anhydrides[85], polyester-polyanhydrides (prepared by the reaction of hydrogenated polydienes with trimellitic anhydride)[86], anhydride-terminated polymers (prepared from polyalkylene glycols or diamines and unsaturated dicarboxylic anhydride) for flexibility[87] and anhydrides containing tetraphenylarsenic tetraphenylborate[88] for long pot life. Fluorine containing anhydrides have been used in the curing of fluorine-containing epoxy resins[89].

5. Carboxylic Acids

Dibasic and polybasic acids are another class of compounds that undergo polyaddition reactions with epoxy groups. These have found limited applications in castings, laminates, adhesives, molding powders and filament windings. However, polymeric acids are widely used in coatings.

Similar to anhydrides, acids also react with epoxides in presence of basic catalysts[90,91].

Aliphatic polymeric fatty acids were employed by Belanger and Klassen[92] for epoxy curing. Examples of new carboxylic acids which have been used include benzimidazole dicarboxylic acids[93](for heat resistant compositions) and amidoimidocarboxylic acids (or bisimido dicarboxylic acids)[94] for improved heat resistant and flame resistant laminated epoxy sheets.

6. Polyphenols

Wegler[95] has reviewed the work on epoxy-polyphenol curing reactions. Most of reported work on curing of epoxy resins with phenolic resins has been on the novolac types[11].

Pflug and Valenta[96] found that bisphenol-A or other dihydroxy diphenylmethane novolacs gave heat resistant compositions especially useful in electrical appliances. Lohse and Schreiber[97] describe the use of a product from methoxy terminated siloxane and a cresol novolac for epoxy resins giving resins with good water resistance.

Catalysts for epoxide-polyphenol reactions include inorganic bases, nitrogenous bases and stannous salts[98].

7. Polyureas

Urea and its derivatives are particularly useful for high temperature curing of epoxy resins[99,100]. The products of urea-formaldehyde reaction may be used as accelerators for anhydride cures[99] and as cocuring agents for glycidated novolac resins[101]. Polythioureas $[R'NHC(=S)NHR'']_nR'''$[102], hydrazides[103], guanidines[104,105], dicyandiamide[105,106] have been found to be useful as epoxy curing agents or as catalysts. Gude et al[107] have found the low molecular weight amine terminated polymers (from m-phenylenediamine and p-phenylene diisocyanate) to be particularly useful for solvent resistant coatings and molding epoxy resin compositions.

(B) Curing of Epoxy Resins by Catalytic Agents[11]
(by Polymerization Reaction)

Catalytic polymerization of epoxy resins occurs with a variety of Lewis bases and acids as well as many salts and complex catalysts. Although epoxy curing by Lewis bases and acids results in basically the same cured polymer having a polyether structure, their modes of initiation, propagation are different. With Lewis bases, anionic polymerization takes place while with Lewis acids, it is cationic.

1. Anionic Catalysts

The cure of epoxy resins, todate, by polymerization using anionic catalysts, has not found wide commercial acceptance because of long cure cycles required and the low heat distortion point of resulting cures. However, the advent of imidazole derivatives offer excellent prospects for minimizing the cure cycle duration.

Tertiary amines are the most widely used catalysts of this class. Pyridine, 2,4,6-tris(di-methyl aminomethyl) phenol (DMP-30), triethyl amine, benzyldimethylamine are widely used and typical of this class.

The use of a variety of metal and organometallic anionic catalysts in epoxy curing has been reviewed by Gaylord[108]. These include triethanol borates and titanates with chelated metal salts[109,110] and tricresyl borate[111]. Imidazoles[112-115], imidazolines and bis-imidazolenes[116] have been used to give high distortion temperatures, and flexible compositions. The recent in this class appear to be polyketones from benzimidazole[117] and bisbenzimidazole[118] isophthaloyl chloride. Epoxy resins cured with these compounds show little or no ignition loss at high temperatures. Imidazole borates[119] are used to improve compatibility and storage stability to epoxy resin curing compositions.

2. Cationic Catalysts

A wide variety of inorganic chlorides and their fluoborates, e.g. $SnCl_4$ serve as cationic catalysts for epoxy resins. The most important compound in this class, in terms of commercial utilization, is boron trifluoride, BF_3. BF_3 is not useful as such because of the difficulties in handling and controlling its reaction with epoxy resins. It is generally used as a complex with ethers and amines[120-122]. Of these only the BF_3 methyl amine complex finds wide usage. Fleming and Martin[123] have reported the use of borontrichloride-amine complexes as latent hardeners, which show good storage properties. Diaryl iodonium fluoroborates[124] have been used in the epoxy resin coating composition which are photochemically hardened and show good oil resistance. Tertiary amine salts of α-substituted carboxylic acids[125,126] which show decomposition in the range 10-200°C have been used to impart improved stability and pot life at room temperature.

In the present work, new aminofunctional curing agents for a liquid epoxy resin were synthesized from polythiol compounds, paraformaldehyde, diethylene triamine or tetraethylene pentamine, phenol or 3-pentadecenyl phenol, which is a readily available indigenous raw-material. The polythiols used were a thiol-terminated polysulfide liquid polymer and bis(thioglycolates) of ethyleneglycol, polyethylene glycols-200,400 and 600. The curing of epoxy resin by these aminofunctional curing agents was studied at room temperature and at 50°C.

PRESENT INVESTIGATION AND RESULTS

Aminofunctional compounds, e.g. polyamines and their reaction products with a variety of compounds, find extensive uses in a multitude of epoxy resin-based applications because of their high versatility. Derivatives of polyamines, which are preferred to parent polyamines for certain advantages, have been prepared with other polyfunctional coupling agents. Some of the sulfur-containing coupling agents that have been used are thiourea[48,49], carbon disulfide[50] and thiol-terminated compounds[58-61].

Berenbaum[61] described the use of aminopolysulfide polymers, prepared by the reaction of a hydroxy or thiol terminated polysulfide polymer with an alkylene imine, in the curing of epoxy resins. This was followed by the work of Bertozzi[59], who reported the use of aminofunctional phenol-containing polysulfide polymers in epoxy resin curing. These compounds were prepared from a thiol terminated polysulfide liquid polymer, phenol, an aliphatic polyamine and paraformaldehyde. The curing by these compounds was characterized by low exotherms, good pot life and room temperature curing. Later, Bertozzi[60] used aminofunctional azomethine-containing polysulfide polymers in the curing of epoxy resins to give hard resinous products which were pliable, stable and useful. The recent work is of

Takeuchi and Tmikuda[58] describing the curing of epoxy resins with the reaction products of a polymercaptan, arylene diamine and an alkyl-substituted phenol. The polymercaptan itself was prepared by adducting hydrogen sulfide with bisphenol-A epichlorohydrin copolymer. These copolymers showed good storage stability.

The present study deals with the preparation of new aminofunctional compounds from thiol terminated compounds and the study of the curing of a liquid epoxy resin using them.

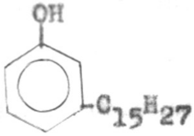
Following materials were used to synthesize the aminofunctional compounds.

i) Diethylene triamine purified by distillation prior to use.

ii) Tetraethylene pentamine used as received.

iii) Phenol purified by distillation prior to use.

iv) 3-Pentadecenyl phenol: Commercial cashewnut shell liquid was distilled under reduced pressure to yield 3-pentadecenyl phenol b.p. 195-200°C/2-3 torr.



v) Paraformaldehyde was used as received.

vi) Glycol bis(thioglycolates) (see Chapter-I). Bis (thioglycolates) of following glycols were used: ethylene glycol, polyethylene glycols-200,400 and 600.

vii) Thiol terminated polysulfide liquid polymer. The synthesis of thiol terminated polysulfide liquid polymer was accomplished as described below:

(a) Preparation of Sodium disulfide Solution of Rank 2.25

Sodium polysulfide solution of desired rank can be prepared using the relation:

$$6NaOH + 2(x+1)S \rightarrow 2Na_2S_x + Na_2S_2O_3 + 3H_2O$$

where x = rank of sulfur.

Sodium polysulfide solution ($Na_2S_{2.25}$) of rank 2.25 and 2 M concentration was prepared by heating the required quantity of aqueous sodium hydroxide solution and sulfur and diluting the resulting solution with water.

(b) Preparation of the Polymer from Dichlorodiethyl formal and Sodium disulfide

Sodium disulfide solution was placed in a flask and heated to 65°C. Magnesium hydroxide, the nucleating agent, was generated in situ by adding sodium hydroxide and magnesium chloride solution to the flask. The contents were heated to 85°C and a mixture of dichlorodiethyl formal and 1,2,3-trichloropropane (99.5:0.5 molar ratio) was added with stirring during 1 hour. The formed disulfide polymer was washed several times with water.

(c) Controlled Reduction of Disulfide Polymer to give the Thiol-Terminated Polymer

The above prepared disulfide polymer was subjected to controlled reduction using sodium hydrosulfide and sodium sulfite. After the reduction, the polymer was recovered by acidification with dilute hydrochloric acid and subsequently washed with water.

Various reactions involved in the reduction process can be written as:

$$\begin{array}{ll} RSSR + NaSH & \rightarrow RSNa + RSSH \\ RSSH + Na_2SO_3 & \rightarrow RSH + Na_2S_2O_3 \\ \hline RSSR + Na_2SO_3 + NaSH & \rightarrow RSH + Na_2S_2O_3 + RSNa \\ \hline RSNa + H^+ & \rightarrow RSH \end{array}$$

Characteristics of the thiol terminated polymer prepared are:

Physical state	liquid
Average mol.wt.	970-980
Mercaptan content	6.8 - 7.0%
pH of water extract	6 - 8
Refractive index	1.55
Density	1.31
Colour and clarity	Amber, clear.

The infrared and NMR spectra are shown in Figs. 2.1 and 2.2 respectively.

Preparation of Aminofunctional Compounds

1. From Polysulfide Liquid Polymer, Phenol (or 3-Pentadecenyl Phenol), Aliphatic Polyamine and Paraformaldehyde

A mixture of polysulfide liquid polymer, phenol (or 3-PDP), aliphatic polyamine (DETA or TEPA) and paraformaldehyde was stirred at 100±2°C for 2 hours, and

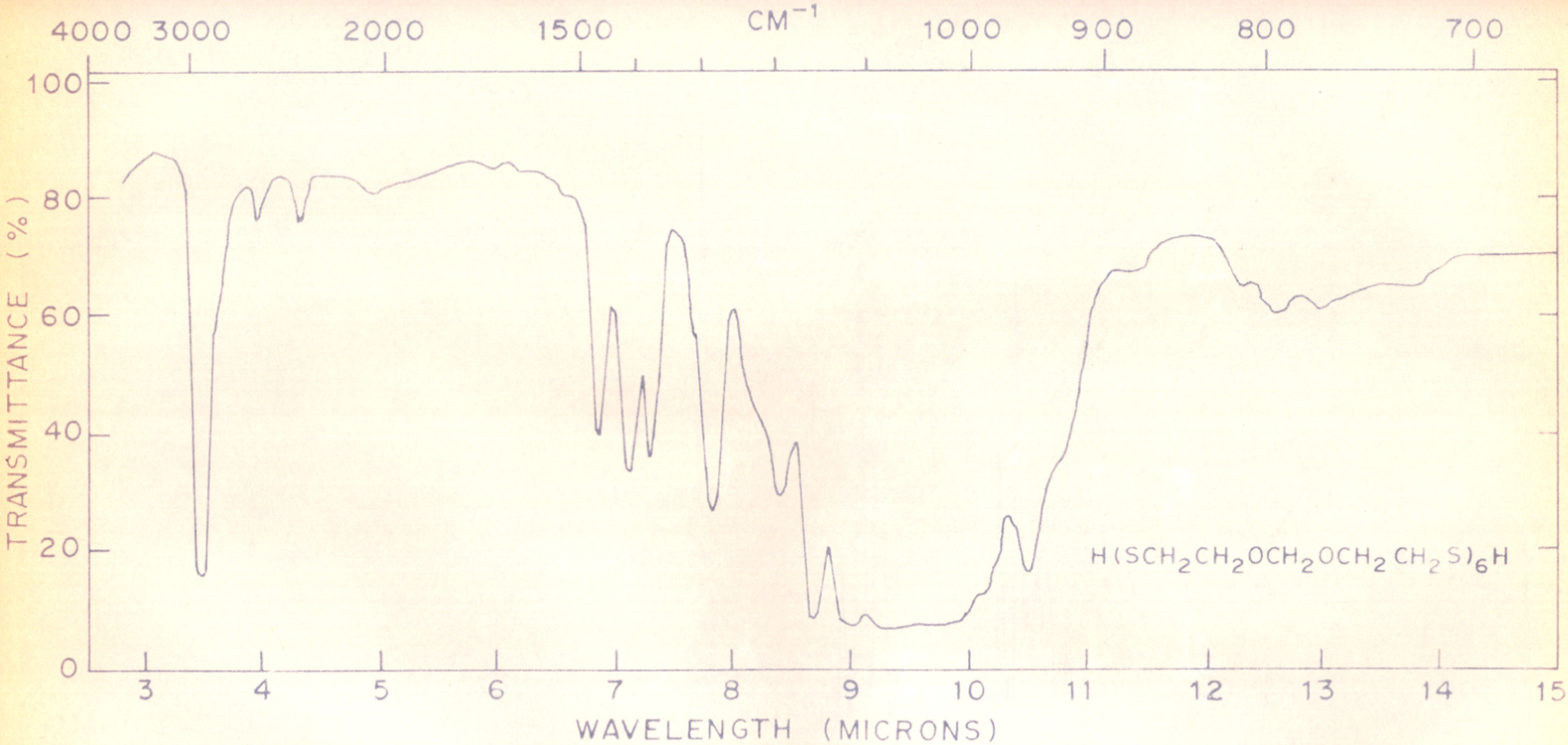


FIG. 2·1 IR SPECTRUM OF POLYSULFIDE LIQUID POLYMER (MW ~ 1000)

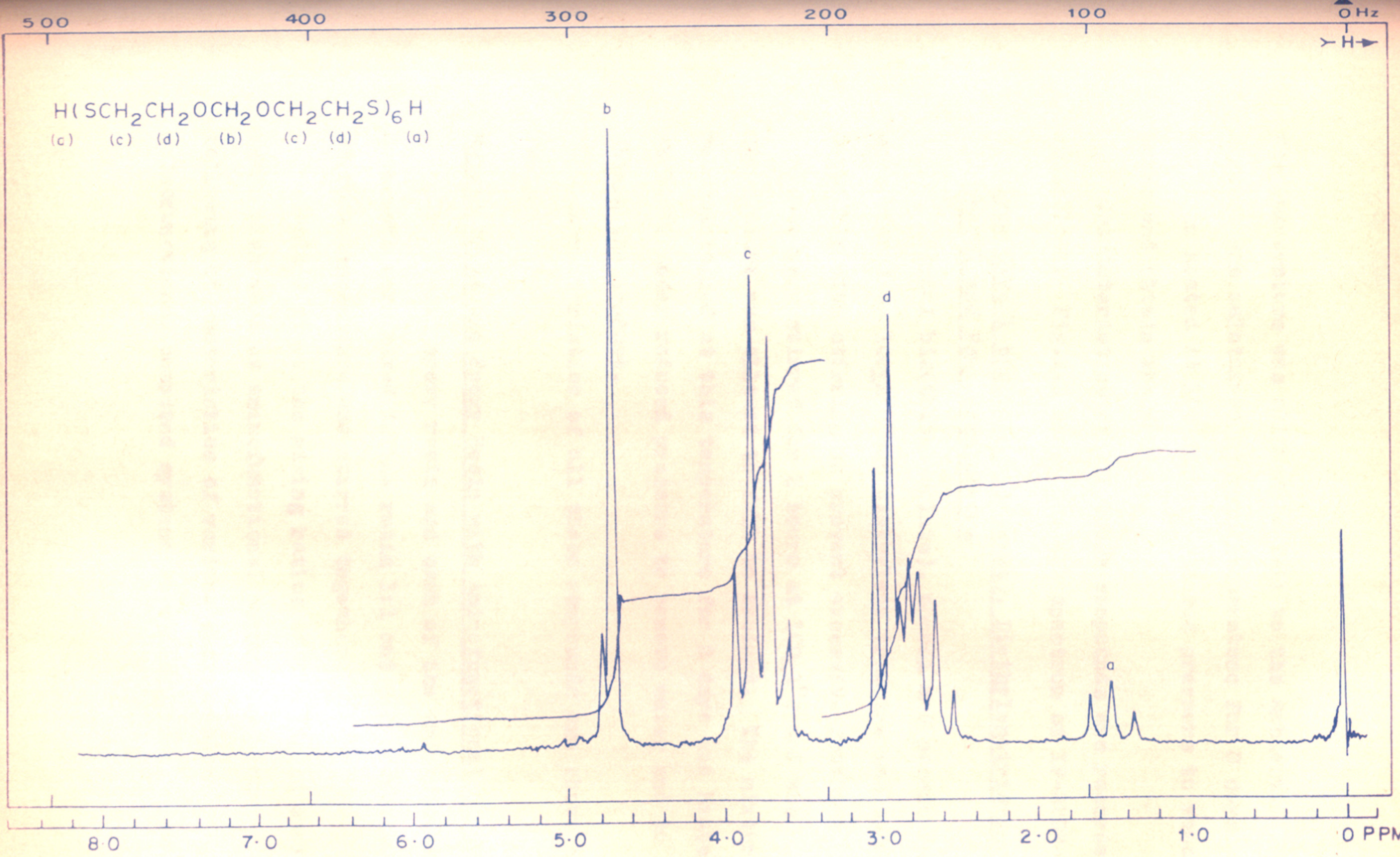


FIG. 2·2 NMR SPECTRUM OF POLYSULFIDE LIQUID POLYMER (MW~1000) the temperature was allowed to fall to the ambient. The mixture was maintained at room temperature for 3 days and then heated at 100°C under reduced pressure to remove water and obtain the product.

Characteristics of all these compounds are recorded in Table-1. Fig.2.3 shows the NMR spectrum of LP-3PDP-TEPA.

2. From Glycol bis(thioglycolates), Diethylenetriamine Phenol and Paraformaldehyde

Glycol bis(thioglycolate), phenol and paraformaldehyde were heated to 100±2°C and diethylene triamine was added carefully with stirring to prevent excessive frothing. The contents were stirred for 2 hours at 100±2°C and the temperature was allowed to fall to ambient. The mixture was maintained at this temperature for 3 days and heated at 100°C under reduced pressure to remove water and to obtain the product.

Characteristics of all these compounds are shown in Table-1.

Mixing of Liquid Epoxy Resin with Aminofunctional Compounds

The liquid epoxy resin and each of the aminofunctional compounds were mixed in the ratio 1:1 and 2:1 respectively at room temperature and stirred together.

Table-2 gives the mixing ratios of the liquid epoxy resin with various aminofunctional compounds. The following characteristics of various epoxy resin-aminofunctional compound systems were determined, viz.

Table-1: Characteristics of Aminofunctional Compounds

No.	Compound	Colour	n_D^{27}	Vertical flow time on a Flow Jig(sec.)	Analysis, % N		Molecular weight
					Calcd.	Found	
1.	LP-Phenol-DETA*	Amber	1.533	18	5.83	6.84	1150 - 1250
2.	LP-3-PDP-DETA	Red	1.535	12	4.53	4.99	1650 - 1700
3.	LP-3-PDP-TEPA	Red	1.534	48-50	6.97	7.49	1350 - 1400
4.	LP-Phenol TEPA	Red	1.530	60	8.72	10.10	1800 - 1900
5.	AFC-EG**	Red	1.572	Very viscous	12.96	11.48	700 - 730
6.	AFC-PEG-200	Red	1.539	15	10.76	10.75	780
7.	AFC-PEG-400	Red	1.536	10	8.35	8.55	970 - 980
8.	AFC-PEG-600	Red	1.531	8	7.13	7.80	1080 - 1100

LP = Polysulfide Liquid Polymer: 3PDP = 3-Pentadecenyl Phenol
DETA = Diethylene Triamine: TEPA = Tetraethylene Pentamine

* Product from Polysulfide Liquid Polymer-Phenol-Diethylenetriamine and Paraformaldehyde, etc.

** Product from Ethylene Glycol bis(thioglycolate)-Phenol-Diethylene Triamine and Paraformaldehyde, etc.

Table-2: Mixing Ratios of Aminofunctional Compounds with Araldite

System	Araldite	Compounds*							
		1	2	3	4	5	6	7	8
A	1**	1							
B	2	1							
C	1		1						
D	2		1						
E	1			1					
F	2			1					
G	1				1				
H	2				1				
J	1					1			
K	2					1			
L	1						1		
M	2						1		
N	1							1	
P	2							1	
Q	1								1
R	2								1

* See Table-1

** Numbers indicate part by weight.

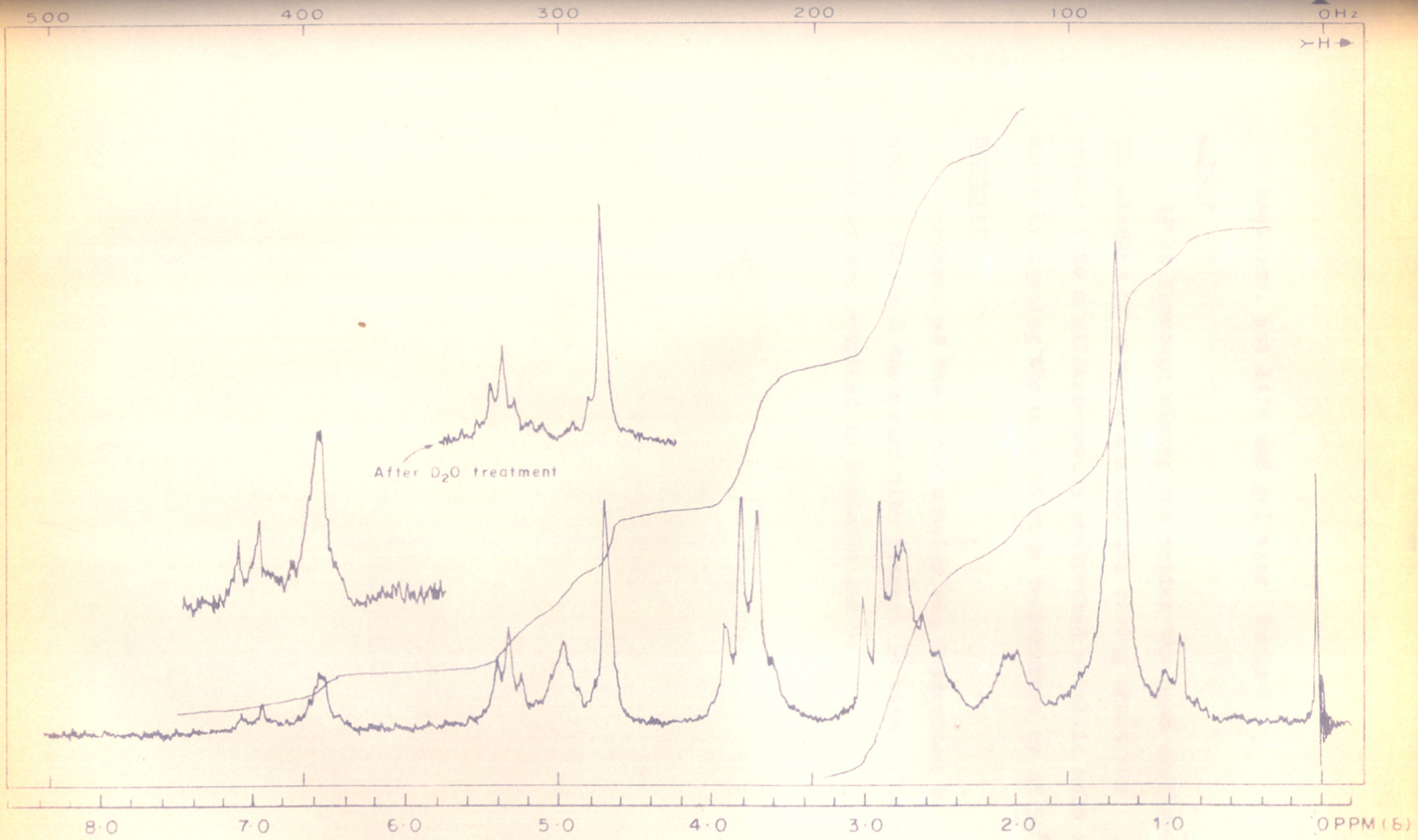


FIG. 2·3 NMR SPECTRUM OF LP-3PDP-TEPA

the exotherm, pot life and gel time (Table-3).

Curing

After thorough mixing and noting the peak exotherm, the mixture of epoxy resin and the curing agent was poured into a silicon-grease pretreated metallic mold and cured by keeping the mold at room temperature or at 50°C.

Hardness

Hardness of the cured samples was determined by using a Shore D durometer with respect to time. These readings are recorded in Tables-4 and 5.

Table-3: Exotherm, Pot life and Gel time of Various Aminofunctional Compound-Araldite Systems

System*	Exotherm °C	Pot life	Gel time
A*	51	2.0 hrs.	2.5 hrs.
B	42	5.0 hrs	7.0 hrs.
C	48	4.0 hrs.	5.0 hrs.
D	39	48.0 hrs.	53.0 hrs.
E	32	4.2 hrs.	6.5 hrs.
F	31	28.0 hrs.	38.0 hrs.
G	45	130 min.	160 min.
H	39	3.0 hrs.	5.0 hrs.
J	40	45 min.	70 min.
K	35	3.0 hrs.	5.0 hrs.
L	34	6.0 hrs.	8.0 hrs.
M	32	24.0 hrs.	48.0 hrs.
N	31	9.0 hrs.	16.0 hrs.
P	30	36.0 hrs.	55.0 hrs.
Q	28	7 days	8 days
R	28	9 days	10 days

* See Table-2

Table-4: Shore-D Hardness of Room-temperature Cured Systems

System**	Time in Days						
	1	3	5	7	10	14	21
A	20,22	25	28	35	42	50	
B	20	*	25	30	35	40,42	
C	10	15	18	20	22	25	28
D		7	*	12	15	17	20,25
E	18	20	23	25	30	35	
F				7	-	10	12.14
G	14	25	30	40	45	50	65
H	7	10	20	22	25	35	45
J	16	22	30	35	*	40	45
K	7	10	12	16	*	20	22
L				10	*	16	20
M						10	16
N				7	*	10	16
P						7	12
Q						SOFT	
R							

* Not determined

** See Table-2.

Table-5: Shore-D Readings of 50°C-cured Systems

System	Time in Days						
	1	3	5	7	10	14	21
A	30	35	45	55	60	65	70
B	25	28	35	45	50	60,61	65
C	20	*	35	40	40,45	50	52,56
D	10	15	*	20	*	32,35	40
E	25	30	35	40		52,55	60
F	18	20	16	25		40,45	50
G	25	30	40	45	50	55	65
H	22	25	30	35	45	50	60
J	20	35	40	50	52	65	80
K	7	30	35	40	45	60	65
L	7	12	16	20		25	30
M		7	*	12	*	15	20
N				12	*	16	20
P						12	16
Q						7	9
R						Soft	7

* Not determined.

DISCUSSION

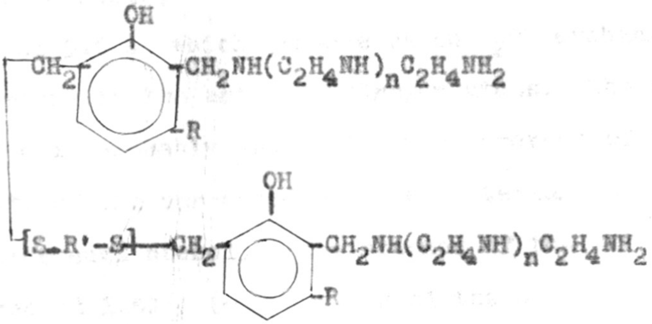
Phenol and substituted phenols (e.g. m-cresol) react with formaldehyde (or paraformaldehyde) to produce products having hydroxy benzylic or ring substituted hydroxy benzylic units respectively. Those condensates containing methylol groups, $-CH_2OH$, can react with active hydrogen compounds (with the elimination of water) to form products having wide commercial utility.

3-Pentadecenyl phenol, (m-HO $C_6H_4C_{15}H_{27}$), is a readily available indigenous raw material (obtained from cashewnut shell liquid). It reacts with formaldehyde similar to other meta-substituted phenols.

Bertozzi[59] reported the use of new aminofunctional compounds, synthesized from phenol, aliphatic polyamine, thiol-terminated polysulfide polymer (a class of active hydrogen compounds) and paraformaldehyde, in the curing of epoxy resin. The present study was intended to synthesize new amino functional compounds and study their curing with a liquid epoxy resin (Araldite of CIBA Ltd.). The aminofunctional compounds were prepared from phenol, 3-pentadecenyl phenol, diethylene triamine, tetraethylene pentamine, a thiol-terminated polysulfide liquid polymer and various glycol bis(thioglycolates). (The characteristics of the aminofunctional compounds so prepared are shown in Table-1). Since efforts to purify these products by known methods were unsuccessful, they were used as such. Also in the process described by Bertozzi, no purity criterion was mentioned.

Attempts to determine amine hydrogens by volumetric procedures were unsuccessful due to the difficulties encountered in end-point detection. Nitrogen contents (determined by microanalysis) were higher than the calculated values (Table-1). The cause for such an observation, however, could not be ascertained.

The probable structure of aminofunctional compounds (AFCs) from thiol terminated polysulfide polymer, aliphatic polyamine, phenol and paraformaldehyde, according to Bertozzi, may be written in general, as:

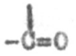


where: $R = H$, for phenol
$R = -C_{15}H_{27}$ for 3-pentadecenyl phenol (3-PDP)
$n = 1$, for diethylenetriamine (DETA)
$n = 3$, for tetraethylene pentamine (TEPA), and
$R' = -(C_2H_4OCH_2OC_2H_4SS)_5\ C_2H_4OCH_2OC_2H_4$ - for polysulfide polymer of mol.wt. 1000.

An attempt was made to get spectroscopic data in support of the above structure.

The infrared spectra of phenol-containing AFCs show strong absorption at 760 cm^{-1} characteristic of 1,2,3-trisubstituted benzene[127]. As can be expected this band is absent in the infrared spectra of AFCs based on 3-pentadecenyl phenol.

The NMR spectrum (Fig.2.3) of the LP-3PDP-TEPA product (see Table-1 for complete name) consists of a doublet centred at 0.95 δ (ascribable to ......CH_2-$C\underline{H}_3$ in the side chain of 3-PDP), a sharp singlet at 1.31 δ (long methylene chain); a triplet centered at 5.3 δ (olefinic protons present in the alkyl chain of 3-PDP); an ill-defined doublet centered at 6.9 δ (two aromatic protons in 1,2,3,4-tetrasubstituted benzene ring) and a signal at 5.0 δ, which disappears on D_2O exchange, may be ascribed to the active hydrogen atoms. The signal at 6.5 δ is probably due to the ring protons of the impurity of the unreacted starting material (namely, 3-pentadecenyl phenol). The absence of the multiplet centered at 1.51 δ (-S$\underline{H}$ protons of the polysulfide polymer, see Fig. 2.2) was also noted. The presence of signals in the range of 2.3 - 4.7 δ is reminiscent of the polysulfide polymer (Fig.2.2). In the case of AFCs prepared from glycol bis(thioglycolates [Glycol bis (thioglycolates) have the structure: $HSCH_2C(=O)O(CH_2CH_2O)_nC(=O)CH_2SH$], we noticed the cleavage of ester linkages from the infrared position of $-C=O$ group, viz.


$\overset{|}{-C}=O$ in the AFC 1650 cm^{-1}

$-C=O$ in parent ester 1735-1750 cm^{-1}


$-\overset{\overset{O}{\|}}{C}-NH-$ at 1250 cm^{-1}

It is likely that the amide formed is an S-substituted thioglycolamide (the infrared spectra of these compounds also contain the 765-770 cm^{-1} band characteristic of 1,2,3-trisubstituted benzene). Hafelle and Broge[128] using methylamine and Minagawa et al[129] using butylamine have found that amidation of thioglycolates (or S-substituted thioglycolates) readily occurs to yield the corresponding amide.

The mixing of Araldite with polysulfide polymer-based AFCs was exothermic, the magnitude of exotherm being dependent on the amount of curing agent in the system. Mixing of more viscous aminofunctional compounds is known to result in low exotherms. The low exotherm from LP-3PDP-DETA, despite its lower viscosity compared to its phenol analogue, may be due to the sterically bulky 3-pentadecenyl substituent in the ring. The somewhat more exotherm of the LP-3PDP-TEPA than LP-3PDP-DETA may be attributed to higher functionality of the former (viz. four more secondary aminogroups in the molecule).

The mixing of AFCs based on glycol bis(thioglycolates) was characterized by low exotherms [except for the AFC from ethyleneglycol-bis(thioglycolate)] which may be due to the presence of amide linkage in the AFC. Kamon et al[130] found that the crosslinking of epoxy resins was dependent on the basicity of the amine. Edwards[131] used the development of exotherm as a measure of the reactivity of the curing agent. Thus, the low exotherm and reactivity of these glycol bis(thioglycolates)-based AFCs can be related to the decreased basicity of the amide. This is in agreement with the observations of Peerman et al[132] and O'Neill et al[133] that polyamines react fully and faster at room temperature than polyamides.

The reactivity of an epoxy resin curing agent system (and hence the peak exotherm) can be related to the pot life and gel time therefrom. It may be reasoned that the magnitude of the exotherm is inversely proportional to the gel time. This is supported by the results recorded in Table-3.

Curing reaction with polysulfide polymer-based AFCs leads to more crosslinking in the earlier stages of curing because of higher functionality. In spite of this greater crosslinking, the long, flexible molecular structure may impart flexibility to the cured polymeric film which will be consequently soft in the earlier stages of curing.

The structure of the AFCs based on glycol bis(thioglycolates), however, remains uncertain. It is likely that the amidation process may result in the free polyol formation. It may, however, be possible to derive the effect of such polyols in epoxy curing. The effect of ether linkages in imparting flexibility to a molecule is well known. Thus the AFC from ethylene glycol bis (thioglycolate), with no ether linkages in the molecule may be expected to give hardest film while PEG-600 bis(thioglycolate) having as many as 13 ether linkages, should give the softest cured polymeric film with epoxy resin. The AFCs from other two glycol-(thioglycolates) may be expected to show intermediate curing properties. This phenomenon is evident from the results recorded in Tables-4 and 5.

EXPERIMENTAL

I. Materials

(1) 3-Pentadecenyl Phenol

Commercial cashewnut shell liquid was distilled under reduced pressure to give 3-pentadecenyl phenol, a pale yellow coloured, clear liquid. b.p. 195-200°C/2 torr. η_D^{27} 1.5080

Anal. $C_{21}H_{32}O$ requires: C, 83.94%, H, 10.76%

Found : C, 83.93%, H, 10.82%

(2) Thiol-terminated Polysulfide Liquid Polymer

Thiol-terminated polysulfide liquid polymer was prepared from sodium disulfide, bis(2-chloroethoxy)methane using 1,2,3-trichloropropane for the creation of crosslink centres. The polymer synthesis is described below:

(a) Preparation of Sodium Disulfide Solution ($Na_2S_{2.25}$)

To an aqueous solution of sodium hydroxide (68.0 g NaOH dissolved in 205 ml water) was added powdered sulfur (58.93 g) and heated to dissolve all the sulfur. Cooled, filtered and diluted with water (to a total volume of 285 ml) to give approximately 2 molar solution of $Na_2S_{2.25}$.

(b) Preparation of Alkyl Disulfide Polymer

Sodium disulfide solution (285 ml) was heated with stirring to 65°C, on a water bath, in a four necked flask equipped with a stirrer, thermowell, dropping funnel and a reflux condenser. The nucleating agent, magnesium hydroxide, was generated '*in situ*' by adding 24% (w/v) aqueous sodium hydroxide solution (4.5 ml) and 56% (w/v) aqueous magnesium chloride solution (6.25 ml) with stirring. The contents were further heated to 85°C and bis(2-chloro ethoxy) methane (100 g) containing 1,2,3-trichloro propane (0.45 g) was added during 60 minutes, keeping the temperature constant at 85°C throughout the addition. After the addition, the flask was heated at 92-93°C for further 60 minutes.

The contents of the flask were transferred to a beaker and washed repeatedly with water. The polymer was obtained as a viscous mass and the yield was 85-90 g.

(c) Reduction of the Polymer using Sodium Hydrosulfide and Sodium Sulfite

A mixture of the polymer (85 g), obtained above, and 20% aqueous sodium sulfite solution (306 ml) were heated in a four necked flask to 80°C. Sodium hydrosulfide solution 23% (42.5 ml) (which was obtained by saturating aqueous sodium hydroxide solution with hydrogen sulfide) was added with vigorous stirring during 30 minutes, keeping the temperature constant at 80°C throughout the addition. Heating was continued for further 90 minutes at the same temperature. The contents were then poured into water and repeatedly washed till the washings were neutral to litmus. The washed product was acidified with 15% HCl. After washing with water, extracted with benzene and the benzene extract was dried over anhydrous Na_2SO_4. The dried benzene extract was filtered and benzene was distilled off under reduced pressure to yield the polymer which was further dried under vacuum.

The characteristics of this polymer are shown on page . This polymer has the structure

$$\underset{d}{H}(S\ \underset{c}{CH_2}\underset{b}{CH_2}O\underset{a}{CH_2}O\underset{b}{CH_2}\underset{c}{CH_2}S)_6\ \underset{d}{H}$$

NMR data: OCH_2O (s , 4.7δ)

$-SCH_2C\underline{H_2}O-$ (m , 3.8δ)

$-S\ C\underline{H_2}CH_2O-$ (m , 2.8δ)

$\underline{H}(SCH_2CH_2OCH_2OCH_2CH_2S)\underline{H}$ (t, 1.51δ)

IR data: 2520 cm^{-1}(-SH).

Infrared and NMR spectra are shown in Figs. 1.1 and 1.2.

(3) Epoxy Resin

The liquid epoxy resin used was Araldite LY 553 (CIBA India). Araldite is a bisphenol-A epichlorohydrin epoxy resin having an epoxy equivalent of 243.4 - 243.6 corresponding to a molecular weight of 485-490.

(4) Diethylene triamine and phenol were purified by distillation.

(5) Tetraethylene pentamine used was of German make.

(6) Bis(thioglycolates). For preparation see Chapter I

(7) Paraformaldehyde used was of B.D.H. make.

II. Methods

Preparation of Aminofunctional Compounds

The method of Bertozzi[59] was followed to prepare the aminofunctional compounds based on:

(i) Polysulfide liquid polymer, and

(ii) Glycol bis(thioglycolates)

A. Based on the Polysulfide Liquid Polymer

Phenol or 3-pentadecenyl phenol (0.0213 mole), polysulfide liquid polymer (0.012 mole, 12 g), paraformaldehyde (0.0465 mole, 1.4 g) and the aliphatic polyamine (0.0204 mole) were stirred together for 2 hours at 100±2°C in a three necked flask equipped with a stirrer, a thermowell and a distillation condenser. After the heating was stopped, the flask was maintained at ambient temperature for 72 hours. Then it was heated on a water bath under reduced pressure to remove water. Yields of the products were all quantitative.

B. Based on Glycol bis(thioglycolates)

The above procedure was slightly modified for the preparation of aminofunctional compounds based on glycol bis(thioglycolates). Phenol (0.0213 mole), glycol bis (thioglycolates) (0.012 mole) and paraformaldehyde (0.0465 mole) were stirred together at 100±2°C and diethylentriamine (0.024 mole) was added carefully to prevent frothing. After the addition, the reaction mixture was heated for 2 hours at 100±2 °C. Rest of the procedure was same as above.

Determination of Viscosity

Viscosity of each of the amino functional compounds was determined as the rate of vertical flow on a flow-jig between two points five centimeters apart.

Properties of all the above aminofunctional compounds are recorded in Table-1.

III. Mixing of Araldite and Aminofunctional Compounds

In each case, weighed amounts of the epoxy resin, and aminofunctional compound were mixed with stirring in the proportion of 1:1 and 2:1 respectively at ambient temperature.

(a) Measurement of Exotherm

As the mixing of liquid epoxy resin and amino functional compounds was exothermic, a thermometer with its bulb dipping well inside the mixture was employed to record the exotherm.

(b) Pot Life and Gel Time

Pot life was taken as the time elapsed from the instant of mixing to the instant when the system became highly viscous.

Gel time was taken as the time elapsed from the instant of mixing to that instant when the surface of the system was tack-free and when the resin surface did not move in 5 minutes with the container tilted to 90° [134].

(c) Curing

After recording the maximum exotherm, the mixture was poured into a silicone grease pre-treated metallic mold and cured by keeping the mold at room temperature or at 50°C.

(d) Hardness

Hardness of the cured samples was determined by a Shore D durometer according to the ASTM designation D 2240-68.

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CHAPTER-III

POLYTHIOURETHANE POLYMERS

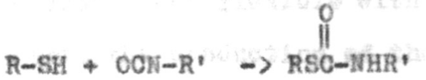
INTRODUCTION

It is not often in high polymer chemistry that one type of material, by virtue of its ability to react with other materials, can give rise to varied types of products adorned with a felicitous versatility, par excellence. And isocyanates present an outstanding example possessing such a remarkable ability[1-6]. Isocyanates by reaction with a variety of compounds, yield products finding extensive uses as fibres, plastics, foams, rubbers, leather substitutes, coating compositions, adhesive formulations etc. - a feature that seldom finds a parallel. The research and development activities in isocyanates are heralding new and glamorous applications for isocyanate products. For example, studies on blood compatible biomedical polymers have indicated a large number of uses for polyurethanes as synthetic blood vessels, intraortic balloons, artificial heart devices, vascular grafts, artificial kidney membranes etc.[7] Polyurethane foams, because of their light weight, coupled with their ability to be sprayed into desired shape, are becoming highly versatile in the world of movie-making[8]. National Chemical Laboratory had been actively engaged in the study of polyurethane coatings, polyurethane rigid foams etc. which are expected to have high industrial utility.

Amongst a variety of isocyanate reactions, reactions with active hydrogen-containing compounds, particularly polyols and polyamines- have been extensively studied. Isocyanate reactions with polyols and polyamines, which provide a versatile approach to a variety of end products, have formed the backbone for major polyurethane industries the world over.

Appreciating these developments and keeping in view the ever-widening commercial importance of thiol compounds, another important class of active hydrogen compounds, it is surprising that no serious efforts seem to have been directed towards the synthesis and study of polythiourethane polymers, which are the thiol-isocyanate addition products.

Thiols react with isocyanates to form thiourethanes[9-12]



$$\text{R-SH} + \text{OCN-R'} \rightarrow \text{RS}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-NHR'}$$

Early kinetic studies of thiol-isocyanate reactions indicate low-reactive nature of the thiol group towards isocyanate function[13]. For the reaction of isocyanates with active hydrogen compounds, which involves the attack on the electrophilic carbonyl carbon of isocyanate group by the nucleophilic centre of the attacking molecule, the following order of reactivity of active hydrogen compounds has been theoretically predicted and experimentally confirmed[14].

$$RNH_2 > ArNH_2 > ROH > ArOH > RSH$$

Thus thiols, compared to hydroxy and amino compounds, are less reactive towards isocyanates. The formation of polythiourethane polymers from polythiols and polyisocyanates may be visualised as:

$$HS{-}R{-}SH + OCN{-}R'{-}NCO \rightarrow \left[SRS\overset{O}{\overset{\|}{C}}NHR'NH\overset{O}{\overset{\|}{C}} \right]$$

Although thiol-isocyanate reactions are well known, the early notable attempt towards the synthesis and use of polythiourethanes was that of Mitchell[15]. Mitchell in 1957, patented a process for the production of polythiourethane cellular foams by the reaction of polyisocyanates with thiol-terminated polysulfide liquid polymers. These products were resilient and flexible with good cellular structure. However, the production of these products was rendered difficult due to the less-reactive nature of the thiol group necessitating the use of extremely reactive catalysts, high reaction temperatures or prolonged reaction period. Isocyanate-blocked, i.e. thiourethane-terminated, polysulfide polymers were described in a process patented by Bertozzi[16], almost a decade later. These polymers were prepared by adducting the thiol-terminated polysulfide polymers with monoisocyanates. These isocyanate-capped polymers, in contrast to the virgin thiol-terminated polysulfide polymers, showed long term ambient-storage stability in admixture with active curing agents but cured to fully vulcanized rubbers at elevated temperatures.

However, a positive and recent approach to the synthesis and study of polythiourethane polymers has been that of Zochniak et al[17], who synthesized polythiourethane polymers from 1,5-pentanediol bis (thioglycolate) with toluene-2,4-diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI). These polymers, which were high melting solids, showed good strength, water resistance, dielectric properties as well as fair thermal resistance.

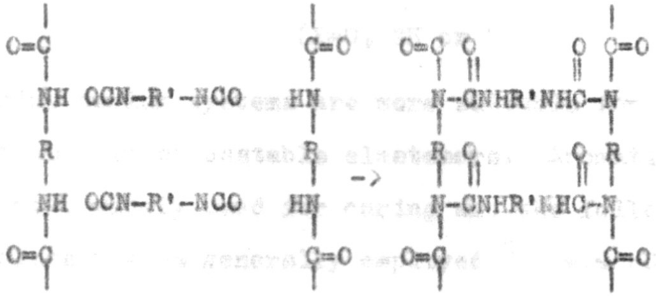
Thus, it is unambiguous that research activities on polythiourethane polymers are still in infant stage and further research is necessary not only to understand their chemistry but also to bring out their advantageous traits and other important innovations to judge their suitability for important applications.

Curing of Polymers from the Reaction of Polyisocyanates and Active Hydrogen Compounds

Polyurethanes and polyureas can be cured by polyisocyanates, polyamines, peroxides, sulfur and formaldehyde. Because of the structural similarities of polythiourethanes to polyurethanes, polythiourethanes may also be cured with the above-mentioned curing agents. The curing process of these polymers is essential since useful properties appear generally after the curing stage. A brief account of the curing action of these curing agents, viz. polyisocyanates, polyamines, peroxides, sulfur and formaldehyde, is given below.

i) <u>Polyisocyanate Curing</u>[4-6,18]

Amide groups, $-NH-\overset{O}{\overset{\|}{C}}-$, which form the backbone of polyurethane (PU), polyurea (PA) and polythiourethanes(PTU) are the active hydrogen centres serving as the potential sites for crosslinking reactions with isocyanates. This reaction which results in the formation of acylurea crosslinks can be shown as:



Crosslinked structure

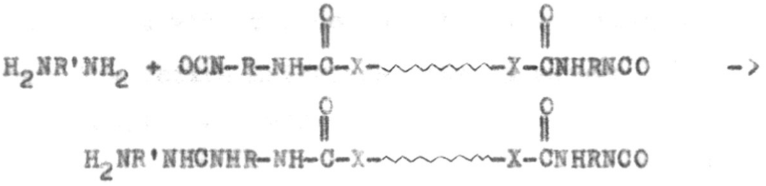
If active hydrogen groups are present at the end of the macromolecular chain, curing by polyisocyanate will proceed by chain extension.

Polyisocyanates generally used for curing are TDI, MDI and dimerized TDI (known as 'Desmodur TT' mp.130°C). For adequate cure, usually excess isocyanate is employed. Diisocyanate-cured vulcanizates are relatively tough.

Generally good physical properties of vulcanizates are obtained for a minimum shore A hardness of 75.

ii) Polyamine-Curing[19-21]

Isocyanate-terminated polyurethanes, polyureas and polythiourethanes are readily crosslinked by polyamines and polyols, although polyamines are most important. These compounds function by a chain-extension curing process, i.e.



$$H_2NR'NH_2 + OCN\text{-}R\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}X\text{-}\sim\sim\sim\sim\text{-}X\text{-}\overset{\overset{O}{\|}}{C}NHRNCO \rightarrow$$

$$H_2NR'NHCONHR\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}X\text{-}\sim\sim\sim\sim\text{-}X\text{-}\overset{\overset{O}{\|}}{C}NHRNCO$$

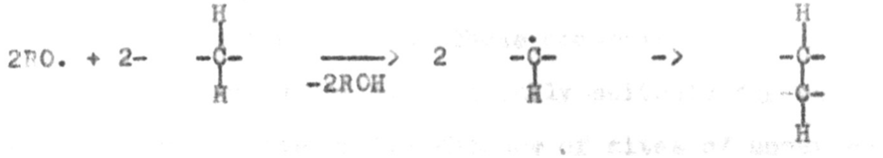
(X=O, NH or S)

Diamine curing systems are more suitable for the production particularly of castable elastomers. Aromatic diamines are most widely used for curing and the following diamines may be generally employed[20]. 4,4'-Diamino diphenylmethane, 4,4'-methylenebis(2-chloroaniline)(MOCA), Benzidine, 3,3'-dichlorobenzidine (DCB), dianisidine, p-phenylene diamine and polymethylene polyaniline. Of these, MOCA is perhaps the best known. DCB has also been found to be suitable for commercial use as it combines workable set time with relative insensitivity to the variations in the cure time or temperature and amount of the curing agent used. Hirosawa and Lee[22] have found (alkylene dithio) dianilines to be effective urethane-crosslinking agents giving highly elastic cellular polyurethanes.

iii) Peroxide-Curing[4-6]

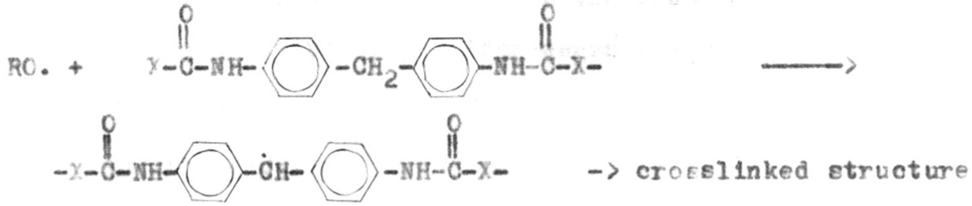
The chemistry of peroxide curing of polyurethane polymers has been studied in much detail. Among the organic peroxides, dicumyl peroxide and benzoyl peroxide are generally used. As can be expected, these curing agents cure by a radical mechanism. The free radicals from the peroxides react with the polymer by abstracting a hydrogen atom from the active methylene site as shown:

$$RO\text{-}OR \rightarrow 2RO\cdot$$



$$2RO\cdot + 2\text{-}\overset{H}{\underset{H}{C}}\text{-} \xrightarrow[-2ROH]{} 2\ \text{-}\overset{\cdot}{\underset{H}{C}}\text{-} \rightarrow \begin{array}{c} H \\ \text{-}C\text{-} \\ \text{-}C\text{-} \\ H \end{array}$$

When peroxides are employed for MDI-based polyurethanes, polyureas and polythiourethanes, the crosslinking reaction occurs primarily within the hard segment, i.e.



It may be expected that crosslinking by peroxides involving hard segments and rubbery segments will show different effects. Cooper and Tobolsky[23] studying benzoyl-peroxide curing of a polyester urethane opined that crosslinking by peroxides within the hard segments of linear elastomers affects the plateau modulus, primarily decreasing it, while crosslinking in the rubbery segments shows itself above the T_g of the hard segments.

Peroxide and diisocyanate cures are compatible and can be used together for specific end properties. The desired final properties of vulcanizates can be achieved by a proper manipulation of peroxide to isocyanate ratio in the curing composition.

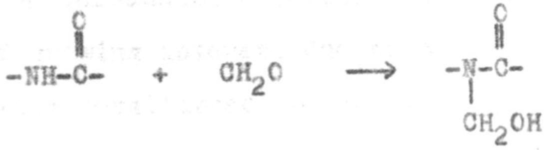
iv) Sulfur-Curing[24-26]

Conventional polyurethane compositions from saturated monomers are not generally suitable for curing with sulfur because of the absence of sites of unsaturation. Sulfur curing may be made effective by synthesizing polymers from unsaturated monomers, for example castor oil based polyurethanes or polythiourethane polymers. Sulfur cures of such polymers is best achieved by using only sulfur or sulfur in combination with the usual sulfur-cure accelerator and activator. Sulfur-cures generally give hard vulcanizates.

v) Formaldehyde-Curing[27]

Saturated or unsaturated elastomers may also be cured by using formaldehyde-releasing substances and a small amount of acid or acid-forming compound. The source of formaldehyde may be paraformaldehyde or amine-formaldehyde condensates.

Formaldehyde first adds to urethane hydrogen to form N-methylol group:



$$-NH-\overset{\overset{O}{\|}}{C}- \quad + \quad CH_2O \longrightarrow -\underset{\underset{CH_2OH}{|}}{N}-\overset{\overset{O}{\|}}{C}-$$

This methylol group further reacts with a $-NH-\overset{\overset{O}{\|}}{C}-$ of another chain resulting in crosslinking of the chains by methylene bridge.

$$-\underset{\underset{CH_2OH}{|}}{N}-\overset{\overset{O}{\|}}{C}- \quad + \quad -\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}- \longrightarrow \begin{array}{c}-N-CO-\\ |\\ CH_2\\ |\\ -N-CO-\end{array} \quad + \quad H_2O$$

Khakimullin[28], studying the vulcanisation of urethane rubbers with paraformaldehyde in presence of alkaline and alkaline earth metal perchlorates, found the resulting rubbers to be best suited for products which are subjected to thermal and dynamic stress. However, in the formaldehyde vulcanization process, water is an undesirable by-product.

The present investigation is an attempt to gain further insight into the synthesis and study of new polythiourethane polymers. In the course of this study, new polythiourethane polymers were synthesized and their tensile properties were determined.

PRESENT INVESTIGATION AND RESULTS

Polyaddition products of isocyanates with active hydrogen compounds, especially polyols and polyamines, are of growing interest due to their many splendoured varieties embellished, often, with unexcelled brilliance of vivid and glamorous applications. The ever-mounting interest that centres around such products originates mainly from the more latitude possible in their synthesis and, more interestingly, due to some of the inherently advantageous and important properties, e.g. good strength, high abrasion resistance, good oil and chemical resistance etc.

Polyols and polyamine-addition products with polyisocyanates (known as 'polyurethanes' and 'polyureas' respectively) are highly versatile and find glamorous applications in various fields. Next to polyols and polyamines, the other important active-hydrogen compounds are thiols. Thiols react with isocyanates similar to their oxygen analogues. Except for the recent work of Zochniak et al[17] the literature reveals scanty work regarding the synthesis and study of polythiourethane polymers. Zochinak et al[17] have reported the synthesis and properties of only two polythiourethane polymers prepared from 1,5-pentanediol bis(thioglycolate) with toluene-2,4-diisocyanate and 4,4'-diphenyl methane diisocyanate.

The present investigation was therefore undertaken to gain further knowledge regarding the synthesis and a few properties of new polythiourethane polymers. These polythiourethane polymers were prepared using the bis(thioglycolates) of polyethylene glycols-200,400 and 600 and castor oil tris(thioglycolate) with toluene-2,4-diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI).

General Synthesis of Polythiourethane Polymers

(1) From TDI and a Glycol bis(thioglycolate) (in 1:1 molar Proportions)

TDI and a glycol bis(thioglycolate) in equimolar proportions were heated under vacuum at 92-93° for 6-7 hours. The characteristics of all these products are recorded in Table-1.

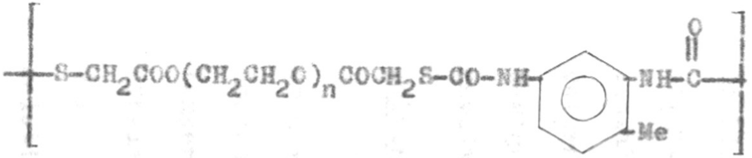
Product from castor oil tris(thioglycolate) (1 mole) and TDI (1.5 mole) was prepared similarly. It was a brittle material. m.p. > 290°C.

(2) From the Mixture of a Glycol bis(thioglycolate) (1 mole) and Castor oil tris(thioglycolate)(1 mole) with TDI or MDI (2.5 mole)

A mixture of a glycol bis(thioglycolate) (1.0 mole) and castor oil tris(thioglycolate) (1.0 mole) and TDI or MDI (2.5 mole) was heated under vacuum for 7-8 hours at

Table-1: Characteristics of Thiourethanes from TDI and Glycol bis(thioglycolates)

General structure of Products :



No.	Bis(thioglycolate) of	n=	Physical state		Analysis	
					C,%	H,%
1.	Ethylene Glycol	1	Clear solid (m.p. 174°C)	Calcd:	46.87	4.16
				Found	46.6	4.58
2.	PEG** - 200	4	Solid (m.p. 92°C)	Calcd:	48.84	5.42
				Found:	49.96	6.47
3.	PEG-400	9	Viscous liquid	Calcd:	49.86	6.43
				Found:	50.02	7.2
4.	PEG-600	13	Viscous liquid	Calcd:	51.31	7.01
				Found:	51.53	7.65

** Polyethylene Glycol

92-93°C till a solid product was obtained. The product after its preparation was kept overnight before testing for physical properties.

Testing

Each rubbery product was mixed with MDI (the cross-linking agent) on a laboratory two-roll mill and the milled material was pressed out at 145°C for 30 minutes. Tensile strength and elongation, and hardness were determined according to the methods described in ASTM designation D 412-68 and D 2240-68 respectively. These results are recorded in Table-2.

Solvent Resistance of Vulcanizates

Solvent resistance of the vulcanizates was determined as percent weight increase, as described in the ASTM designation D 471-64, after 15 days of immersion at room temperature. The liquids used were toluene, acetone, ethylacetate, carbontetrachloride, 20% aqueous sulfuric acid (v/v) and 10% aqueous sodium hydroxide (2.5 N) solution. The results are presented in Table-3.

Table-2: Properties of Polythiourethane Polymers

Polymer	From castor oil tris (thioglycolate) and bis(thioglycolate) of	Diisocyanate	Shore A hardness	Relative extension %	Tensile strength MPa
I	PEG-200	TDI	80	50	10.39
II	PEG-200	MDI	85	55-60	10.93
III	PEG-400	TDI	78	55	9.7
IV	PEG-400	MDI	80	70	9.38
V	PEG-600	TDI	70	60	8.07
VI	PEG-600	MDI	75	75	8.57

Table-3: Solvent Resistance of Polythiourethane Polymers
(Weight Percent Increase)

Solvent	Polymer **					
	I	II	III	IV	V	VI
Acetone	22.0	42.9	25.8	51.0	30.2	59.5
CCl_4	78.3	55.0	64.37	40.5	43.23	27.35
Ethyl Acetate	35.8	25.6	36.1	26.2	36.7	28.2
Toluene	48.2	37.0	44.4	32.1	37.4	25.0
20% Aq.H_2SO_4	5.2	10.3	3.81	8.5	2.2	6.4
10% Aq.NaOH	D	D	D	D	D	D
Water	6.3	3.8	6.8	4.1	7.0	4.5

D = Complete Degradation
** = See Table-2

DISCUSSION

Ever since their brilliant discovery by Prof.Bayer in 1937, the growth of polyurethane polymers has been relentless and splendid. These polymers have been the focus of universal attraction bedecked with a host of important properties which can be engineered to a variety of diversified applications. It is not outside the realm of possibility to envision these isocyanate-based polymers becoming, with the advent of new techniques of preparation and processing, the most sought-after materials in not too distant future.

The important properties of polymers based on the reaction of isocyanates with active hydrogen compounds, viz. hydroxy, amino or thiol compounds, have been attributed to the presence of $-NH-\overset{O}{\overset{\|}{C}}-X$ linkage (X=O, NH or S). When X is different in $-NH-\overset{O}{\overset{\|}{C}}-X$, the linkage $-NH\overset{O}{\overset{\|}{C}}-X$ and the corresponding product are known by different names as shown below:

X =	Name of the $-NH-\overset{O}{\overset{\|}{C}}-X$ linkage	Name of the corresponding polymer
O	Urethane	Polyurethane
-NH-	Urea	Polyurea
S	Thiourethane	Polythiourethane

Among the uses of polyurethanes, it is especially to their use as elastomers that much of the literature has been devoted[29]. Their use as elastomers arises mainly due to the good strength, abrasion resistance, oil and chemical resistance. The urethane groups contribute polarity and hydrogen bonding necessary for improved strength, elasticity and abrasion resistance, and also for providing good chemical resistance.

Apart from polyurethanes and polyureas, the synthesis and study of the properties of polythiourethanes have not been looked into extensively. The work of Zochniak et al[17] happens to be the only published report dealing in some detail with the synthesis and a few properties of two polythiourethane polymers from 1,5-pentanediol bis (thioglycolate) with TDI and MDI.

The present work was undertaken to synthesize and study the tensile properties of a few new polythiourethane polymers. The following materials were employed for their synthesis.

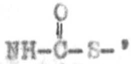
(a) Toluene-2,4-diisocyanate (TDI)
(b) 4,4'-Diphenyl methane diisocyanate (MDI)
(c) Bis(thioglycolates) of polyethylene glycols-200, 400 and 600 respectively, and
(d) Castor oil tris(thioglycolate) (COTT).

The polythiourethane polymers, which were tested for their tensile strength, elongation at break and hardness, were synthesized from the mixture of a glycol bis(thioglycolate) (1.0 mole), castor oil tris (thioglycolate) (1.0 mole) and the aromatic diisocyanate (2.5 moles).

The synthesis was accomplished without the use of any solvent. Some of the conclusions that seem to be immediately evident from this synthesis regarding the characteristics of the resulting polythiourethane polymers may be summarized as follows:

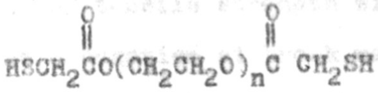
(1) The molar quantities of the diisocyanate, glycol bis (thioglycolate) and COTT being constant, the number of thiourethane linkages (N_t) can be assumed to be the same for all elastomers. Although N_t is same, the concentration of thiourethane linkages (W_t), expressed as weight percent content, will be different for each product.

(2) COTT, which may be considered as a trifunctional crosslinking agent, was used in a fixed molar quantity in the preparation of all polythiourethane polymers. Hence, the number of crosslinks imparted by COTT may be assumed to be same while the crosslink density, obviously will be different for each polymer.

(3) Urethane groups contribute polarity, hydrogen bonding and rigidity etc. into a polyurethane polymer molecule[29]. Since oxygen and sulfur occur in the same group (Group VI) in the periodic table, a similar effect of the thiourethane linkage,  $NH-\overset{\overset{O}{\|}}{C}-S-$, on the polythiourethane molecule may be expected. The effects, evidently of -NHC(O)O- and -NH-C(O)S- may not be identical because of the inherent differences in the properties of oxygen

and sulfur, and -C-O and C-S bonds. It is also known that the ultimate properties of elastomers like tensile strength and elongation at break, depend on the degree of crosslinking, extent of hydrogen bonding etc.

(4) It is known that for a given series of polyurethane polymers synthesized from one isocyanate and a particular series of difunctional aliphatic active-hydrogen compounds, in fixed molar quantities, properties such as tensile strength, glass transition temperature (T_g) of the resulting polymers, will be guided primarily by the structure of the aliphatic difunctional compound[18,30]. The above three properties decrease with an increase in the aliphatic chain length while elongation at break increases. In the present case, the only variable factor in the synthesis of polythiourethane polymers is the structure of the glycol bis(thioglycolate), the general structure of which may be represented as:



$$HSCH_2\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_n\overset{O}{\overset{\|}{C}}\,CH_2SH$$

where n = 4, for PEG-200
n = 9, for PEG-400, and
n =13, for PEG-600

Thus it may be considered that the ultimate properties of the elastomers using these glycol bis(thioglycolates) will depend primarily on the value of 'n'.

From the above generalizations, it is clear that although N_t is same for all polythiourethane elastomers based on these glycol bis(thioglycolates), W_t decreases with a corresponding increase in the molecular weight of the glycol bis(thioglycolate), i.e. in the order:
PEG-200 bis(thioglycolate) > PEG-400 bis(thioglycolate) > PEG-600 bis(thioglycolate).

Edgar[31] and Chichagova et al[32] consider that high content of urethane linkage in the polymer backbone increases stiffness, rigidity and, thus, strength in a polyurethane polymer. Smith and Magnusson[18], while studying the properties of a given series of polyalkylene glycol-polyurethanes, found the T_g to be linearly dependent on the content of urethane linkage in the polyurethane. They also found a linear relationship of tensile strength with T_g. The results of Chen et al[30] indicate for a series of polyether glycol-based polyurethanes a reciprocal relationship of tensile strength with the polyether chain length. The elongation at break was found to increase with increasing polyether chain length. Thus, all these above suggest high tensile strength, hardness (which is a measure of degree of crosslinking) to the polythiourethane elastomer from COTT-PEG-200 bis(thioglycolate) which decrease with an increase in the molecular weight of the glycol. But elongation at break may be expected to show an increasing trend. The results recorded in Table-2 are in complete agreement with these views.

The aromatic unit, -- , in the polymer backbone chain is especially effective in inducing stiffness in a molecule. This effect arises due to the resonance and planarity of the aromatic ring. This produces a rigid structure which raises the T_g of the polymer[33-35]. If more aromatic units are present in the chain, the effect on strength and rigidity would be more pronounced. Thus, we can expect an increase in strength and hardness for the MDI-based polythiourethane elastomers compared to those based on TDI. This is supported by the results recorded in Table-2.

The complete degradation of the vulcanizates in 10% aqueous sodium hydroxide (2.5 N) solution may be due to the complete hydrolysis of the ester linkages present in the elastomer. It was also observed that all glycol thioglycolates, in pure state, show a high degree of susceptibility for hydrolysis even in mildly basic environment.

EXPERIMENTAL

General Remarks

Tensile strength and elongation tests of vulcanisates were performed dumbbell specimen at room temperature using a Scott tensile testing machine. Hardness was determined at room temperature using a Shore-A Durometer.

Tensile strength of vulcanisates is expressed in 'Mega Pascal' (MPa), the recommended SI unit for tensile strength[36]. The conversion factor is:

$$\begin{aligned} 1000 \text{ psi.} &= 70 \text{ kg. cm}^{-2} \\ &= 6.9 \times 10^{6} \text{ Pa(or Newton/meter}^{2} = \text{N/m}^{2}) \\ &= 6.9 \text{ MPa} \end{aligned}$$

Melting points are uncorrected.

Materials

1. Castor oil tris(thioglycolate) and bis(thioglycolates) of polyethylene glycols-200, 400 and 600 (see Ch. I).
2. Toluene-2,4-diisocyanate (TDI) was used without further purification. 4,4'-diphenylmethane diisocyanate (MDI) was distilled under reduced pressure prior to use (m.p. 37°C).
3. All solvents used for solvent-resistance studies of vulcanizates were purified by known methods.

Methods

Synthesis of Polythiourethane Polymers from TDI and a Glycolbis(thioglycolate)

Ethylene glycol bis(thioglycolate) (2.1 g, 0.01 mole) and TDI (1.74 g, 0.01 mole) were heated under vacuum (1-0.5 torr) at 92-93°C for 6-7 hours to give the polymer.

Polythiourethane polymers from TDI and bis(thioglycolates) of polyethylene glycols (PEG)-200, 400 and 600 were prepared similarly.

The characteristics of all these polymers are recorded in Table-1.

Polythiourethane Polymers from glycol bis(thioglycolate)-Castor oil tris(thioglycolate) mixture and TDI

PEG-200 bis(thioglycolate) (0.01 mole, 3.52 g) and castor oil tris(thioglycolate) (0.01 mole, 11.54 g) were dried under vacuum at 92-93°C. TDI (0.025 mole, 4.35 g) was added and the contents were heated under vacuum for a period of 7-8 hours until a solid, rubbery product resulted. The product, which was pale yellow in colour, was removed and kept overnight before testing for its physical properties.

Polymers from the mixtures of castor oil tris (thioglycolate) (0.01 mole with PEG-400 bis(thioglycolate) or PEG-600 bis(thioglycolate) (0.01 mole) and TDI (0.025 mole) were prepared similarly.

Polymers from the mixture of glycol bis(thioglycolate), castor oil tris(thioglycolate) and MDI were also synthesized similarly.

Testing

The rubbery product was passed through a two-roll laboratory mill to get a sheet. It was mixed with MDI (10 parts per 100 parts of rubber by weight) and again given several passes to get a sheet. This was pressed out in a metal mold in a hydraulic press at 145°C for 30 minutes. Dumbbell specimen were cut from the vulcanizates using a standard dumbbell punch of width 0.125". Tensile strength and elongation were determined at room temperature according to ASTM designation D 412-68. Shore-A hardness was found out according to ASTM designation D 2240-68.

Solvent resistance of the vulcanizates was determined in acetone, carbon tetrachloride, ethylacetate, toluene, 20% aqueous sulfuric acid, 10% aqueous sodium hydroxide and water as percent weight increase after 15 days of immersion according to ASTM designation D 471-64.

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CHAPTER-IV

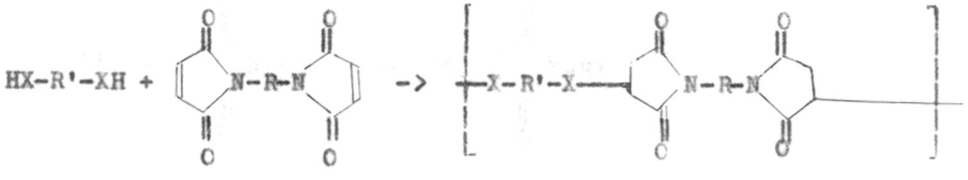
POLYIMIDOTHIOETHER POLYMERS

INTRODUCTION

The search for new polymeric materials - both thermoplastic and thermoset - is being pursued with new enthusiasm and increasing interest in recent years. This activity has been very well aided by ingeneous technical and technological developments for their processing, and the changes possible in the polymerization systems which allow much more latitude in the control of microstructure and physical properties of these polymers. Furthermore, modification of many of these polymers can be achieved to better their range of utility without sacrificing some of the other key properties. In some cases, the exceptional clarity and/or improved physico-chemical properties of these new plastics make them desirable replacement for the conventional polymers in many applications[1].

New interest has been shown in the synthesis and study of some new thermoplastic polymers which have, as an integral part of the polymer backbone, alternating 'hard' and 'soft' domains. The 'hard' units arise from high melting monomers while the 'soft' units are from low melting or liquid monomers. Since such polymers are generally not crosslinked, they display typical thermoplastic behaviour. The solution-polymerization techniques make it possible to synthesize these addition polymers having a wide variation in their physical properties by a proper manipulation of the molar ratios of monomers. Typical of this class are the polyimidothioether polymers, a recent class of polymers reported by Crivello and Juliano[2] in 1975. These polymers are made by the addition polymerization of bismaleimides with polythiols. Bismaleimides have the structure:

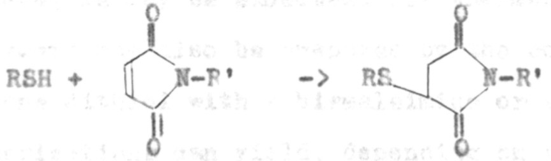
Because of the flanking carbonyl groups on either side of the double bonds, maleimide double bonds are highly reactive and susceptible to facile reduction, Diels-Alder reactions, 1,3-dipolar addition reactions as well as an attack by a large number of nucleophiles. Maleimides are also capable of radical or photoinitiated homopolymerization[3-5]. Maleimides readily react with active hydrogen compounds, to yield polymers having succimimide rings in the backbone.



($X=S,O,NH,SO_2-$)

The polyamino bismaleimide (also called polyaspartimides) formation is very general. The reaction takes place readily, usually in presence of an organic acid, with any maleimide or amine. These polyaspartimides possess high thermal stability[6,7] and mechanical strength, and also exhibit interesting properties useful in electrical, friction and ablative applications etc.[8,9]. Maleimide-aryl sulfonic acid polymers have also been reported to have better heat resistance. Apart from these, maleimides and their derivatives find use as rubber vulcanizing agents[10-12], polyester-crosslinking agents[13,14], epoxy curing agents[15-17] and many other applications.

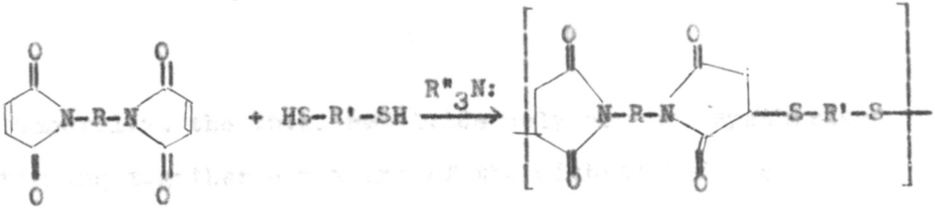
Significant progress in the synthesis and characterization of polyimidothioethers comes from the work of Crivello and Juniano[2] and Crivello[18]. Thiol-maleimide addition reactions are facile. Thiols and thiolate anion are among the most powerful nucleophiles known and the literature contains ample examples of their addition to maleimide compounds[19-23]. Thiol addition to maleimide can be shown, in general, as:



Succinimidothioether

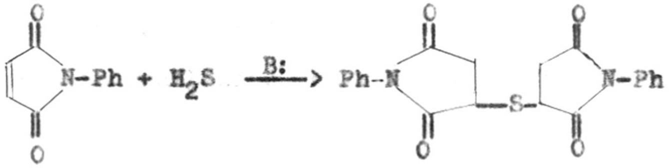
e.g. mercapto acids, alkyl and aryl thiols have been shown to add to N-substituted maleimides in presence of a basic catalyst, usually a tertiary amine, to give good yields of addition products.

Tertiary amine catalyzed addition reactions of bismaleimide and bisthiols have been shown to yield polymers, known as 'polyimidothioethers'[2,18]. These reactions which may be shown as



are highly general and facile, and both the bismaleimide and bisthiol of widely differing structures react to give polyimidothioether polymers. Crivello and Juliano[2] reported the synthesis of a series of bismaleimide-polysulfide polymers which showed good mechanical and solvent resistant properties. Recently, Crivello[18] has described the synthesis of polyimidothioether polymers from bismaleimides and various low-molecular weight dithiols. These and the above polymers, as may be expected, are thermoplastic in nature. Copolymers may also be prepared by the combinations of more than one dithiol with a bismaleimide or vice-versa. Such polymerizations can yield, depending on the method of synthesis, random copolymers or block copolymers[2,18].

Still more interesting are the reactions of maleimides with hydrogen sulfide. These reactions occur readily to yield the imidothioether in which hydrogen sulfide behaves like a typical dithiol, e.g. reaction of hydrogen sulfide with N-phenylmaleimide proceeds as shown:



Generally, the thiol-maleimide polymers are synthesized by stirring together a mixture of the dithiol and the bismaleimide in m-cresol (using a tertiary amine catalyst) or in dimethyl formamide (using acetic acid as the catalyst).

The present work was undertaken to synthesize the polyimidothioether polymers from bismaleimides and bis (thioglycolates) of ethylene glycol and various polyethylene glycols and to characterize the resulting polymers.

PRESENT INVESTIGATION AND RESULTS

It has been emphasized earlier that our aim has been to synthesize monomeric dithiol compounds and using some of them to synthesize polymers or derivatives, e.g. amino-functional curing agents for epoxy resins, polythiourethanes polymers and polyimidothioether polymers.

The study of polyimidothioether polymers is interesting because of the high generality of reactions, the ease of synthesis, the variations possible in the synthesis of these polymers and copolymers and most important of all, their thermoplastic nature. Although these polymerization reactions were applicable to almost all the bismaleimides, the present study has been limited to the utilization of only two bismaleimides in the synthesis of title polymers.

Following compounds were used in the synthesis of polyimidothioether polymers.

(i) 1,1'-(methylene di-4,1-phenylene) bis[1H-Pyrrole-2,5-dione]; commonly known as N,N'-bismaleimido-4,4'-diphenyl methane (henceforth abbreviated as DMB)

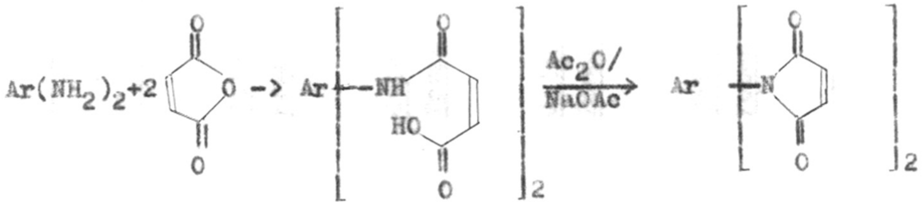
(ii) 1,1'-(1,2-phenylene)bis[1H-Pyrrole-2,5-dione]; commonly known as o-phenylene-N,N'-bismaleimide (henceforth referred to as OPBM)

(iii) Bis(thioglycolates) of ethylene glycol, polyethylene glycol-200 (PEG-200), polyethylene glycol-400 (PEG-400) and polyethylene glycol-600 (PEG-600).

General synthetic methods for various materials are briefly described below:

Bismaleimides

These were prepared by slightly modifying the method of Searle[24]. The aromatic diamine and maleic anhydride, in required molar quantities, were mixed at room temperature in a neutral aromatic hydrocarbon solvent. The reaction product after filtration, was cyclodehydrated using acetic anhydride and fused sodium acetate. The resultant bismaleimide was recrystallized from benzene-ethanol mixture.



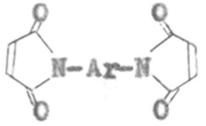
Melting point and elemental analysis data of the synthesized bismaleimides are presented in Table-1. Infrared and NMR spectra of DMB are shown in Figs.4.1 and 4.2 respectively.

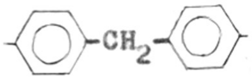
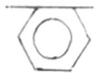
N-phenyl Maleimide

This was synthesized from equimolar quantities of aniline and maleic anhydride by the method described for the bismaleimides and recrystalized from water. m.p. 88°C.

Glycol bis(thioglycolates) : For synthesis, see Chapter I.

Table-1: Characteristics of Aromatic Bismaleimides Prepared



No.	Ar	Melting point		Analysis		
				C,%	H,%	N %
1.		158°C	Calcd	70.39	3.91	7.82
			Found	69.25	4.47	7.95
2.		241°C	Calcd	62.68	2.95	10.44
			Found	62.90	3.16	10.58
3.		198°C	Calcd	62.68	2.95	10.44
			Found	62.75	3.28	10.60
4.		> 345°C	Calcd	62.68	2.95	10.44
			Found	62.83	3.21	10.57

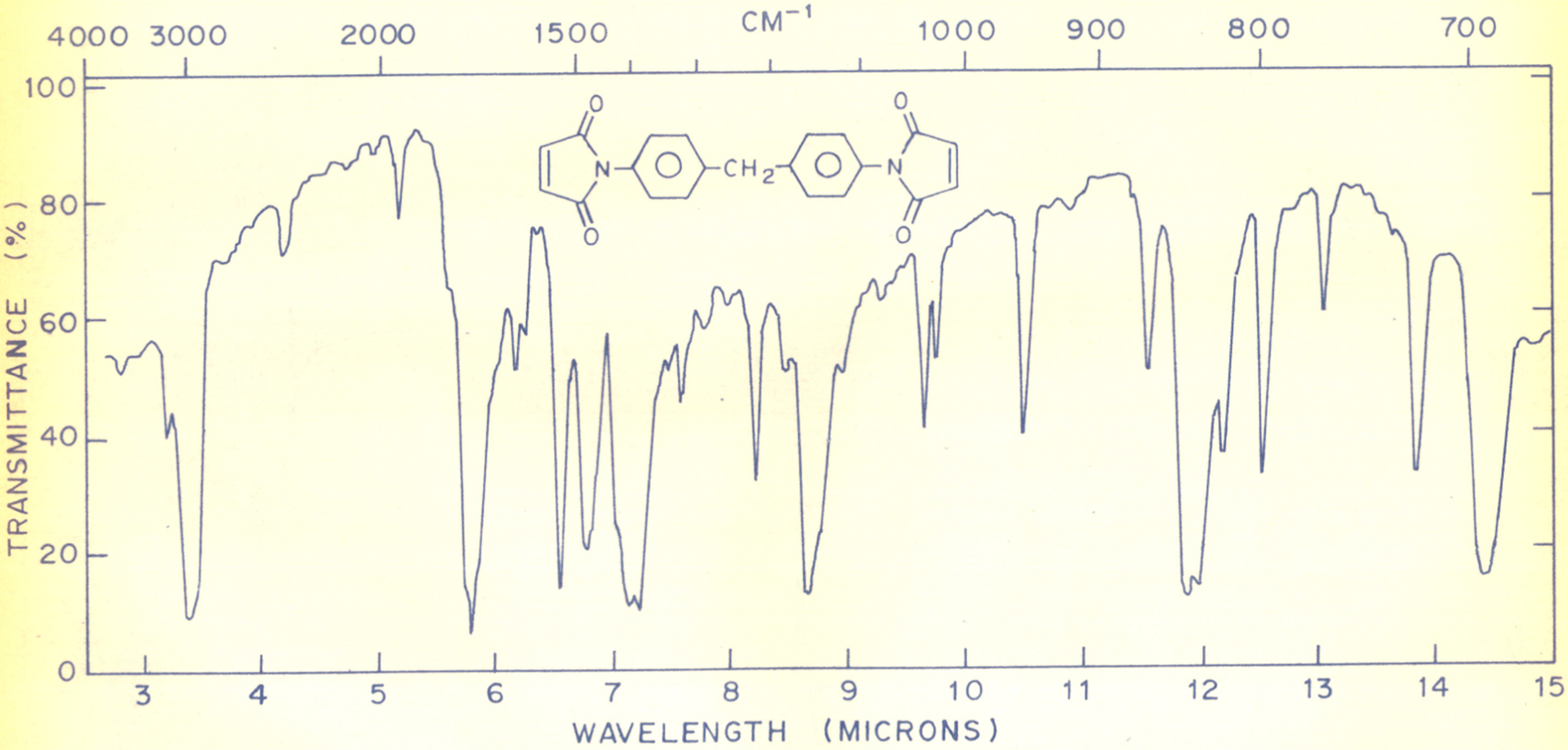


FIG. 4·1 IR SPECTRUM OF N, N'-BISMALEIMIDO-4,4'-DIPHENYLMETHANE (DMB)

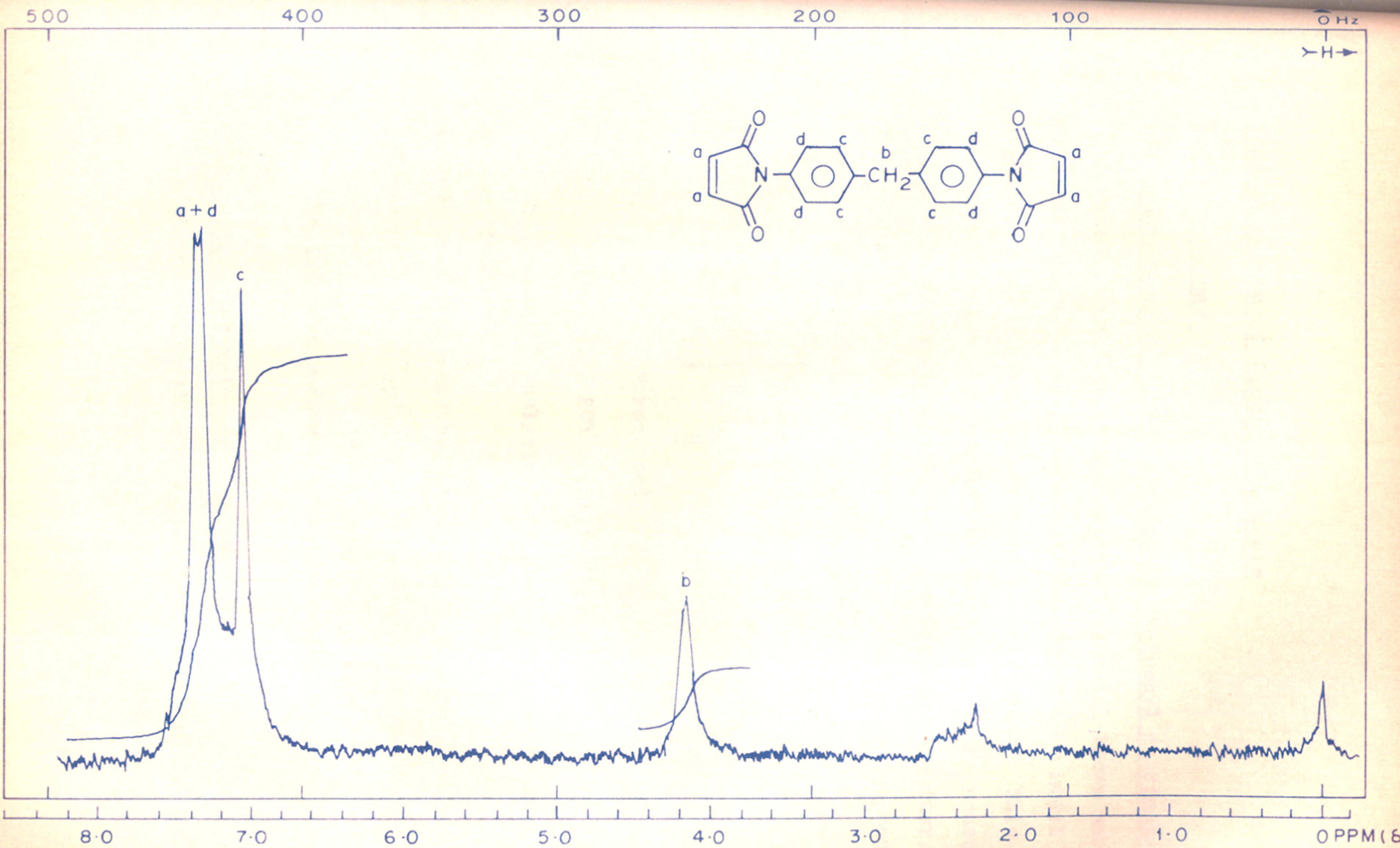


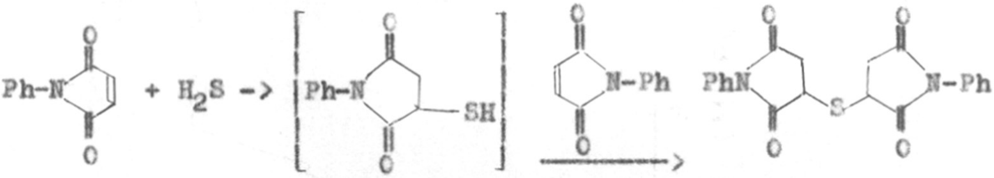
FIG. 4·2 NMR SPECTRUM OF N, N'– BISMALEIMIDO – 4,4' – DIPHENYLMETHANE

General Method of Polymer Synthesis

Model Reactions

(i) Reaction of Hydrogen Sulfide with N-Phenyl maleimide

Hydrogen sulfide is the simplest bisthiol known and its addition to N-phenyl maleimide was tried as a model reaction, viz., the thiol addition to maleimides. This reaction has also been studied by Crivello[18]. The reaction of H_2S with N-phenyl maleimide in m-cresol is very fast. The addition does not stop at the monoaddition stage and compound I is the final product obtained.



Monoadduct

I

M.p. of I 201°C (Lit. 202-204°C)[18]

The elemental analysis data shown below also corresponds to the diadduct I.

Anal: Calcd. for monoadduct ($C_{10}H_9O_2NS$): C, 57.97%, H, 4.34%

for diadduct (I) ($C_{20}H_{16}O_4N_2S$): C, 63.15%, H, 4.24%

Found : C, 63.42%, H, 4.43%

The infrared spectrum of this compound is shown in Fig. 4.3.

(ii) Addition of Thiophenol to DMB

Thiophenol readily adds to DMB in m-cresol in presence

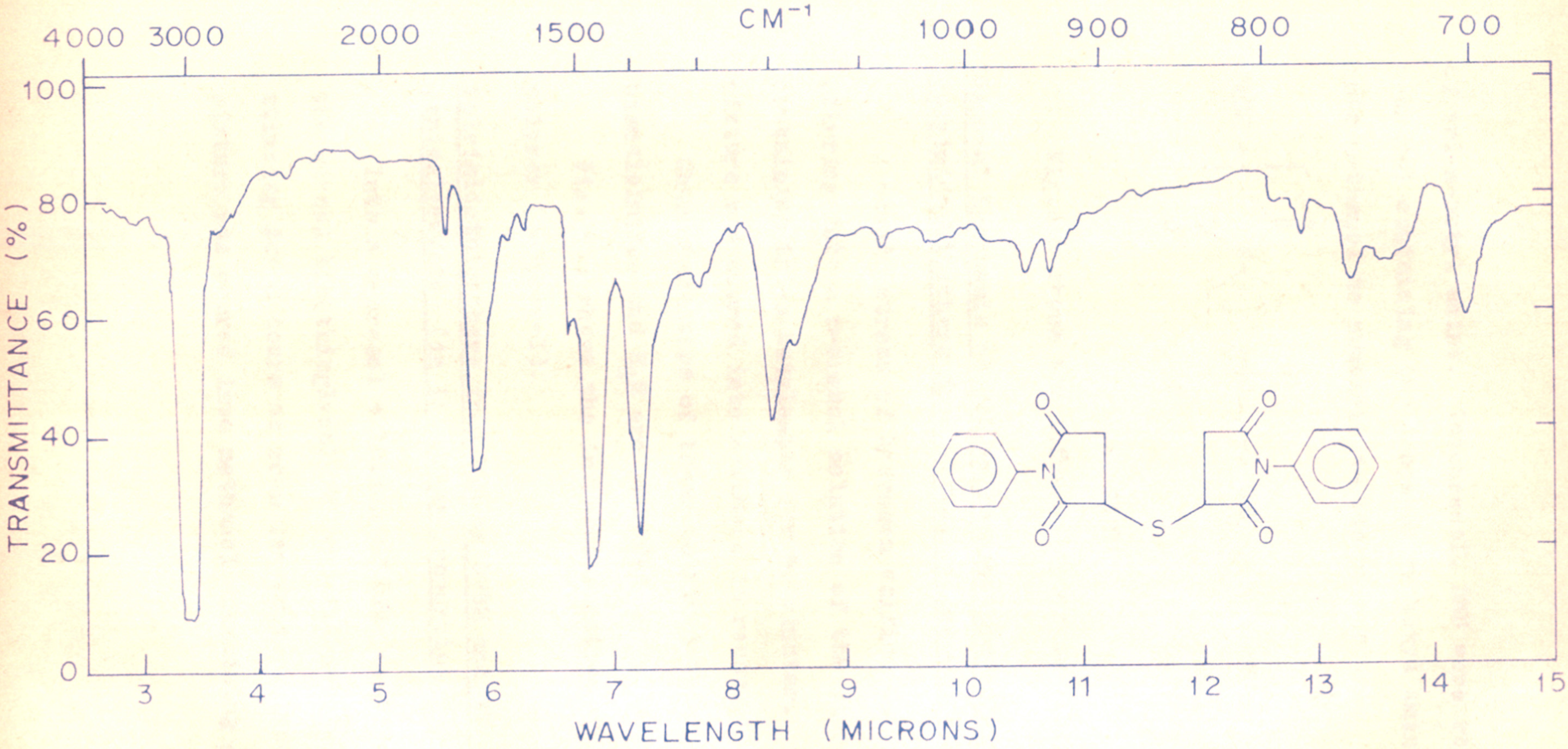
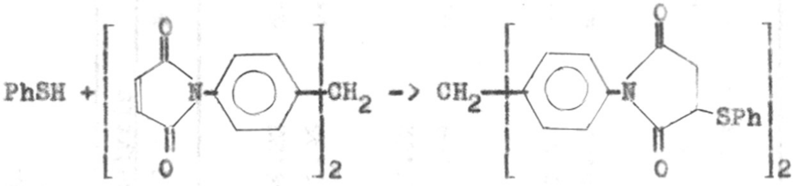


FIG. 4·3 IR SPECTRUM OF N-PHENYLMALEIMIDE–H_2S ADDUCT of tri-n-butyl amine. Thiophenol, DMB were stirred in m-cresol containing two drops of tributyl amine and poured into methanol to precipitate the product.



M.p. 142°C

Fig.4.4 shows the infrared spectrum of this new compound.

General Synthesis of Polyimidothioether Polymers

Polyimidothioethers from Bismaleimides and H_2S

A steady stream of hydrogen sulfide was passed with stirring into a m-cresol solution of the bismaleimide containing tri-n-butylamine for 60 minutes. The reaction mixture was poured into methanol to recover the product.

Characteristics of these polyimidothioethers from bismaleimides and H_2S are recorded in Table-2.

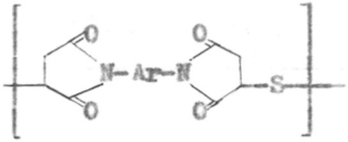
Fig. 4.5 shows the infrared spectrum of the DMB-H_2S polymer (Polymer-I).

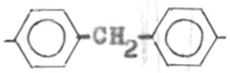
Polyimidothioethers from DMB or OPBM and Glycol bis (thioglycolate) (in 1:1 molar Proportion)

Into a m-cresol solution of DMB (or OPBM) was added the glycol bis(thioglycolate) and tri-n-butylamine. After stirring for 3 hours at room temperature, the reaction mixture was poured into methanol containing glacial acetic

Table-2: Properties and Elemental Analysis Data of Polyimidothioethers from Bismaleimides and Hydrogen Sulfide

General Structure of these Polymers:



Polymer	Ar	Yield %	Melting point °C*	Inherent viscosity dl/g **	Analysis		
						C %	H %
I		95	272	0.493	Calcd	64.23	4.02
					Found	63.96	5.29
II		97	307	0.047	Calcd	55.62	3.31
					Found	55.04	4.38
III		96	260	0.097	Calcd	55.62	3.31
					Found	56.37	4.15
IV		95	272	0.297	Calcd	55.62	3.31
					Found	55.39	4.08

* For literature values see Ref.(16)

** 1% solution in DMF at 30°C

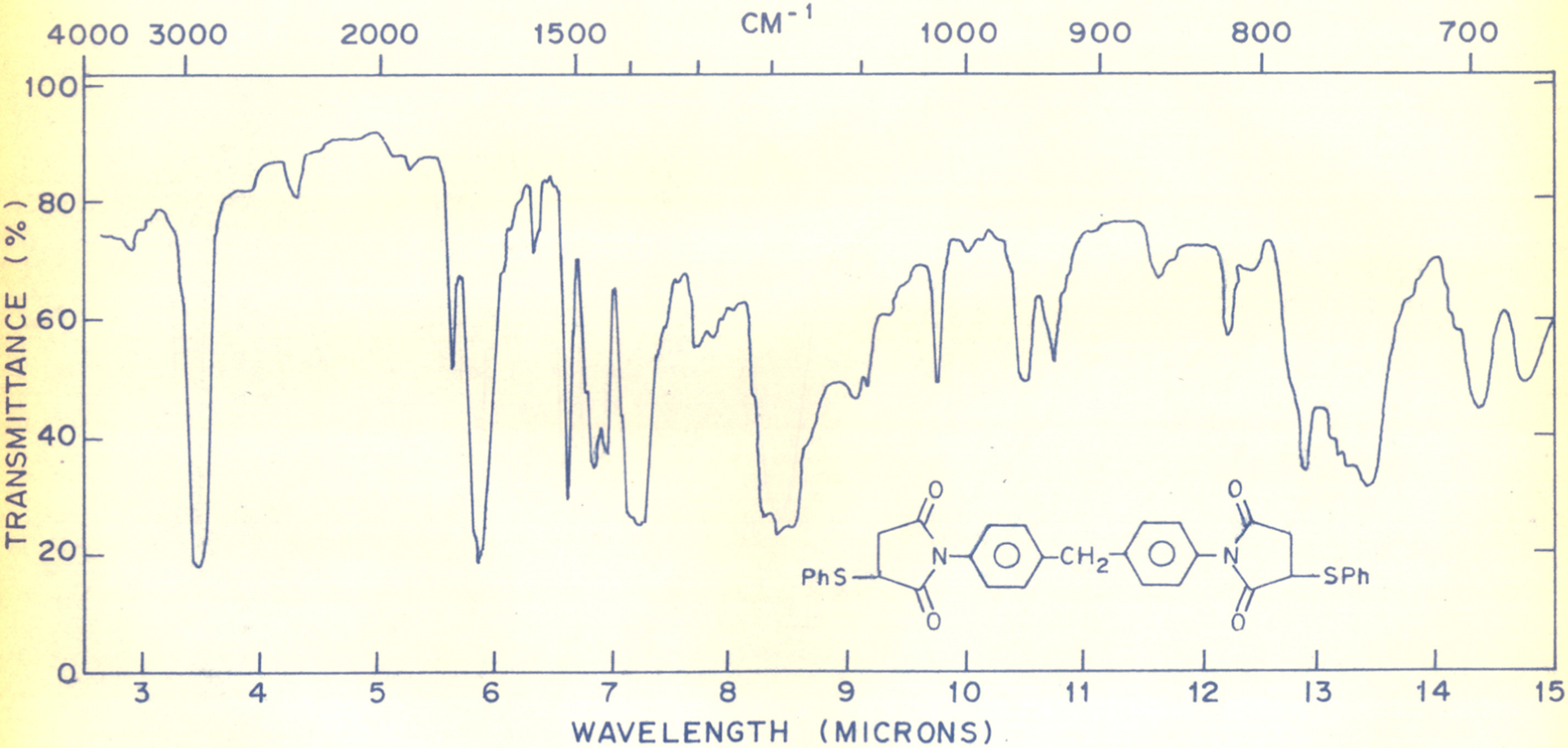


FIG. 4·4 IR SPECTRUM OF DMB–THIOPHENOL ADDUCT

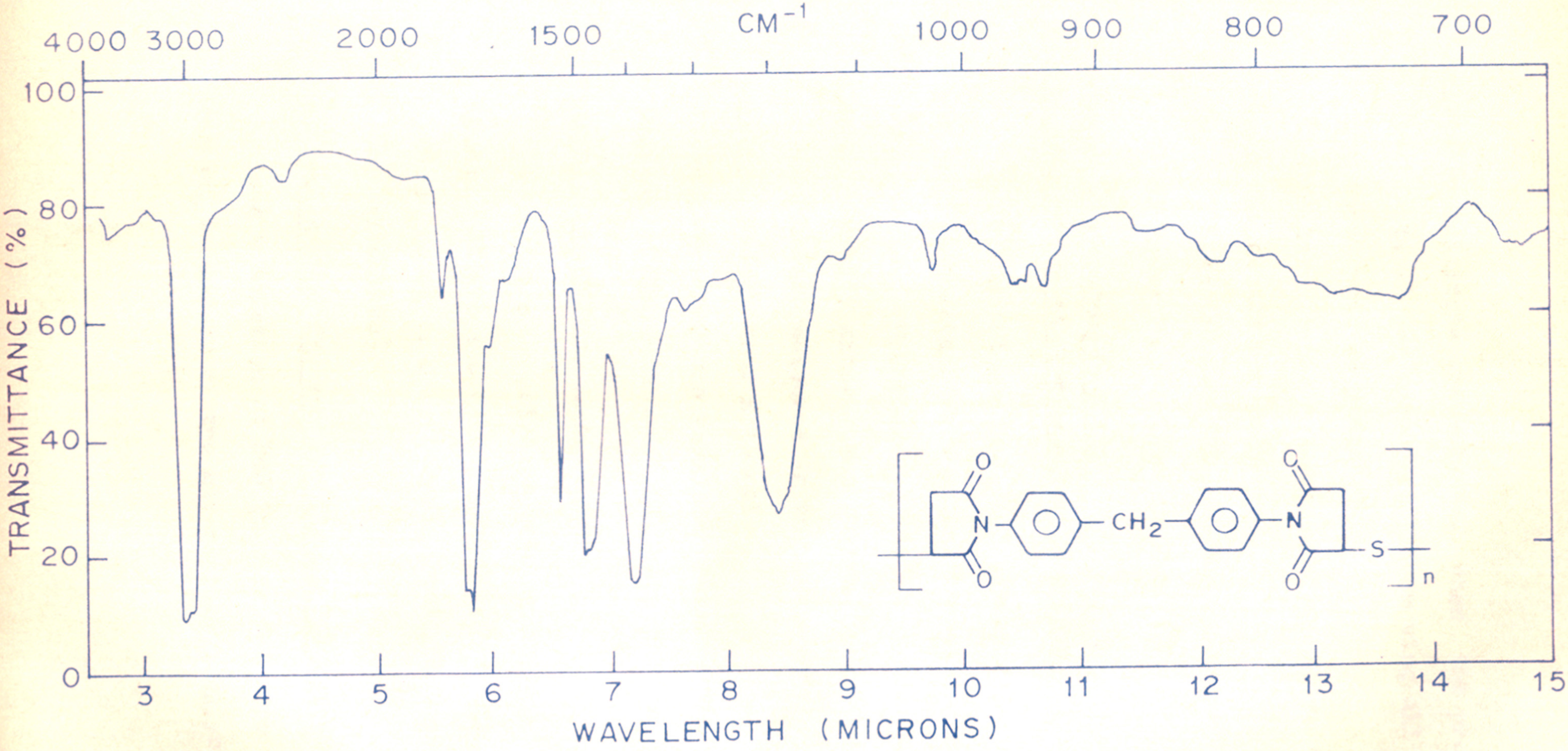


FIG. 4·5 IR SPECTRUM OF DMB–H_2S POLYMER (POLYMER I) acid to precipitate the polymer. When the product did not separate out, it was recovered by removing all organic liquids under reduced pressure.

In Tables-3 and 4 are recorded the characteristics of the polyimidothioether polymers from DMB and OPBM respectively.

The IR spectrum of DMB-PEG-400 bis(thioglycolate) polymer (Polymer V) is shown in Fig. 4.6.

Polyimidothioethers from DMB and Glycol bis(thioglycolate) (in 10:1 molar Proportions) and Hydrogen Sulfide

DMB (0.1 mole) and a glycol bis(thioglycolate) (0.01 mole) were stirred together in m-cresol containing tri-n-butyl amine for 30 minutes. Hydrogen sulfide was bubbled in for 60 minutes and the reaction mixture was stirred for further 60 minutes. The product was recovered in the usual way by pouring the reaction mixture into methanol.

Table-5 gives the physical characteristics and elemental analysis data of all these polymers.

General Synthesis of Copolymers

Two types of copolymers were synthesized.

(a) From DMB and two glycol bis(thioglycolates)

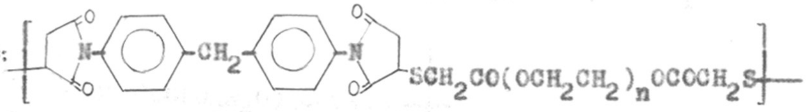
(b) From the mixture of DMB and OPBM and a glycol bis (thioglycolate)

Copolymers from DMB and two Glycol bis(thioglycolates)

Into a solution of DMB in m-cresol were added with stirring a mixture of two glycol bis(thioglycolates)

Table-3: Characteristics of Polyimidothioethers from DMB and Various Glycol bis(thioglycolates)

General Structure of the Polymers:

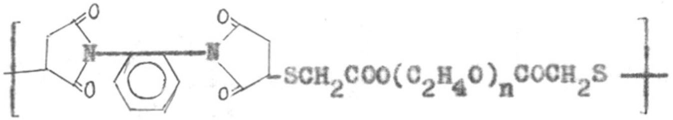


Polymer	Bis(thioglycolate)	n= (in the structure)	Melting point °C	η_{inh} dl/g*	Analysis		
						C,%	H,%
V	EG[a]	1	73	0.155	<u>Calcd</u>	57.04	3.87
					<u>Found</u>	57.69	4.20
VI	PEG-200	4	VL[c]	0.234	<u>Calcd</u>	56.55	5.15
					<u>Found</u>	55.84	6.16
VII	PEG-400	9	VL	0.093	<u>Calcd</u>	56.10	6.08
					<u>Found</u>	56.00	6.11
VIII	PEG-600	13	VL	0.050	<u>Calcd</u>	55.83	6.56
					<u>Found</u>	54.58	6.83

a = Ethylene Glycol
b = Polyethylene Glycol
c = Viscous brown liquid
* = 1% solution in DMF at 30°C

Table-4: Characteristics of Polyimidothioethers from OPBM and Glycol bis(thioglycolates)

General structure of Polymers



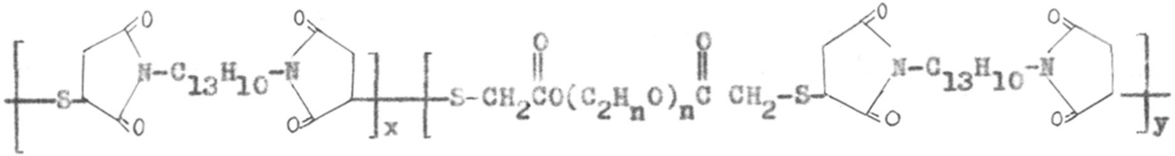
Polymer	Bis(thioglycolate) of	n= (in the structure)	Melting point °C	η_{inh}, dl/g **		Analysis	
						C,%	H,%
IX	EG*	1	55-58	0.123	**Calcd**	50.2	3.76
					Found	49.9	4.43
X	PEG-200	4	VL*	0.156	**Calcd**	51.14	4.91
					Found	50.96	5.23
XI	PEG-400	9	VL	0.080	**Calcd**	52.04	6.02
					Found	51.13	6.29
XII	PEG-600	13	VL	0.038	**Calcd**	52.48	6.56
					Found	51.98	6.97

* See Table-3

** 1% solution in DMF at 30°C

Table-5: Characteristics of Polyimidothioethers from DMB, Glycol bis(thioglycolates) and H_2S

General structure of these Polymers:



Polymer	Bis(thioglycolate) of	n= (in the above structure)	Melting point ^{o}C	η_{inh}, dl/g **	Analysis		
						C,%	H,%
XIII	EG*	1	65–70	0.181	Calcd	63.39	4.19
					Found	62.48	4.6
XIV	PEG-200	4	57–61	0.222	Calcd	63.08	4.24
					Found	63.73	4.8
XV	PEG-400	9	50–54	0.110	Calcd	63.74	4.46
					Found	64.59	5.36
XVI	PEG-600	13	45–48	0.103	Calcd	64.83	4.6
					Found	65.79	5.57

* See Table-3

** 1% solution in DMF at 30°C

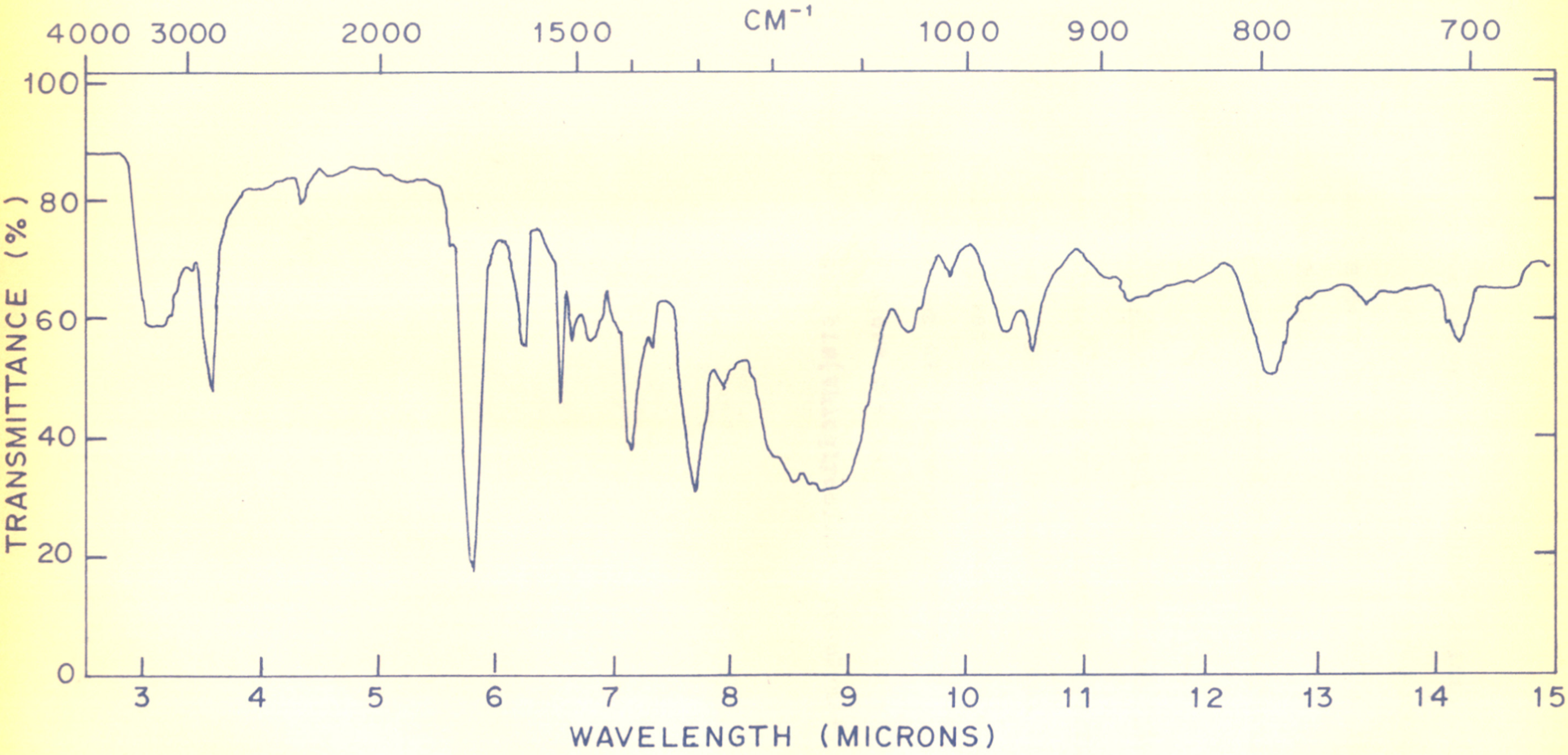


FIG. 4·6 IR SPECTRUM OF DMB – PEG400 BIS (THIOGLYCOLATE) POLYMER (POLYMER VII) followed by two drops of tri-n-butyl amine. After stirring for 3 hours at room temperature, the product was isolated in the usual manner by pouring the reaction mixture into acidified methanol.

In Table-6 are recorded the characteristics of these copolymers.

Copolymers from DMB-OPBM and a Glycol bis(thioglycolate)

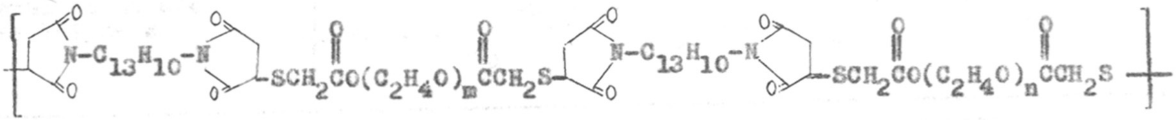
These polymers were synthesized as described above from a mixture of DMB and OPBM and a glycol bis(thioglycolate).

Table-7 gives the characteristics and elemental analysis data for all these copolymers.

Fig. 4.7 shows the infrared spectrum of DMB-OPBM ethylene glycol bis(thioglycolate) copolymer.

Table-6: Characteristics of Copolymers from DMB and two Glycol bis(thioglycolates)

General structure of these copolymers:

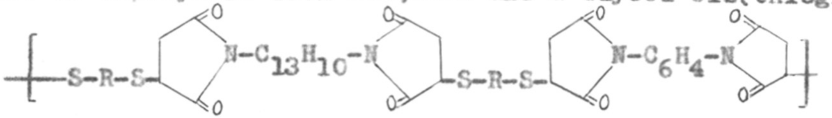


Polymer	Bis(thioglycolate) of 1	Bis(thioglycolate) of 2	Melting point, °C	η_{inh},*** dl/g		Analysis Calcd.	Analysis Found
XVII	EG(m=1)	PEG-200(n=4)	60-65	0.058	C+ H	56.76 4.7	61.53 5.14
XVIII	EG	PEG-400(n=9)	NVL*	0.107	C H	56.44 5.37	56.32 5.78
XIX	EG	PEG-600(n=13)	NVL	0.081	C H	56.24 5.71	55.25 5.58
XX	PEG-200(m=4)	PEG-400(n=9)	NVL	0.183	C H	56.3 5.67	55.81 6.00
XXI	PEG-200	PEG-600(n=13)	VL**	0.255	C H	56.1 6.01	56.34 6.32
XXII	PEG-400(m=9)	PEG-600(n=13)	VL	0.211	C H	55.95 6.32	54.72 6.48

* Non-tacky viscous liquid
** Viscous liquid
\+ Analysis in duplicate of two samples gave the same value
*** 1% solution in DMF at 30°C.

Table-7: Characteristics of Copolymers from DMB,OPBM and a Glycol bis(thioglycolate)

General structure of these Polymers:



Polymer	Bis(thioglycolate) of, (R)	Physical state	η_{inh}^{**} dl/g		Analysis	
					Calcd.	Found
XXIII	EG	Solid(mp.78°C)	0.179	C	52.97	52.62
				H	4.01	4.32
XXIV	PEG-200	VL*	0.250	C	54.04	53.92
				H	5.03	5.97
XXV	PEG-400	VL	0.106	C	54.18	53.45
				H	6.05	5.96
XXVI	PEG-600	VL	0.053	C	54.24	53.72
				H	6.56	6.93

* Viscous liquid

** 1% solution in DMF at 30°C

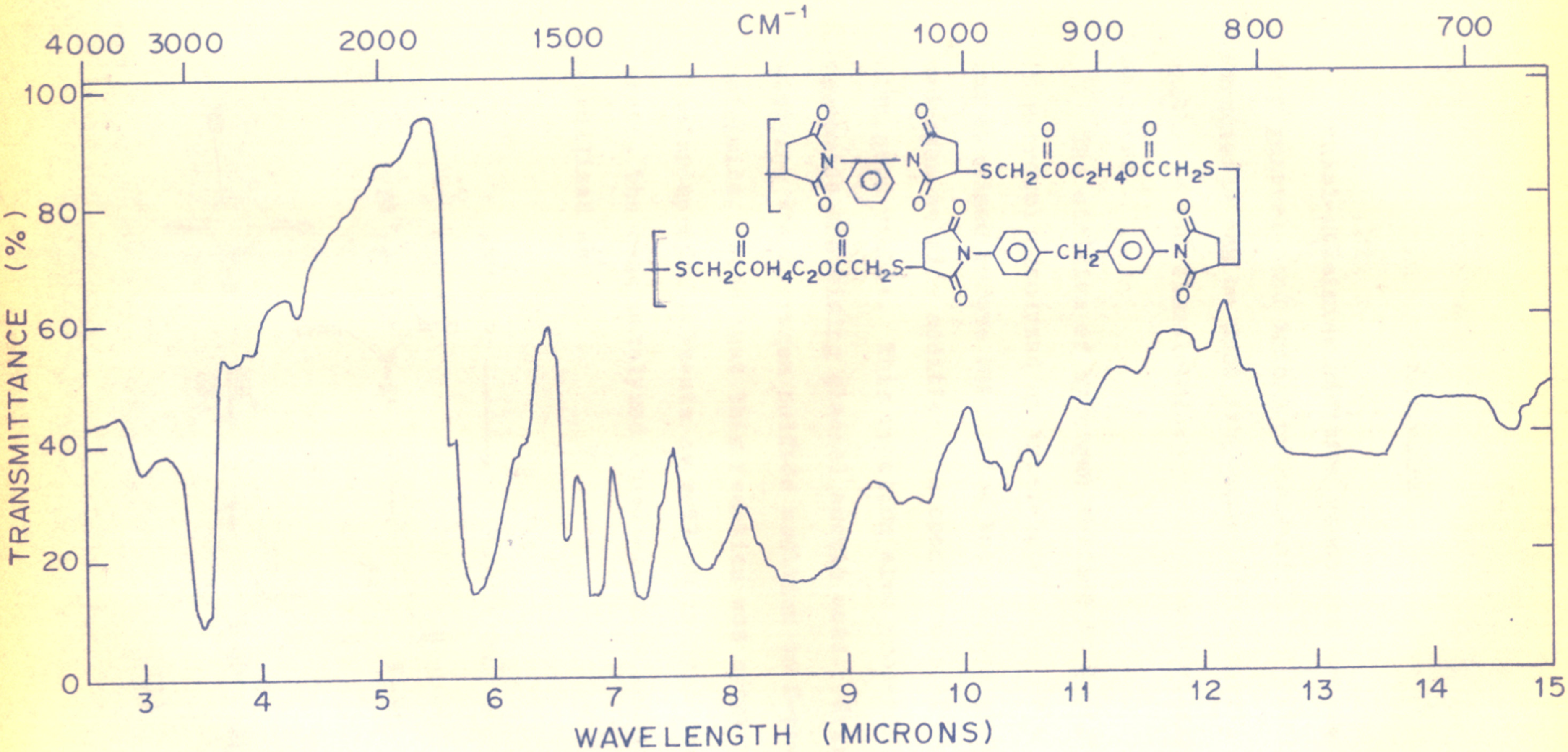


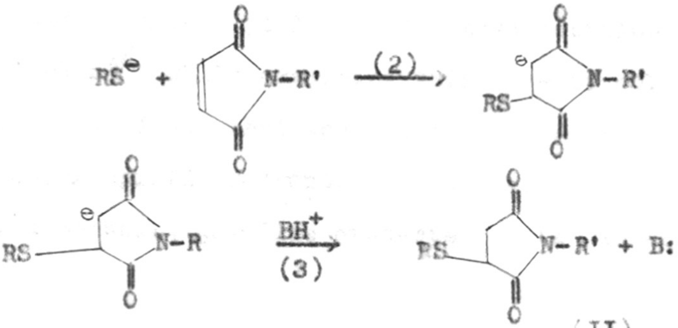
FIG. 4·7 IR SPECTRUM OF DMB-OPBM-ETHYLENEGLYCOL BIS(THIOGLYCOLATE) COPOLYMER

DISCUSSION

Thiol-maleimide addition reactions are facile and very general, and thiols or maleimides of widely differing structures can be used like other difunctional monomers, bisthiols and bismaleimides yield linear polyimidothioether polymers.

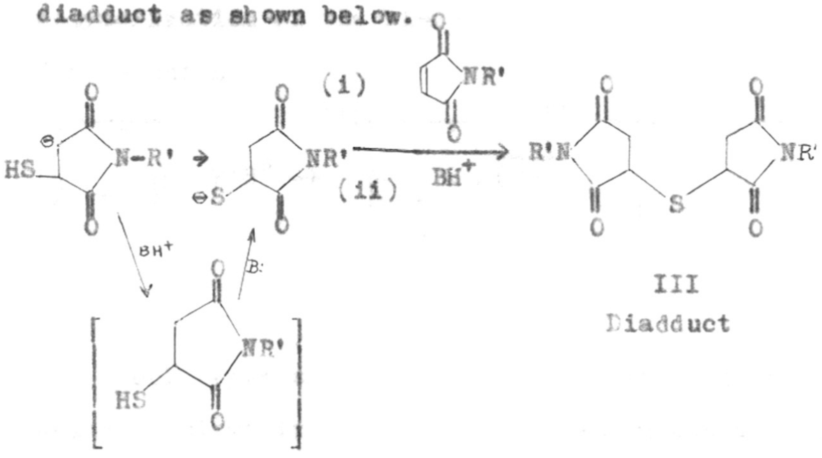
The addition of hydrogen sulfide to N-phenyl maleimide in m-cresol catalyzed by tri-n-butylamine as a model reaction was examined before attempting the polymer synthesis. The hydrogen sulfide addition was spontaneous at room temperature with good yields. This reaction also proceeds in dimethyl formamide containing glacial acetic acid. Crivello[18], while studying the hydrogen sulfide addition to N-phenyl maleimide, found that this reaction was spontaneous in basic dipolar aprotic solvents as well as in pyridine. Based on these, the base catalyzed thiol-addition mechanism can be visualized as:

$$RSH + B: \xrightarrow{(1)} RS^{\ominus} + BH^{+}$$



(II)

When R=H (for H_2S), further reaction of II with another molecule of maleimide is possible and this leads to the diadduct as shown below.

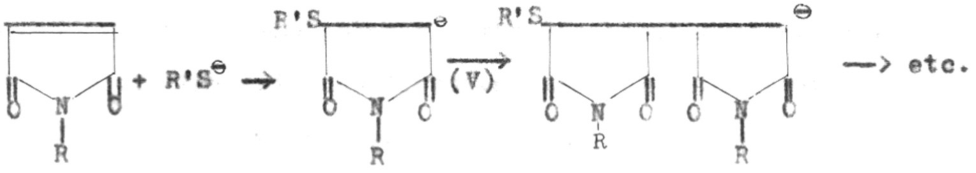


III
Diadduct

IV

Since the mono adduct IV could not be isolated (as described earlier), it may be considered that the ensuing reactions are relatively faster. Such thiol-maleimide reactions are facile with bisthiols and monomaleimides, and bismaleimides and monothiols, e.g. thiophenol addition to DMB was found, in the present work, to be facile to yield the adduct.

Similar additions of bisthiols or hydrogen sulfide to bismaleimides yield linear polyimidothioether polymers. Crivello[18], while examining this type of polymerization reaction, found that the polymerization reactions in dipolar aprotic solvents and in absence of catalysts, lead to insoluble, gel-like products. This was attributed to a seriously competing bismaleimide-self polymerization reaction. The reaction was considered to be an anionic polymerization of the bismaleimide initiated by the thiolate ion as shown:

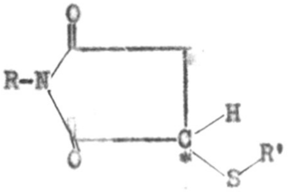


(V) (VI)

Such types of alkoxide or hydroxide ion-initiated anionic polymerization of maleimides in non-aqueous medium have been shown to take place rapidly even at low temperatures[25-27]. Decker[28] found that even pyridine, a weak base, catalyzes the polymerization of maleimide in aqueous medium. Crivello[18] suggested that the homopolymerization can be minimized or prevented by intercepting the species VI by protonation. This can be achieved (i) by using glacial acetic acid in DMF or DMSO or (ii) m-cresol containing a tertiary amine e.g. N,N,N',N'-tetramethylene ethylene diamine or triethylamine. Crivello found that m-cresol containing the t-amine suited best for the purpose.

A study of infrared spectra of polyimidothioether polymers (Tables 2-7) gives an insight into the probable structure of these polymers. In Fig. 4.1 (IR of pure DMB), the strong imide carbonyl absorptions appear at 1720 and 1800 cm^{-1}. The unsaturation bands appear at 3100 cm^{-1}

due to C-H stretching vibration, at 850 and 690-700 cm^{-1} due to the out of place deformation vibration[29,30], and characteristic of CH=CH form. The band at 1380 cm^{-1} (strong) may be assigned to assymmetrical stretching vibrations of C-N-C[29]. In all the polymers from the bismaleimides, the absence of ethylenic-unsaturation bands at 690, 840-850 and 3100 cm^{-1} is conspicuous indicating thiol addition to maleimide double bonds. The strong band at 1180-1200 cm^{-1} in the IR spectra of imidothioether polymers, has been assigned to the C-S-C stretching vibration[18]; expectedly this band is absent in the original bismaleimide and the thiol. The absence of a band at 2500 cm^{-1} (-SH) and the presence of a band at 1180-1200 cm^{-1} (C-S-C) conclusively indicates the thiol addition to maleimide double bonds (Figs. 4.2 - 4.7). Crivello[18] has indicated a band due to succinimide ring methylene protons at 1380-1400 cm^{-1}; however this is overlapped by the band due to C-N-C stretching vibration. Interestingly, these polymers carry an asymmetric centre on the carbon atom in the succinimide ring carrying sulfur substituent, i.e.



The physical properties of these polymers show a high degree of dependence on the aliphatic chain length of the thiol as it forms the aliphatic backbone (the soft domain) of the polymer. As the carbon chain length between the thiol groups is increased, the tendency towards low viscosity becomes apparent. These are evident from the results recorded in Tables#2 to#7. In the present case this trend with the use of long-chain ethyleneoxide units (i.e. ether units) may be expected to be more pronounced because of the flexibilizing nature of ether linkages. This flexibility increases with increasing ether content.

Polyimidothioether copolymers, as mentioned earlier, may be prepared by using two different thiols with a bismaleimide or vice-versa. The copolymers prepared are shown in Tables-6 and 7. The infrared spectra revealed just the basic features described earlier and only the elemental analyses data seem to support, at least partially, the structure assigned for these copolymers.

EXPERIMENTAL

General Remarks

Melting points were determined using a 'Tempo Melting Point Apparatus' and are uncorrected.

Viscosity is reported as 'inherent viscosity'. Viscosity measurements were made using an Ubbelohde Viscometer on a 1% solution of the polymer in DMF at 30°C.

Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer and using trifluoroacetic acid as solvent.

IR spectra were recorded either as nujol mulls (for solids) or as liquid films (for liquids).

'Work up' referred to frequently in the experimental section, means the following: the reaction mixture was poured into 500 ml methanol (containing 10 ml glacial acetic acid) and the precipitated product was filtered, washed with methanol, many times and dried. When the reaction mixture formed a homogeneous phase with acidified methanol, the product was recovered by removing all organic liquids under reduced pressure. All polymerization reactions were performed at room temperature.

Materials

All amines were purified by either recrystallization or distillation. Maleic anhydride was purified by mixing the crude material with a little acetic anhydride and distilling at normal pressure. The fraction boiling at 195-196°C was collected and used. Cresol means m-cresol which was purified by distillation (b.p. 201-202°C). All other organic solvents used were purified by known methods. Bis(thioglycolates) were synthesized as already described (Chapter-I).

Methods

All maleimide compounds were prepared by a slight modification of Searle's method[24].

Synthesis of N-Phenyl Maleimide

A solution of aniline (9.3 g) in toluene (20 ml) was added with stirring to a solution of maleicanhydride (9.81 g) also in toluene (250 ml) in a 500 ml beaker. The addition was highly exothermic and the precipitation of N-phenyl meleamic acid was instantaneous. After the completion of addition, the contents were allowed to stand for 30 minutes to complete the reaction. The precipitated product was filtered through a Buchner funnel and was washed with several fresh portions of warm toluene. The precipitate was then placed in a 500 ml round bottom flask with a reflux condenser and acetic anhydride (150 ml) was added followed by fused sodium acetate (5 g) and heated on a water bath for 80 minutes. The reaction mixture was cooled and poured into 3 litres of ice-water when N-phenyl maleimide separated out as a crystalline, canary-yellow solid. It was filtered, washed many times, with ice-water and dried. N-phenyl maleimide was recrystallised from water to yield yellow needles. m.p. 88°C.

Anal.$C_{10}H_7O_2N$: Requires: C, 69.36%, H, 4.04%, N, 8.09%
Found : C, 69.17%, H, 4.21%, N, 8.17%

Synthesis of Bismaleimides

A solution of the aromatic diamine (0.05 mole) in toluene (100 ml) was added with stirring to a solution of maleic anhydride (0.10 mole) in toluene (250 ml) contained in a 500 ml beaker. The mixing was exothermic and accompanied by rapid formation of the bismaleamic acid precipitate. After the completion of addition, the contents were allowed to stand for 30 minutes, filtered and the solid was washed several times with toluene. The bismaleimide was obtained after the cyclodehydration process of bismaleamic acid using acetic anhydride (150 ml) and fused sodium acetate (5-6 g) as described for N-phenylmaleimide. All bismaleimides were recrystallized from benzene-ethanol mixture.

Melting points and elemental analysis data of bismaleimides are recorded in Table-1. Bismaleimides were characterized by comparing the above data with literature values[18] and also by infrared spectral characteristics. IR spectrum of 4,4'-diphenylmethane-N,N'-bismaleimide(DMB)

(Fig.4.1): 1720(C=O), 690, 840-850 and 3100 cm^{-1}(C=C).
NMR = δ 4.0 (S $-C_6H_4-\underline{CH_2}-C_6H_4-$) , 7.2-7.8 (m, aromatic and olefinic protons).

Model Reactions

(1) Reaction of Hydrogen Sulfide with N-phenyl Maleimide

Into a mixture of N-phenyl maleimide (2.5 g), cresol (20 ml) and 2-3 drops of tri-n-butylamine contained in a 3-necked flask equipped with a stirrer, a gas inlet tube hydrogen sulfide gas was bubbled with stirring. The reaction was exothermic. After 30 minutes, hydrogen sulfide passage was stopped and the product was obtained, as reported in the 'work-up' (see General Remarks). The product was a nearly-white solid. Recrystallized from acetonitrile. m.p. 202°C, yield: 2.45 g.

Anal. $C_{20}H_{16}O_4N_2S$ Requires: C 63.15%, H, 4.24%
Found : C, 63.42%, H4.43%

The same product was also obtained by performing the above reaction of N-phenylmaleimide in dimethyl formamide (25 ml) containing glacial acetic acid (5 ml) .
IR (Fig. 4.3): 1720, 1790 (C=O), 1180 (C-S-C), 690 cm^{-1}($-C_6H_5$).

(2) Reaction of Thiophenol with DMB

Thiophenol (1.10 g), N,N'-bismaleimido-4,4'-diphenyl methane (DMB) (1.80 g) were stirred together at room temperature for 3 hours in cresol (25 ml) containing 2 drops of $n-Bu_3N$. The product, obtained after the usual work up, was a white solid. m.p. 142°C, yield: 1.6 g.

Anal.Calcd. for $C_{33}H_{26}O_4N_2S_2$ Requires: C,68.51%, H, 4.5%

Found : C,68.83%, H, 4.8%

IR spectrum of this compound is shown in Fig. 4.4. Characteristic bands are: 1710, 1780 cm^{-1}(C=O), 1180-1190 cm^{-1} (C-S-C), 700 cm^{-1}($-C_6H_5$).

Synthesis of Polyimidothioether Polymers

Synthesis of Polyimidothioethers from Bismaleimides and Hydrogen Sulfide

In a 3-necked flask equipped with a stirrer and a gas inlet tube were placed 4,4'-diphenylmethane-N,N'-bismaleimide (DMB) (2.0 g) and cresol (25 ml) and stirred gently to effect solution. Hydrogen sulfide was bubbled into the mixture for 5-10 minutes and 2-3 drops of tri-n-butylamine was added. Hydrogen sulfide stream was continued for a total of 60 minutes. The reaction was mildly exothermic. The polymer was obtained after the usual 'work-up'. The product was a white solid.

Polyimidothioethers from hydrogen sulfide and other bismaleimides were prepared similarly. Characteristics of all these polymers are shown in Table-2.

Fig.4.5 shows the IR spectrum of DMB-H_2S polymer. Characteristic bands are: 1730 cm^{-1} (C=O), 1190 cm^{-1} (C-S-C).

Synthesis of Polyimidothioethers from Bismaleimides and Glycol bis (thioglycolates)

In these syntheses the preparation of title polymers was limited to DMB and o-phenylene-N,N'-bismaleimide (OPBM).

(1) Polyimidothioether Polymers from Bismaleimide and Glycol bis(thioglycolate) in 1:1 molar Proportion

DMB (1.79 g) and cresol (25 ml) were gently stirred together in a 3-necked flask to effect solution. Ethylene glycol bis(thioglycolate) (1.05 g) was added to the solution followed by the addition of 2-3 drops of n-Bu_3N. The mixture was stirred for 3 hours. The reaction was slightly exothermic. The product was obtained after the usual 'work-up'.

Polyimidothioethers from DMB and bis(thioglycolates) of PEG-200, 400 and 600 were prepared similarly. Characteristics of all these polymers are shown in Table-3.

Polyimidothioether polymers from o-phenylene-N,N'-bismaleimide (OPBM) and the glycol bis(thioglycolates) were prepared similarly. Characteristics of these polymers are shown in Table-4.

The IR spectrum of DMB-PEG-400 bis(thioglycolate) polymer: 1720 (C=O); absence of bands due to C=C vibrations is conspicuous.

(2) Polyimidothioethers from DMB and Glycol bis(thioglycolates) in 10:1 Molar Proportion and Hydrogen sulfide

DMB (3.58 g) and cresol (25 ml) were placed in a 3-necked flask equipped with a stirrer and a gas inlet tube. Ethyleneglycol bis(thioglycolate) (0.21 g) and 2-3 drops of n-Bu_3N were added into the flask and the mixture stirred for 30 minutes. Hydrogen sulfide gas was then bubbled into the reaction mixture with stirring. Hydrogen sulfide stream was continued for a period of 60 minutes and then stopped. The reaction mixture was stirred for further 60 minutes and the product was isolated after the working up the reaction mixture.

Similarly polymers from DMB and bis(thioglycolates) of PEG-200, 400 and 600 were prepared by the method described above.

Physical properties of all these polymers are recorded in Table-5.

Synthesis of Copolymers

(1) Synthesis of Polyimidothioether Copolymers from DMB (1 mole) and two glycol bis(thioglycolates)(0.5 mole each)

DMB (3.58 g) and cresol were placed in a 3-necked flask equipped with a stirrer. Ethyleneglycol bis (thioglycolate) (1.05 g) and PEG-200 bis(thioglycolate) (1.71 g) were added to the solution followed by the addition of 2-3 drops of n-Bu_3N. The reaction was slightly exothermic. The reaction mixture was stirred for 3 hours and worked up to obtain the product.

Similarly copolymers from DMB and the various mixtures of glycol bis(thioglycolates) were prepared by the method described above.

Characteristics of all the copolymers prepared are recorded in Table-6.

(2) Polyimidothioether Copolymers from a Mixture of DMB and OPBM with a Glycol bis(thioglycolate)

A mixture of DMB (1.79 g) and OPBM (1.34 g) was gently stirred in cresol (25 ml) in a 3-necked flask to effect solution. Ethyleneglycol bis(thioglycolate) (2.1 g) was added to it followed by the addition of 2-3 drops of n-Bu_3N and the contents were stirred for 3 hours. The copolymer was obtained after the working-up of the reaction mixture. Other copolymers from DMB-OPBM and other glycol bis(thioglycolates) were prepared similarly.

In Table-7 are recorded the characteristics of all these copolymers.

IR spectrum of DMB-OPBM-ethyleneglycol bis(thioglycolate) copolymer has been given in Fig.4.7. Characteristic bands are: 1736 cm^{-1} (C=O), absence of ethylenic unsaturation bands at 700 cm^{-1}, 845 cm^{-1} and 3100 cm^{-1} is conspicuous.

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CHAPTER-V

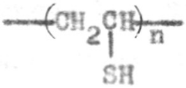
RUBBERY PRODUCTS FROM CASTOR OIL TRIS(THIOGLYCOLATE)

INTRODUCTION

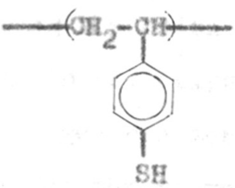
An increasing spur of activity in research on sulfur-containing polymers is being witnessed for the past two decades. In the wake of such newer interest, as may be rightly anticipated, several sulfur-containing compounds having interesting properties, and new reagents for the polymerization of sulfur compounds, have been added to the ever-growing repertoire of sulfur compounds[1-6]. Such an interesting development may not come as a complete surprise remembering the many important uses of sulfur compounds (see General Introduction). The chemistry of sulfur compounds itself is quite fascinating because of the wide spread array of chemical and physical properties exhibited by many different sulfur containing functions[1]. These range from high reactivity to chemically inert character. Some of the sulfur containing compounds are of high academic interest while some others are of profound commercial importance.

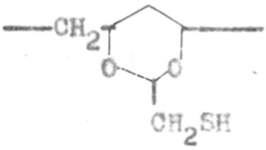
The chemistry of organosulfur compounds - including organosulfur polymers - centres around thiols. The multi-faceted industrial applications of thiols are too well known and numerous to be recounted here (see General Introduction). Many polymers containing sulfhydryl group have been synthesized having interesting applications not only in biology and medicine, but also in the domain of commercial adhesives and coatings. Some of the well known polymers are:

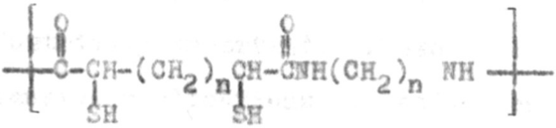
$H(SCH_2CH_2OCH_2OCH_2CH_2S)_nH$ - the well known LP-series of polymers of Thiokol Chemical Corporation



$-(CH_2\underset{SH}{CH})_n-$

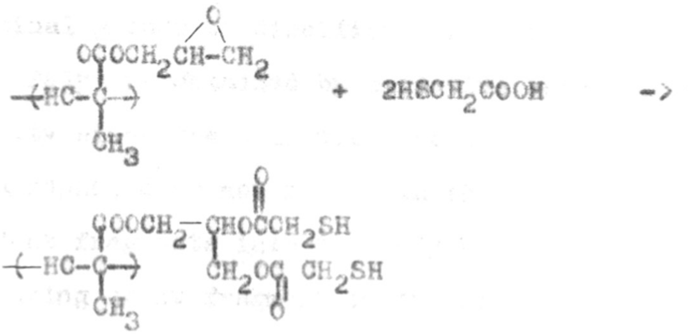






$\left[\overset{O}{\overset{\|}{C}}-\underset{SH}{CH}-(CH_2)_n\underset{SH}{CH}-\overset{O}{\overset{\|}{C}}NH(CH_2)_n\ NH\right]$

Sulfhydryl containing polymers have also been prepared by treating the corresponding polyglycidyl compounds with mercaptocarboxylic acids. For example, poly(glycidyl methacrylate) and thioglycolic acid give.



Many of these mercaptan containing polymers are useful as sequestering agents for heavy metals, as model compounds in understanding the reactivity of enzymic sulfhydryl groups[5], as redox resins etc[5].

A multitude of important chemical properties exhibited by thiols are of an exquisite character. Of these, the propensity for facile oxidation to disulfide structures with a wide variety of inorganic and organic oxidizing agents is of importance in industrial applications. Among the thiol group-containing organic polymers, thiol-terminated polysulfide liquid polymers (the well known 'LP' generic series of Thiokol Chemical Corporation) are by far the representative type of this class and are industrially important. These LP-series polymers find extensive applications in sealant compositions. In a majority of applications, these thiol terminated polymers owe their high utility to their ability to form high molecular weight solid rubbery products by the action of oxidizing agents[4]. The essential process behind the formation of these products is the oxidation of thiol terminal groups to disulfide structures.

Polymers obtained by oxidative cure are of more utility since the oxidation process (described in following paragraphs) does not result in the introduction of oxidant fragments into the polymer backbone. The presence of curing agent fragment in the polymer backbone will have undesirable effects on the final properties of the cured product. The following classes of oxidizing curing agents are used in the oxidation process of thiol group containing compounds[7].

1. Metal Oxides

Oxides of lead, zinc, magnesium, calcium, barium, iron [Fe(II) and Fe(III)], cobalt and copper [Cu(II)].

2. Metal Peroxides

Peroxides of lead, zinc, magnesium, calcium, manganese, tellurium, selenium, tin, iron (FeO_2), arsenic (As_2O_3) and antimony (Sb_2O_3 and Sb_2O_5).

3. Other Inorganic Oxidizing Agents

Chromates, dichromates and perchlorates of sodium and potassium.

4. Organic Peroxides

Benzoyl and dicumyl peroxides, cumene and t-butyl hydroperoxides and t-butyl perbenzoate.

5. Other Organic Oxidizing Agents

Mono- and poly nitroderivatives of benzene, trinitrotoluene and other organonitro compounds. p-Quinone dioxime is also an important and widely used oxidizing agent.

6. Miscellaneous Organic Curing Agents

Organic titanates, borates and silicates; quinone, 2-furfural and reactive phenols; di-, and poly isocyanates and epoxides.

A large number of basic catalysts are also employed for accelerated cures. These include aliphatic, aromatic and heterocyclic tertiary amines, polyamines, and amine salts. Acid catalysts used include acid anhydrides and Lewis acids.

A brief account of the curing action of the above listed compounds is presented below.

1. Metal Oxides

Generally, the compounds of this class are not very active and lead to the formation of mercaptide structures with the metal atom in the main chain, e.g. with ZnO,

$$2RSH + ZnO \rightarrow RS\text{-}Zn\text{-}SR + H_2O$$

These mercaptides, which usually give higher volatility loss at high service temperatures, probably catalyze a structural rearrangement at those temperatures resulting in high heat aging losses. But satisfactory cures are possible with oxides of zinc, magnesium, calcium, cadmium, cobalt, copper or lead when processed at 158°F for longer periods.

2. Metal Peroxides

These form a very important class of thiol-oxidizing agents and generally give complete cures. In this class, lead peroxide (PbO_2) is one of the commonly used and most versatile curing agents, which functions at both room or elevated temperatures[8-10].

The reactions of lead peroxide with thiol group, as a typical example of curing by inorganic peroxides, may be shown as:

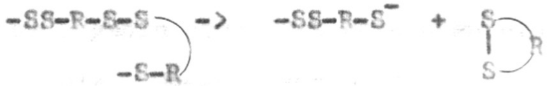
$$2R\text{-}SH + PbO_2 \rightarrow RSSR + PbO + H_2O \tag{i}$$

$$2RSH + PbO \rightarrow RS\text{-}Pb\text{-}SR + H_2O \tag{ii}$$

$$RS\text{-}Pb\text{-}SR \xrightarrow{\Delta \text{ or } h\nu} RSR + PbS \tag{iii}$$

$$RS\text{-}Pb\text{-}SR + PbO_2 \rightarrow RSSR + 2PbO \text{ etc.} \tag{iv}$$

The presence of lead mercaptide bond, as shown in reaction (ii), introduces a number of deficiencies and is undesirable[8]. The conversion of mercaptide bond to monosulfide, i.e. reaction (iii), is of higher concern as it leads to a loss of adhesion. The presence of the mercaptide linkage also contributes to a weight loss by cyclodepolymerization reaction, shown in reaction (v).



(v)

(in commercial polysulphide rubbers, R= $C_2H_4OCH_2OC_2H_4$-)

Since the mercaptide bond is regenerated, the continued interchange reaction may result in the volatalization of a major part of the original polymer unless the mercaptide formation is reduced. One of the ways of minimizing the concentration of mercaptide groups is by incorporation of a very small amount of elemental sulfur. The reaction with sulfur may be shown as:

$$RS\text{-}Pb\text{-}SR + S \rightarrow RS\text{-}SR + PbS$$

The presence of disulfide linkage is essential for good chemical resistance. Elemental sulfur is usually employed in trace amount (0.25 g/100 g of the polymer). Larger proportions of elemental sulfur contribute to thermal instability (by the attack of sulfur on the polymer hydrocarbon backbone) adversely affecting the adhesion characteristics and aggravating stress-relaxation characteristics.

Numerous studies have revealed tellurium dioxide, manganese dioxide and various chromate salts to be particularly useful for cures with fewer side reactions than lead peroxide. Fatty acids- stearic acid is widely used- act as retarders to control the cure rate.

3. <u>Organic Peroxides</u>

Various organic peroxides have been used for oxidative curing of thiols. Cumene hydroperoxide is a soluble curative. The cumene hydroperoxide-thiol reaction may be shown as:

Cumene hydroperoxide is only moderately active and activators such as diphenyl guanidine or triphenyl guanidine are generally used with it.

It has been found that generally the tertiary alcohols formed, being mildly acidic, lower the high temperature serviceability of cured products.

4. Dioximes

Among the organic oxidizing agents, dioximes, particularly p-quinone dioxime, give effective cures for thiol terminated low-molecular weight polymers. The reaction may be written as:

Aliphatic diamines, formed from aliphatic dioximes may act as chain-scission promoters because of higher basicity. Thus, the usefulness of dioximes is limited to aromatic dioximes. p-Quinone dioxime is generally used in conjunction with diphenyl guanidine.

5. Organic Nitro Compounds

Aromatic nitro compounds, e.g. dinitro benzene, trinitrobenzene, or trinitrotoluene, have been found to be effective in the oxidative curing of thiol-terminated liquid polymers. The stoichiometric reaction involved may be written as:

However, these are not as effective as the reaction indicates because, in reality, a number of oxidation levels between the nitro and amino groups are possible. Diphenyl guanidine is employed as the basic catalyst with nitro compounds.

6. Aldehydes

In this class, 2-furfuraldehyde is widely used in the curing of thiol terminated liquid polymers. The curing is generally accomplished in an acidic environment, e.g. furoic acid.

As can be seen, the product is characterized by the presence of thioacetal linkage[7,8]. These compositions, however, have no advantage over other general cure systems and exhibit poor elevated temperature serviceability. Other acid catalysts useful include organo-substituted phosphoric acids, formic acid and salicylic acid.

7. Epoxy Resins and Polyisocyanates

Many aliphatic and aromatic polyepoxide resins and polyisocyanates react with thiol-terminated compounds and such additive curing reactions are of prime importance in adhesive applications because in these reactions no by-products (e.g. H_2O) are formed. (Chapters II and IV).

8. Miscellaneous

Quinone reacts with thiols and, in the absence of water, yields hydroquinone as a by-product. Many organotitanium derivatives have been evaluated as curing agents for thiol compounds. Tetraisopropyl titanate and tributyl borate have been found to be very reactive with polymers having hydroxy or thiol end groups.

In the present study, castor oil tris(thioglycolate), a new polythiol, was synthesized from castor oil and thioglycolic acid. This polythiol exhibits a strong tendency to form transparent, brittle and insoluble film on exposure to air. The thiol compound also formed solid products with metal peroxides and p-quinone dioxime. The present work was, therefore, aimed at a study of curing of castor oil tris(thioglycolate) with lead peroxide and p-quinone dioxime using various inorganic fillers. Tensile properties of the cured products were determined.

PRESENT INVESTIGATION AND RESULTS

Esters containing at least three thiol groups prepared by the reaction of polyhydric alcohols with mercaptocarboxylic acids are known to form films on exposure to air which are insoluble in organic solvents[11]. And castor oil tris(thioglycolate), a new trithiol prepared by the reaction of castor oil with thioglycolic acid, was no exception. It showed a strong tendency to form transparent and brittle film on exposure to air and the film was found to be insoluble in organic solvents. It was, therefore, thought that it might be possible to obtain solid rubbery products by curing with the usual oxidative curing agents which are used in the curing of thiol terminated polysulfide liquid polymers.

The aim of the present work was to investigate the possibility of using lead dioxide and p-quinone dioxime/ diphenyl guanidine curing systems to cure castor oil tris (thioglycolate) and determination of the physical properties of the cured products.

For the synthesis of castor oil tris(thioglycolate) [COTT] see Chapter I. Curing of COTT by lead peroxide and p-quinonedioxime is described below.

(i) Lead Dioxide (PbO_2) Curing System

Due to high specific gravity of lead dioxide (9.375) and its tendency to settle from the mix, it is not practicable to use it as such. Therefore it was used as a dispersion in dibutyl phthalate (C-5 paste). The C-5 paste was prepared by mixing thoroughly the following:

Lead dioxide	50 parts
Dibutyl phthalate	45 parts
Stearic acid	5 parts

The compounding recipe for the lead dioxide curing of COTT is shown below:

COTT	100 parts
Filler*	x
Sulfur	0.25 part
Stearic acid	1.0 part
C-5 paste	15 parts

* Fillers used: Carbon black 30; TiO_2 50; or silica 15 parts .

Set times of various mixes are shown below:

Filler	Set time at 70°C, hrs.
Carbon black	20
TiO_2	16
Silica	10

Physical testing of the vulcanizates was carried out according to ASTM designations D 412-68 and D 676-59T. These results are shown in Table-1.

In case of TiO_2 and silica filled products, the vulcanizates were too brittle for the properties to be determined.

Table-1: Properties of PbO_2 cured vulcanizates pressed out at 160°C for 10 minutes.

Filler	Tensile strength MPa	Relative extension %	Shore A hardness
Carbon black	0.568	20	65
TiO_2	-	-	55
Silica	-	-	50

(ii) p-Quinonedioxime(GMF)/diphenyl guanidine(DPG) Cure System

This system is effective for thiol-terminated low molecular weight polysulfide liquid polymers where lead dioxide curing system is not so useful. p-Quinone dioxime was used in combination with an amine accelerator, diphenyl guanidine (DPG).

Compounding recipe for p-quinone dioxime/DPG cure system for COTT used was as follows:

COTT	100 parts
Filler*	X parts
p-Quinonedioxime	10.5 parts
DPG	4.5 parts

*Fillers used: Carbon black 30, TiO_2, 50 or silica 15 parts.

Set times of various mixes are shown below:

Filler	Set time at 70°C in hrs.
Carbon black	12
TiO_2	72
Silica	70

The physical properties of the vulcanizates are recorded in Table-2.

Table-2: Physical properties of p-quinone dioxime/DPG cured vulcanizates

Filler	Tensile strength MPa	Relative extension %	Shore A hardness
Carbon black	0.64	20	70
TiO_2	0.26	20	55
Silica	0.38	10	50

Curing of the Mixture of Castor oil tris(thioglycolate) and thiol-terminated polysulfide liquid polymers (MW 4000)

It was thought that the addition of other thiol terminated polymers to COTT would help in improving the overall physical properties of COTT vulcanizates. Our immediate choice for this purpose was the two thiol terminated polysulfide liquid polymers, namely, LP-2 (mol.wt. 4000, 2% crosslink) and LP-32 (mol.wt. 4000 and 0.5% crosslink).

Lead dioxide Curing System for COTT & LP-32 Combinations

LP-32 was mixed with COTT in different proportions and cured with lead dioxide.

The compounding recipe is shown below

COTT	*
LP-32	*
Sulfur	0.25 part
Stearic acid	1.0 part
C-5 paste	15 parts

*mixing ratios of COTT and LP-32 and their set times are shown below.

System	COTT	LP-32	Set time at 70°C, hrs
I	25	75	33
II	50	50	36
III	75	25	43

The physical properties of these vulcanizates are given in Table-3.

Table-3: Physical properties of lead peroxide cured COTT-LP-32 vulcanizates

System	Tensile strength MPa	Relative extension %	Shore A hardness
I	1.28	110	45
II	0.68	30	53
III	0.66	20	55

p-Quinone dioxime/DPG Curing System for COTT-LP-32 and COTT-LP-2 Combinations

COTT was cured separately with LP-32 and LP-2 in the ratio 1:1 by weight using the p-quinone dioxime/DPG cure system.

The compounding recipe used is shown below:

COTT	50 parts
LP-32 or LP-2	50 parts
Carbon black	30 parts
p-Quinone dioxime	10.5 parts
DPG	4.5 parts

<u>Set Time:</u> i) COTT-LP-32 8 hrs. at 70°C
ii) COTT-LP-2 8 hrs. at 70°C.

The physical properties of the vulcanizates are given in Table-4.

<u>Table-4</u>: Physical properties of p-Quinone dioxime/DPG-cured Vulcanizates pressed out at 160°C for 10 minutes

System	Tensile strength, MPa	Relative extension %	Shore A hardness
COTT-LP-32	1.51	80	60
COTT-LP-2	1.72	50	65

Solvent resistance of lead dioxide-cured COTT and the COTT-LP-32 vulcanizates (shown in Table-3) was determined as percent weight increase after 30 days of immersion at room temperature in the following solvents: benzene, toluene, xylene, ethyl acetate, carbon tetrachloride, methyl alcohol, isopropyl alcohol and water. These results are recorded in Table-5.

Table-5: Solvent Resistance of Vulcanizates Determined as Equilibrium Percent Weight Increase

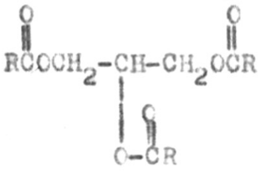
Solvent	Lead dioxide-cured Vulcanizates			
	COTT	I	II	III
Benzene	97.3	153.0	161.0	183.0
Toluene	97.25	122.5	131.3	142.0
Xylene	95.1	107.5	127.4	130.5
Ethyl acetate	59.3	48.4	66.5	67.0
Carbon tetrachloride	146.0	176.0	184.0	193.0
Methyl alcchol	7.0	7.3	6.0	5.0
Isopropyl alcohol	5.0	7.6	6.0	2.0
Water	4.6	4.3	8.5	6.0

DISCUSSION

Polymers having thiol groups, preferentially at the end of the chain, are of high academic interest and industrial importance. These find wide utility in sealant compositions in the preparation of solvent-resistant elastomers, as repair and coating materials, as fuel tank and pressurized cabin sealants in aircraft industry, oil seals and plotting compounds in electrical industry, as deck and hull caulking materials in marine industry etc. Some of such important properties arise due to their ability to get converted, on reaction with oxidizing agents, to products having elastomeric properties. These oxidized products are characterized by the presence of recurring disulfide, -SS-, units necessary for high resistance to fuels, oils, solvents as well as impermeability to gases.

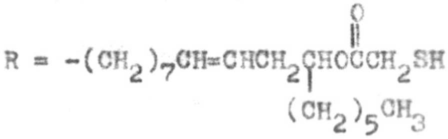
Mercaptan containing esters, formed by the reaction of hydroxy compounds with mercatocarboxylic acids, and having at least three or more thiol groups are known to form insoluble films on exposure to air[11]. And castor oil tris(thioglycolate (COTT), belonging to the above class, also behaved similarly. It showed a propensity to form a clear, brittle and insoluble film on exposure to air and even on storage in closed containers. Hence, it was attempted to cure COTT with the oxidizing agents used usually for curing thiol terminated polymers, viz., lead peroxide and p-quinone dioxime (GMF) using the fillers carbon black, silica and titanium dioxide.

COTT has the following structure (neglecting the double bond configuration in the molecule, see p.



$$R\overset{O}{\overset{\|}{C}}OCH_2-\underset{O-\underset{}{\overset{O}{\overset{\|}{C}}}R}{\underset{|}{C}H}-CH_2O\overset{O}{\overset{\|}{C}}R$$

where



$$R = -(CH_2)_7CH{=}CHCH_2\underset{(CH_2)_5CH_3}{\underset{|}{C}H}O\overset{O}{\overset{\|}{C}}CH_2SH$$

From the structure of COTT, the following conclusions are evident.

i) COTT is monomeric in nature

ii) As COTT contains three thiol groups, it will be extensively crosslinked in the cured state. Consequently elongation will be low and hardness will be more.

iii) R group in the molecule shown in the structure contains 16 carbon atoms, and the $-(CH_2)_5CH_3$ group present therein may be considered to be pendant. Such a bulky pendant group may be expected to enforce less compact packing of individual chains resulting in low modulus and strength.

The tensile strengths of both the lead peroxide and GMF cured COTT vulcanizates were low (Tables-1 and 2 respectively). Silica and titanium dioxide filled lead peroxide-cured vulcanizates of COTT were too brittle for the physical properties to be determined. This may probably be due to the relatively poor reinforcing action of these fillers.

The effect of monomeric nature of COTT and the extensive crosslink in cured state was better understood by admixing COTT with other thiol containing polymers having relatively high molecular weight, flexible structure and low crosslink density. Our immediate choice was the two thiol-terminated polysulfide liquid polymers shown below:

LP-32: Molecular weight 4000, 0.5% crosslink
LP-2 : Molecular weight 4000, 2.0% crosslink

The crosslinks in these polymers are imparted by 1,2,3-trichloropropane. These polymers have the structure:

$$H(SCH_2CH_2O\ CH_2O\ CH_2CH_2S)_{23}H$$

and when cured individually, show high strength, elongation and low shore A hardness[11,12]. By gradually increasing the LP-32/COTT ratio, a corresponding increase in tensile strength, elongation may be expected. This is supported by the results recorded in Table-3. On the basis of the results recorded in Tables-1 and 2, relatively better improvements may be expected by employing the GMF-curing system. The LP-32-COTT system should result in better strength and extension, while the LP-2-COTT combination should show comparatively more strength and more hardness but low extension. These are fully supported by the results recorded in Table-4.

EXPERIMENTAL

General Remarks (see page 108)

Materials

Castor oil tris(thioglycolate) preparation and characterization are given in Chapter I page

Lead peroxide was used as C-5 paste prepared by mixing 50 parts of lead dioxide, 45 parts of dioctyl phthalate and 5 parts of stearic acid.

p-Quinone dioxime and diphenyl guanidine were used without further purification.

All solvents, used for solvent resistance studies, were purified by known methods.

Methods

Curing of Castor oil tris(thioglycolate) with lead dioxide

Castor oil tris(thioglycolate) was weighed into a mixer and the filler added in three portions in the intervals of 10 minutes and mixed well. Stearic acid and sulfur were added and thoroughly mixed for further 15 minutes. C-5 paste was added, mixed well for another 30 minutes and allowed to set in an oven at 70°C.

Curing of castor oil tris(thioglycolate) with p-quinone dioxime and diphenyl guanidine

Castor oil tris(thioglycolate) and the filler were mixed thoroughly as described above. p-Quinone dioxime and diphenyl guanidine were added, mixed thoroughly and allowed to set in an oven at 70°C.

Curing of the Mixture of Castor oil tris(thioglycolate) and Polysulfide Liquid Polymers with lead dioxide

Separately weighed amounts of castor oil tris (thioglycolate) and the polysulfide liquid polymer (LP-2 and LP-32) were transferred into a mixer and mixed thoroughly with carbon black. Then sulfur and stearic acid were added and mixed well. C-5 paste was finally added and after mixing thoroughly was allowed to set in an oven at 70°C.

Curing of the mixture of castor oil tris(thioglycolate) and Polysulfide liquid polymer with p-quinone dioxime and diphenyl guanidine

Separately weighed amounts of castor oil (thioglycolate) and the polysulfide liquid polymer (LP-2 or LP-32) were transferred into a mixer and mixed thoroughly with carbon black. p-Quinone dioxime and diphenyl guanidine were added and after being mixed thoroughly, allowed to set in an oven at 70°C.

All the tack-free cured products were kept overnight before testing for their tensile properties.

Testing

The tack-free products, after being crumbled on a laboratory rubber mixing two-roll mill, were pressed out at 160°C for 10 minutes in a metal mold. Tensile strength, elongation and hardness were determined at room temperature on dumbbell-shaped specimens. according to ASTM designations D 412-68 and D 2240-68.

Solvent Resistance of Vulcanizates

Equilibrium swelling of vulcanizates was found out according to ASTM designation D 471-64B as percent weight increase after 30 days immersion at room temperature in the following solvents: benzene, toluene, xylene, ethyl acetate, carbon tetrachloride, methyl alcohol, isopropyl alcohol and water.

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PART-II

ORGANOTHIOSILICON COMPOUNDS IN THE THERMAL STABILIZATION OF POLY(VINYL CHLORIDE)

INTRODUCTION

Poly(vinyl chloride) (popularly known as PVC)- one of the earliest thermoplastics to be produced industrially and which still holds a major place amongst industrial plastics - has grown from a state of academic curiosity at a relentless and impressive rate to a fullfledged fascinating topic of endless interest. Even more interesting, the fact remains that over the years, investigations relating to the degradation and stabilization of PVC have captured the imagination of a multitude of workers and continues to be one of the most active areas of research in polymer chemistry. Such an ever-increasing universal interest unveils the world-wide economic importance of this highly versatile and low cost plastic. Probably there is no other thermoplastic that exhibits, on plasticization, such a broad spectrum of enormously important properties.

In spite of such a portentous interest the reality remains that PVC happens to be one of the few polymers that shows low resistance to thermal and photodegradation. Under the influence of heat, light and high energy radiation, PVC progressively splits off hydrogen chloride resulting in a general deterioration of physical and electrical properties accompanied by discoloration.

PVC presents an ideal and outstanding example of the few polymers that degrade by sequential elimination without monomer loss.

Initial Sites of Dehydrochlorination

Available experimental results of many authors seem to support the view that neither the idealized head-to-tail structure (also called 1,3-structure) of PVC:

$$\sim\sim\mathrm{CH_2CHClCH_2CHCl}\sim\sim$$

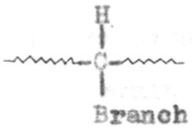
nor the abnormal head-to-head structure (1,2-structure)

$$\sim\sim\mathrm{CH_2CHClCHClCH_2}\sim\sim$$

is the prime cause of initiation of dehydrochlorination, which once induced, proceeds by a 'zipper-like' elimination of more hydrogen chloride resulting in extended polyene structure contributing to the discoloration of the polymer. Therefore, attention has been focussed on some of the structural irregularities in the polymer that function as potential sites of inherent instability. Many review articles have been published dealing with the thermal dehydrochlorination and stabilization of PVC[1-5]. The following structural irregularities have been studied more extensively[6,7].

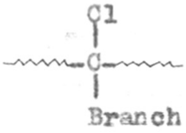
(i) Branching Sites

Branch sites in PVC presumably arise by a chain transfer between a chain radical and an already formed polymer, and can be of two kinds:



Tertiary Hydrogen

and/or



Tertiary chlorine

Although the existence of branch points has been confirmed by spectroscopic investigations[8], the structure of the branch itself is not clear. Chloromethyl (CH_2Cl) group containing branches are presumed to be present.

The recent calculations of Valko et al[8] show that differently branched structures have different reactivities and that these also contribute to the hydrogen chloride elimination reactions.

(ii) End Groups

PVC can have two types of end groups. Those containing initiator fragments or terminally unsaturated groups arising from chain transfer reactions. The results of many workers show conflicting evidences e.g. while Park and Skene[9] found that the end groups from peroxide initiator fragments were more effective in inducing dehydrochlorination, Meyer[10] observed the opposite. Thus, this ever-recurring problem of reconciliation of the results of different investigators still clouds the issue and this is partly attributed to the widely variant sensitivities of the different techniques employed for estimating evolved hydrogen chloride and other decomposition products.

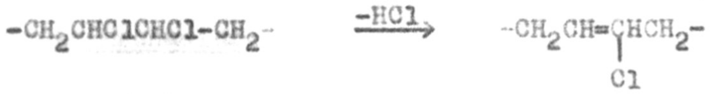
Studies with model compounds suggest no remarkable effect of terminal unsaturations on dehydrochlorination[11,12] of PVC.

(iii) Internal Unsaturation and Allylic Chlorine

Thermal dehydrochlorination studies of low molecular weight model compounds in gaseous phase, liquid phase[7,11,13,14] and the semi-empirical calculations of Valko and Tvaroska[12] indicate that internal unsaturation with allylic chlorine is thermally more labile than terminal unsaturation and it is likely that these may act as potential initial sites of instability during thermal degradation. Recently, Buruiana et al[15], by NMR studies, and Petiaud and Pham[16] by 'NMR-spectrum accumulation-technique' have confirmed the existence of internally unsaturated units in PVC and also found such a polymer to be more unstable.

(iv) 1,2-Dichloro Structures[7]

Although 1,2-dichloro structures formed by head-to-head units are less stable, there is no conclusive proof for their existence in the polymer. The α-chloro saturated structure obtained at the beginning of dehydrochlorination, i.e.



$$-CH_2CHClCHCl-CH_2- \xrightarrow{-HCl} -CH_2CH{=}\underset{\overset{|}{Cl}}{C}HCH_2-$$

has been shown to be more stable than allylic chlorine-containing structures[11]. The relatively increased stability of α-chloro unsaturated structure, which would probably inhibit zipper-elimination of hydrogen chloride, probably explains the increased thermal stability of chlorinated PVC and poly(vinyledene chloride).

(v) Stereoregularity of the PVC Polymer

Macoveanu et al[17] have indicated that the PVC synthesized at constant temperature in a given temperature range (45, 52 and 60°C) has practically the same degree of syndiotacticity and crystallinity (5%). Abbas and Servik[7] suggest that the syndiotactic sequences might affect the propagation of polyene sequences but cannot be considered as specific initiation sites for dehydrochlorination reaction.

Mechanism of Thermal Dehydrochlorination

Three distinct mechanisms have been proposed to explain the thermal dehydrochlorination of PVC and all have evidences in their favour. But it is quite interesting that all the three mechanisms have unanimity in that the dehydrochlorination is the prime cause for polymer instability and once initiated, is followed by a zipper-like elimination of more hydrogen chloride.

(i) Ionic Mechanism

Liquid phase thermal decomposition studies of low molecular weight model compounds[14], the catalytic effect of Lewis acids, protic acids, bases and acceleration of dehydrochlorination in polar solvents favour an ionic mechanism for dehydrochlorination in PVC. The accelerating effect of Friedel-Crafts compounds[18], which are known to react by an ionic mechanism, and the catalytic reaction of hydrogen chloride with degrading PVC[19] also suggest an ionic pathway.

$$\mathrm{RCl} \xrightarrow{\text{slow}} \mathrm{R^+ + Cl^-}$$

$$\mathrm{RCl + HCl} \rightleftharpoons \mathrm{R^+HCl_2^-} \rightleftharpoons \mathrm{R^+ + HCl_2^-}$$

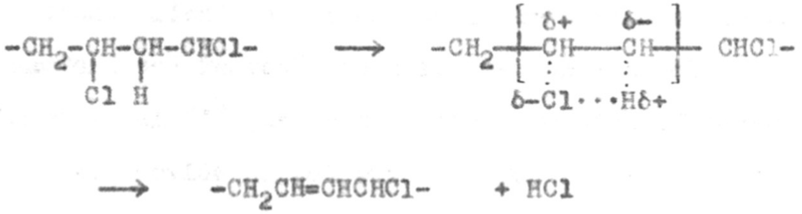
$$\mathrm{R^+} \rightleftharpoons \mathrm{H^+} + \text{olefin}$$

$$\mathrm{H^+ + HCl_2^-} \rightleftharpoons \mathrm{2\,HCl} \quad \text{etc.}$$

The existence of such intermediates has been proved by various methods[20-23]. Further evidence for the ionic mechanism comes from the works of Meyer et al[14] and Onozuka[3] which support Schlimper's postulation of the presence of [Polyene .....$\mathrm{H^+}$]$\mathrm{Cl^-}$ type complex in degraded PVC[24].

(ii) Unimolecular Mechanism

Gas phase hydrogen halide elimination reactions of halogen containing hydrocarbons have been shown to proceed via 4-center unimolecular transition states[25]



$$-CH_2-\underset{Cl}{CH}-\underset{H}{CH}-CHCl- \longrightarrow -CH_2-\left[\underset{\delta-Cl\cdots H\delta+}{\overset{\delta+\qquad\delta-}{CH-CH}}\right]-CHCl-$$

$$\longrightarrow -CH_2CH{=}CHCHCl- \quad + HCl$$

Theoretical calculations of the bond energy required to polarize C-Cl to C^+-Cl^- [26], and the work of Asahina and Onozuka[3] support the above mechanism. Activation energy calculations of Valko et al[8] and Valko and Tvaroska[12] suggest that unimolecular elimination reactions via a 4-center transition state are permitted and also that structural irregularities seem to contribute to polymer instability by such an elimination.

(iii) Free Radical Mechanism

Evidences in favour of free radical mechanism for the dehydrochlorination for the pure polymer under controlled conditions and in inert atmosphere are quite impressive and more in number. Many authors[27-29] consider the chlorine atom, formed by the homolytic cleavage of C-Cl bond, to be responsible for inducing chain reaction.

$$Cl^{\bullet} + \quad -CH_2CHCl- \quad \longrightarrow \quad -\dot{C}HCHCl- \quad + HCl$$

$$-\dot{C}HCHCl- \quad \longrightarrow \quad -CH{=}CH- \quad + Cl\cdot$$

The accelerating effect of free radical sources[30], uv and γ-radiation[31-34] on dehydrochlorination, and ESR studies[35,36] manifest indirect evidence for radical formation. Liquid phase dehydrochlorination experiments of Bamford and Fenton[37] in tritium-labelled toluene, and Leibman et al[36,38] indicating the formation of macro-radicals, provide direct evidence for the free radical process. Degradation experiments on polymer mixtures and graft copolymers of PVC also indirectly point to the active participation of chlorine atoms in dehydrochlorination process[37,39-43]. The work of Yousufzai et al[44], which conclusively showed the existence of chlorine atoms in the dehydrochlorination of PVC has been cited as an exciting evidence for the free radical mechanism. Atmospheric oxidations are mostly free radical in nature and an increased rate of dehydrochlorination in air should also be regarded as further evidence for the free-radical process[45,46].

It is interesting to note that most of the evidences for these mechanisms stem from the liquid phase studies of model compounds. These leave enough speculations how best these results can be correlated to the gaseous decomposition studies because of different rates. Equally interesting, still, is that no convincing argument has yet been advanced to indicate that the dehydrochlorination of PVC is different from that of low molecular weight model compounds.

Poly(vinyl chloride) is normally processed at high temperatures (around 180°C) in air and with a variety of polar and nonpolar additives. Under such rigorous conditions, it is rather difficult to assess the currently available evidence in support of any of the three mechanisms. Hence, it may well be assumed that both ionic and radical processes may be concomitant and the preponderance of one over the other will be governed by many factors. Nolan and Shapiro[47] have presented evidence in support of the manifestation of such a dual mechanism during thermal dehydrochlorination of PVC. They found that at 194°C, PVC degrades thermally via a dual mechanism - the unimolecular process preceding a radical chain process and that the latter was predominant.

An interesting suggestion has been made regarding the influence of conjugated sequences in promoting dehydrochlorination[48]. It is suggested that conjugated sequences with a large number of double bonds may become excited to the triplet state even at room temperature and certainly at high temperature of processing. Relaxation of the polyene back to the singlet state yields energy that may excite the C-Cl bond and initiate further degradation reactions and/or crosslinking.

Thermal Stabilization of PVC using Stabilizers

The technology of stabilizing PVC against degradative influences has advanced faster than the understanding of the degradation process itself. It is immediately obvious that these degradative reactions necessitate the incorporation of stabilizers to improve physical and electrical properties and enhance the life of PVC articles. The stabilization of PVC using various additives has been dealt in detail in many reviews[1-6].

These stabilizing additives, which vary widely in chemical structure, are selected and combined in various ways to satisfy processing and end-use requirements. The manufacture, selection and proper combination of these stabilizers comprise the art and science of PVC technology.

It is now generally recognized that the stabilizers, to be most effective, should possess one or more of the following salient features supplementing their prime function of binding (or destroying) hydrogen chloride evolved from the polymer.

(i) An ability to replace labile chlorine atoms (e.g. at allylic position) to give thermodynamically more stable groups in the polymer thus lowering the number of potential sites of inherent instability.

(ii) An ability to modify chain reactions and thus inhibiting the 'zipper'-like elimination of hydrogen chloride.

(iii) The ability to interrupt conjugated polyene-sequences in the polymer and hence the colour formation.

(iv) The capacity to render prodegradent substances (including impurities in the polymer and by-products produced during the stabilization process) innocuous.

A higher capacity of the functional groups (or ligands) in the stabilizer or of the cleaved products to interact with hydroperoxides and/or the polyene sequences in the polymer would be a highly valuable additional asset to the stabilizer efficiency.

In addition to these, and equally important, the stabilizer should be colourless, compatible with PVC, non-migrating, non-toxic, effective in small quantities, non-staining and, to a large extent, should not adversely affect other properties of the polymer.

Types of Stabilizers used

Stabilizers have been classified into the following general types[49]:

(i) Salts of Mineral Acids

These include carbonates, sulfates, silicates, phosphates and phosphites of the metals, e.g. sodium, lead, and calcium. Organic phosphites are by far the most important class from the technological point of view.

(ii) Salts of Carboxylic Acids

(a) Salts of fatty acids (stearates, laurates, ricinoleates)

(b) Salts of other acids (e.g. maleates, phthalates etc.)

The above acid salts of Ba, Cd, Zn and Ca find extensive applications commercially.

(iii) Organotin Compounds

These organometallic compounds represent by far the most efficient class of PVC stabilizers in vogue commercially. Organotin carboxylates, mercaptides and mercapto alkanoates (thioglycolates and mercapto propionates) are representative types in this class. Of these, the mercaptoalkanoates are most efficient and remain supreme.

(iv) Other organic compounds of metals and metalloids, e.g. alcoholates and mercaptides.

(v) Epoxies

Common types are epoxidized soyabean oil and linseed oil epoxidized ethers and esters.

(vi) Polyols and Nitrogen Compounds

These include pentaerythritol, sorbitol, amino compounds of all types - notably derivatives of ureas, thioureas, guanidines, various amines, amides and imides.

(vii) Synergistic combinations of two or more stabilizers.

Mechanism of Stabilization

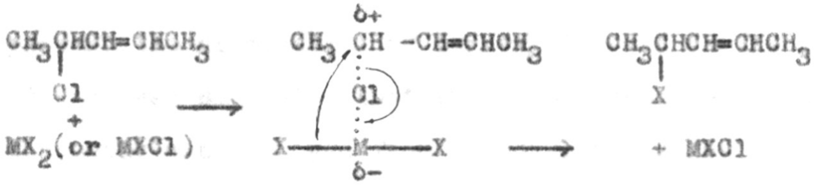
Metal soaps and organotin compounds, which were used in the present study, constitute a very important class of commercial stabilizers widely used. So, presently, a discussion of the mechanism of stabilization will be limited to these two classes of stabilizers only.

(A) Metal Soap Stabilizers

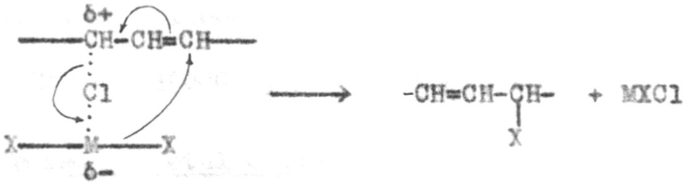
Important in this group are the fatty acid salts and maleates, acetates of barium, cadmium, zinc and calcium.

Frye and Horst[50,51] suggested that metal soaps functioned by replacing a labile chlorine atom with the metal soap ligand. The work of Shimura et al[52] supported the above mechanism of Frye and Horst and also revealed that the esterification of the polymer by metal soaps is closely related to the stabilization of PVC. Evidence for the ester-exchange reaction also comes from the work of many authors[53-56] and esterification studies of model compounds with metal soaps, by Bengough and Onozuka[57], indicated that only allylic chlorine and not tertiary chlorine is esterified.

Klemchuk[58], in view of the complexing ability of metal atoms in the metal soaps, postulated the following scheme of reactions depicted below.



Another possibility involving allylic shift, also exists for the ester-exchange



It is evident that complexing of labile chlorine with metal chloride (MCl_2) will not lead to any stabilization but probably will enhance the degradation. Therefore, the species responsible for stabilization are MX_2 and MXCl but not MCl_2. It was also argued that stabilizing effect of the metal soaps is dependent on the complexing ability of the metal as well as the size and nucleophilicity of ligands attached to it.

The work of Bengough and Onozuka[57] revealed that ester-exchange reaction is not necessarily linked to stabilization and the stability by these materials appears to be due to their ability to react with double bonds and thus limit the discoloration.

The addition of basic substances such as pyridine, epoxy compounds and metal soaps, is found necessary to prevent the elimination of carboxylic acid during processing. It has been suggested that the base functions by shielding the methylene hydrogen from carboxylate oxygen[51]. The reactivities of metal soaps have been shown to correlate with the ionization potentials of the metals (in metal soaps). The reactivity of metal soaps, accordingly, may be shown as follows:

$Zn(OCOR)_2 > Cd(OCOR)_2 > Pb(OCOR)_2 > Ca(OCOR)_2 > Ba(OCOR)_2$

Synergism of Metal Soaps

One of the most important factors influencing the effectiveness of PVC stabilization is the phenomenon of synergism. The virtue of this interesting and very important phenomenon lies in the significantly enhanced efficiency of higher magnitude from the use of synergistic combinations than might be expected from the additive action of the individual components in the mixture. Synergistic mixtures can contain monotypic or different types of stabilizers. The necessity for employing a mixture of two or more different stabilizers arises because generally the individual components will not possess all the salient features for efficient functioning.

Soaps of metals Ba, Cd, Ca and Zn are hardly ever used alone but always in Ba-Cd and Zn-Ca couples. These mixtures absorb 82-95% of the theoretical quantity of hydrogen chloride. Ocskay et al[89], using zinc and calcium oleates, found an effective optimum ratio of Ca to Zn of 2:3 when initial colour was of prime importance and 4:1 for delayed induction period before the onset of catastrophic discoloration.

Significant progress in the understanding of the manifestation of metal soap-synergistic action comes from the work of Onozuka[54] by a study of model compounds. The results of the work indicate a minimization of dehydrochlorinating-catalytic effect of reactive metal chlorides (zinc chloride and cadmium chloride) through an ester-exchange reaction with another metal soap (calcium or barium soaps; it may also be noted that these two soaps have metals of low ionization potential).

The presence of metal soap of low reactivity in the mixture is necessary to prevent the elimination of carboxylic acid.

Klemchuk[58] attributed the Ba-Cd synergism to a rapid exchange of chloride ions from CdClX to BaX_2,

$$CdClX + BaX_2 \longrightarrow CdX_2 + BaCl\,X$$

and presence, probably, of a following type metallic complex:

$$X - Ba\overset{X}{\underset{Cl}{\diamond}}Cd - X$$

Recently Iida et al[60] have suggested the intense coloration of the metal soap stabilized (Ba, Cd, Zn and Ca) PVC film to be due to the formation of a metal chloride-polyene complex susceptible to rearrangement from the remaining metal soap in the system. The presence of such complexes has been supported by experiments with model compounds. Significant differences in the ionization potentials of group II metals employed seems to be a necessary criterion for effective synergism[54]. The greater initial stabilization evinced by group II B metals was attributed to their high ionization potential (lower electropositivity), increased tendency to covalency and capacity to engage in free radical processes. Enhanced ionic character, consequent upon low ionization potential (high electropositive nature) was thought to be responsible for low effectiveness of group II A metal laurates and these soaps are also thought to be less prone to radical processes. They exhibit weak stabilizing action but total discoloration is considerably delayed. The efficiency of the group II A - II B metal laurate couples may be due to the dual mechanism operation[61] but there is no evidence to support this hypothesis.

Organotin Stabilizers

Among the organometallic stabilizers, quadrivalent tin compounds are most widespread and some tin stabilizers are outstanding in their efficiency. Remarkable progress in blow-molding, particularly in food packaging, has ensured glamour applications for these stabilizers, as these applications demand extraordinary clarity and higher thermal stability.

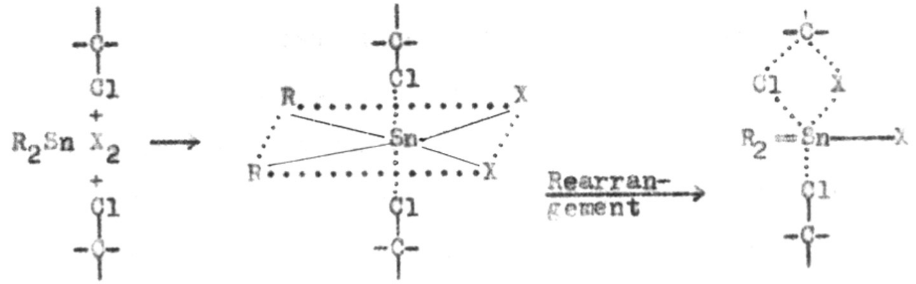
Organotin compounds most often used have the general formula:

$$R_nSn\,X_{4-n}$$

where R = Organic radical
X = Organic (or rarely inorganic) function bonded to tin through oxygen or sulfur

The high effectiveness of stabilizing action of organotin compounds is due to their polyfunctionality. Organotin compounds generally used are carboxylates (of fatty acids or dienophilic acids), mercaptides and thioglycolates, of which the thioglycolates reign supreme.

Frye et al[62], observing a gradual loss of radioactivity from the polymer, stabilized by labelled organotin compounds, on repeated dissolution - precipitation cycles, attributed the phenomenon to the presence of a coordination link between the stabilizer and the polymer. This can be shown as:



Octahedral complex

$$\longrightarrow R_2Sn\,XCl + -\overset{|}{\underset{|}{C}} - X + -\overset{|}{\underset{|}{C}} - Cl$$

The complex once formed, with a further possibility of rearrangement as shown, is susceptible for cleavage with hydrogen chloride. There is no evidence, however, that such complexes indeed exist.

Spectral studies[63,64] have indicated that the ester-exchange reaction has no profound effect in thermal stabilization of PVC and that the stabilization by the organotin compounds (or their cleaved products) may be governed by the ability of the stabilizer to react with unsaturation sites in the polymer. The spectral studies[63] further indicated little or no addition to double bonds (in the polymer) either with organotin esters or the aliphatic acids formed after reaction with hydrogen chloride. Mufti and Poller[65] while demonstrating Diels-Alder reactions of organotin maleates found that such type of Diels-Alder reactions are even more likely with free maleic acid (or its half-esters) liberated from the stabilizers. In case of organotin mercaptides or thioglycolates it is highly probable that the thiols formed from the stabilizer (after reaction with hydrogen chloride) will add to the double bonds either by free radical or ionic mechanism[66-70]. Yamaguchi et al[71] studying the acid-catalyzed addition of thiols to diene polymers have shown that acids are also capable of promoting thiol-addition to double bonds. Another well known and equally important reaction of thiols is the capacity for hydroperoxide decomposition.

It was found that the relative ease of exchange of the X groups in R_2SnX_2 (X=carboxylate or sulfur derivative) with tertiary chlorine atoms in the polymer has no greater effect on their efficiency and that the stabilizing efficiency is decided mostly by their readiness and capacity to exchange with allylic chlorines as well[72,73]. The high efficiency of organotin mercaptides and thioglycolates has been attributed to their readiness to exchange with both types of chlorine atoms efficiently[73,74].

It is well known that the tin atom in organotin compounds, which has normal σ bonds, is capable of forming donor-acceptor (coordination) bonds by participation of its d-orbitals with various nucleophiles (N,S,O etc)[58,64]. Minsker et al[64] have advanced an interesting argument regarding a possible interaction of tin atom with π-bonds of PVC, involving the 5d-orbitals of tin. Accordingly, the π electrons of the conjugated double bond system in the polymer (analogous to the electron pair present on nucleophiles) will form d_π-p_π bonds with the tin atom. The formation of these complexes can be depicted as:

The effect of such complexes would be, obviously, to destabilize conjugated systems.

Internal Stabilization

Another new and definitive approach towards the problem of PVC stabilization is the art of internal stabilization[75]. This involves the incorporation of thermally stable and chlorine-free monomers during the vinyl chloride-polymerization stage itself. The idea is obviously to limit the number of adjacent vinyl chloride units in the polymer backbone.

No apparent difference in the stabilization action seems likely between the stabilizers externally admixed and chemically incorporated. However, it is not clear whether the ligands of the stabilizer replace labile chlorine atom or add to unsaturation sites produced on dehydrochlorination.

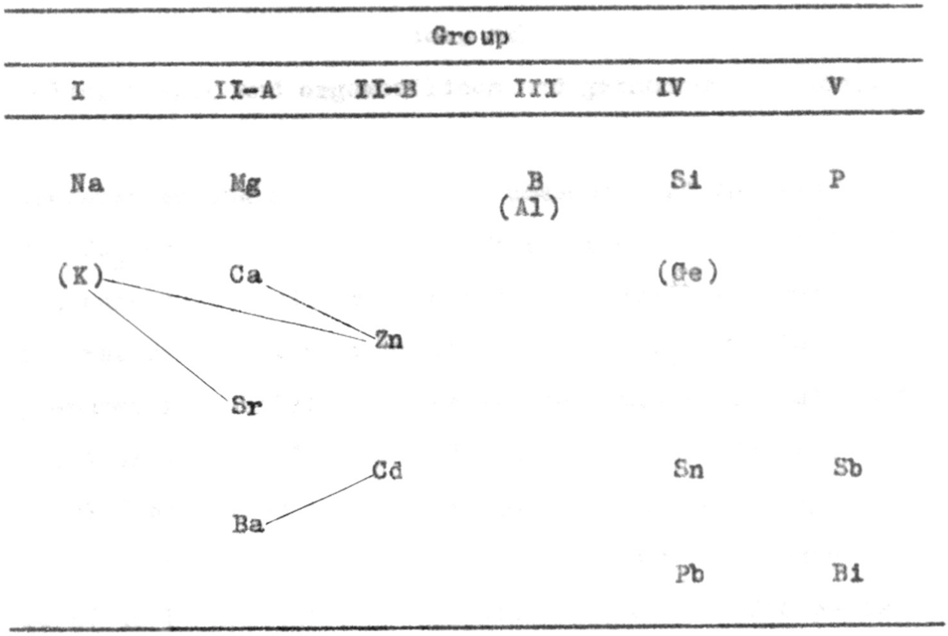
Heat and light stabilized PVC polymers have been obtained by polymerization of vinyl chloride containing 0.1 - 10% polyvalent metal salts of C_6-C_{18} carboxylic acids[76].

The present work was aimed at the synthesis of two new organothiosilicon compounds for evaluation in plasticized PVC as thermal stabilizers. Synergistic combinations of one of the two organothiosilicon compounds were employed with metal soaps as well as an organothiotin thioglycolate.

PRESENT INVESTIGATION AND RESULTS

Polyfunctional organic derivatives of metals, non-metals, and silicon play a major role in the synthesis and stabilization of polymers. The use of these compounds is of paramount importance in the thermal stabilization of poly(vinyl chloride (PVC), one of the oldest and most used thermoplastics. The principal elements on which the stabilizers are based, are shown below.

Periodic arrangement of stabilizer elements[77]



Group					
I	II-A	II-B	III	IV	V
Na	Mg		B (Al)	Si	P
(K)	Ca			(Ge)	
		Zn			
	Sr				
		Cd		Sn	Sb
	Ba				
				Pb	Bi

The fatty acid salts of group II elements invariably are used in sub group A-B couples (as shown in Table above)

Besides lead compounds, currently the most commonly used commercial stabilizers are the fatty acid salts and mercaptides of Ca, Zn, Cd, Ba and tin. Particularly the introduction of mercaptides (alkyl mercaptides and thioglycolates) of tin has been a landmark in thermal stabilization of PVC. The commercial utility and efficiency of organotin compounds, particularly the sulfur derivatives, remains unsurpassed even today.

Apart from tin and lead, the other element in Group-IV whose derivatives have also been used in PVC stabilization is silicon. Some of the organosilicon compounds which have been tried as PVC stabilizers are the silazanes (having Si-N bonds), silyl urethanes, silicon-urea derivatives, polysiloxanes and organosilicon and germanium hydrides.

Willis, in 1965, first patented the use of silazanes, prepared by the ammonolysis of compounds of the type R_2SiCl_2 and $RSiCl_3$, in the stabilization of PVC[78,79]. In the same year, Thinius reported the stabilizing properties of urea derivatives of silicon[80], e.g. $Bu_2Si(NHCONHR)_2$ prepared from silyl diisocyanate and amines, and also of silyl urethanes[81,82]. The following year, Andrianov et al[83] described the use of polysiloxanes and poly (aryl aluminosiloxane) as PVC stabilizers which were found to be effective in an amount 1 part per 100 parts of resin. Sangalov et al[84,85] and Hongu et al[86] have used many organopolysiloxanes for heat resistant PVC resin compositions. Recently, Mironov et al[87] found a composition containing silsesquioxanes with dibutyltin sulfide to impart enhanced heat stability to poly(vinyl chloride). Some silicon and germanium organic hydrides have also been found to delay the thermal decomposition and the onset of discoloration in PVC[88,89].

Tin compounds, mostly the quadrivalent tin derivatives, currently in use as PVC stabilizers, are relatively of high cost. The resources of silicon are more widely distributed in nature unlike than those of tin and thus it is possible that organosilicon stabilizers for PVC would be, comparatively, of lower cost. Although organosilicon compounds, reported so far in literature, are not as efficient as organotin compounds as stabilizers for PVC, it is evident that further work is necessary in this direction.

It is interesting to note that all the organosilicon compounds tested for PVC stabilization so far, had only Si-O and Si-N linkages, and no compounds with Si-S linkage had been tested for their thermal stabilizing action in PVC. With this fact in mind, coupled with the high cost of tin derivatives and ready availability of many silicon compounds, the present study was aimed at synthesizing quadrivalent organosilicon compounds characterized by the presence of two or more Si-S linkages for evaluation as stabilizers for PVC. Two new organothiosilicon compounds, di(phenylthio)diphenyl silane and tris(phenylthio) phenyl silane were synthesized. Of these two, di(phenylthio) diphenyl silane was used in combination with laurates of zinc and calcium and bis(mono-2-ethyl hexyl maleate) of barium and cadmium. A combination of di(phenylthio) diphenyl silane with dibutyltin-S,S'-bis(2-ethylhexyl thioglycolate) was also used. These combinations were evaluated for their thermal stabilizing action in PVC.

(i) Synthesis of Organothiosilicon Compounds

These were synthesized by reacting the corresponding phenylchlorosilane with the sodium salt of thiophenol in benzene.

$$Ph_2SiCl_2 + 2NaSPh \longrightarrow Ph_2Si(SPh)_2 + 2NaCl$$

$$PhSiCl_3 + 3NaSPh \longrightarrow PdSi(SPh)_3 + 3NaCl$$

$Ph_2Si(SPh)_2$, di(phenylthio) diphenyl silane and $PhSi(SPh)_3$, tris(phenylthio) phenyl silane were pale clear yellow colored liquids with index of refraction of 1.614 and 1.643 respectively.

Diphenyl dichlorosilane and phenyl trichlorosilane were synthesized according to the method of Rosenberg et al[90] from silicon tetrachloride and phenyl-magnesium bromide and using 2,2,4-trimethyl pentane as the solvent.

$$PhMgBr + SiCl_4 \rightarrow PhSiCl_3 + MgBrCl$$

$$2PhMgBr + SiCl_4 \rightarrow Ph_2SiCl_2 + 2MgBrCl$$

The physical properties of these are shown overleaf.

Ph_2SiCl_2: b.p. 122°C/2 torr: n_D^{27} 1.577
Yield 53%

$PhSiCl_3$: b.p. 62-65°C/1.5 torr, n_D^{27} 1.524
Yield 55%

(ii) Zinc laurate was synthesized according to the method of Whitmore and Lauro[91] from zinc acetate and sodium laurate in aqueous medium.

$$Zn(OAc)_2 + 2NaO_2C(CH_2)_{10}CH_3 \rightarrow Zn(O_2C(CH_2)_{10}(CH_3)_2 + 2NaOAc$$

m.p. 127°C, white, fluffy powder.

(iii) Calcium laurate was synthesized according to the method of Yoke[92] from calcium chloride and sodium laurate in aqueous medium.

$$CaCl_2 + NaO_2C(CH_2)_{10}CH_3 \rightarrow Ca(O_2C(CH_2)_{10}CH_3)_2$$

m.p. 130°C, white, fluffy powder.

(iv) Cadmium and barium bis(mono-2-ethylhexyl maleate) were synthesized by treating the sodium salt of mono-2-ethyl hexyl maleate with the respective metal chloride in aqueous medium. Both the organometallic compounds were clear, colorless liquids. Their formation may be shown as follows:

$$MCl_2 + NaO_2CCH{=}CHCO_2C_8H_{17} \rightarrow M(O_2CCH{=}CHCO_2C_8H_{17})_2$$

(M= Ba,Cd)

(v) Dibutyltin -S,S'-bis(2-ethyl hexyl thioglycolate) was prepared by the reaction of dibutyltin oxide and 2-ethyl hexyl thioglycolate in benzene. It is a clear colorless liquid.

$$Bu_2SnO + 2HSCH_2COOC_8H_{17} \rightarrow Bu_2Sn(SCH_2COOC_8H_{17})_2$$

Compounding and Testing

The compounding recipe for the evaluation of stabilizers in PVC is shown below:

PVC resin (SR-10 suspension polymer of K value 66)	100 parts
Dioctyl phthalate	50 parts
Stabilizer (or stabilizer composition)*	2 parts
Stearic acid	1 part

* various stabilizer composition used are shown in Table-1

After mixing all the ingredients, sheets were taken out by milling on a two-roll mill. These sheeted out materials were then subjected to oven aging test at 180°C. The results obtained are recorded in Table-2.

<u>Table-1</u>: Different Stabilizer Systems Used in PVC Stabilization Study

Compounds	Systems									
	A	B	C	D	E	F	G	H	I	J
Ph $Si(SPh)_3$	2*									
$Ph_2Si(SPh)_2$		2		1	1	1	1	1		
$Bu_2Sn(SCH_2CO_2C_8H_{17})_2$			2	1						
Zinc laurate					1		0.5		1	
Calcium laurate							0.5		1	
Barium bis(2-ethyl hexyl maleate)						1		0.5		1
Cadmium bis(2-ethyl hexyl maleate)								0.5		1

* Numbers indicate parts per 100 parts of PVC resin.

Table-2: Relative Efficiencies of Different Stabilizer Systems Used

No.	Stabilizer system*	Time at initial discoloration (in minutes)	Time at blackening (in minutes)	Relative efficiency as a thermal stabilizer
1.	A	60	a	Good
2.	B	60	a	Good
3.	C	100	a	Very Good
4.	D	90	a	Very Good
5.	E	-	20	Poor
6.	F	30	a	Fair
7.	G	50	70	Fair
8.	H	50	a	Fair
9.	I	40	50	Fair
10.	J	40	a	Fair

* See Table-1

a = More than 120 minutes.

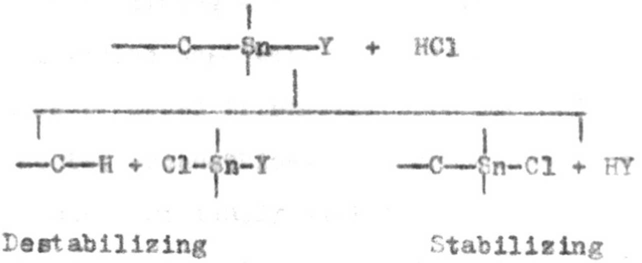
DISCUSSION

The technology of PVC stabilization has developed faster than the efforts made towards the understanding of the mechanism of its thermal degradation. There is general agreement between the available experimental results of a number of workers that the thermal, non-oxidative decomposition of PVC involves sequential loss of hydrogen chloride. This process results in polyene sequences, and these, when of considerable length, lead to undesirable colour in the polymer. A positive catalytic effect of liberated hydrogen chloride on the dehydrochlorination reaction in PVC has also been suggested by Van der Wen and de Wit[19].

Therefore, it is evident that the prime function of a stabilizer should be to offset the balance of evolved hydrogen chloride either by decreasing the rate of dehydrochlorination or by reacting with it, or both. In addition, stabilizing ability of the cleaved products of the stabilizer also contributes to the stabilization of the polymer. The most widely used stabilizers are organometallic compounds of the general formula MY_2 where M can be R_2Sn^{2+} (R=aliphatic), Zn^{2+}, Cd^{2+}, Ba^{2+} or Ca^{2+} whereas Y may be $-OR'$ (alkoxides), $-OCOR'$ (esters), $-SR''$ (mercaptides) or $-SCH_2-R''-COOR'''$ [thioglycolates or mercapto propionates ($R''=CH_2$)]. The most efficient stabilizers in vogue are the organo tin sulfur compounds.

In the present study two organosilicon sulfur compounds were synthesized and evaluated as thermal stabilizers for PVC. They were: di(phenylthio) diphenyl silane (DPTDS) and tris(phenylthio) phenylsilane (TPTPS).

It has been demonstrated that when organotin stabilizers R_2SnY_2 are heated in aprotic, low-polarity solvents with gaseous hydrochloric acid, released at rates comparable with those obtained in degrading PVC, the cleavage of Sn-Y bonds occurs and not R-Sn bonds. Even in excess acid, this mode of cleavage remains unaffected[93]. The cleavage of Sn-Y, and not R-Sn bonds, is of paramount importance in the PVC stabilization process by R_2SnY_2 compounds. These can be shown as follows:



The importance of Sn-Y bond cleavage is readily appreciated because in the cleavage of C-Sn bond, the final product stannic chloride is a powerful catalyst for dehydrochlorination reaction[94].

Organothiotin compounds have been shown to undergo Sn-S bond cleavage by reaction with hydrochloric acid in liquid phase[95,96]. Similarly, organothiosilicon compounds, with dry hydrogen chloride, also undergo facile Si-S cleavage[97]. Such reactions are also possible with the liberated hydrogen chloride in degrading PVC. These reactions can be shown as:

$$R_nM(SR')_{4-n} + (4-n)HCl \rightarrow R_nMCl_{(4-n)} + (4-n)\ HSR'$$

These reactions liberate the corresponding organic thiol, R'SH, which can either act as transfer agents for the termination of radical chain degradation reactions or add directly to double bonds.

Rockett et al[96] while examining similar cleavages of a series of organothiotin compounds with hydrochloric acid in non-aqueous aprotic solvent medium, observed better thermal stabilizing action in PVC for those organothiotins which liberated more thiol (the liberated thiols were estimated by usual titrimetric procedures). It was found that the two organothiosilicon compounds used in the present study behaved similarly yielding the thiol and, further, that the tin compound namely, dibutyltin-S,S'-bis(2-ethyl hexyl thioglycolate) liberated more thiol than either of the two organothiosilicon compounds used, viz., di(phenylthio) diphenyl silane or tris(phenylthio) phenyl silane. The higher efficiency of the tin compound (see Table-2) therefore, may be partly attributed to the above phenomenon.

As there was no difference in the stabilization efficiency between the two organothiosilicon compounds used (see Table-2) and, also because of the ease of its synthesis, di(phenylthio) diphenyl silane was employed for further studies. This included its synergistic combinations with zinc laurate and calcium laurate, barium bis(mono 2-ethyl hexyl maleate) and cadmium bis(mono 2-ethyl hexyl maleate) and their evaluation in PVC for thermal stabilizing action. Also, the combination of di(phenylthio)diphenyl silane with dibutyl tin-S,S'-bis(2-ethyl hexyl thioglycolate) was evaluated as thermal stabilizer in PVC (see Table-1).

The stabilizing efficiency of the mixture of dibutyltin-S,S'-bis(2-ethyl hexyl thioglycolate) and di(phenylthio) diphenyl silane (System 'D' in Table-1) as may be expected, was found to be intermediate of efficiencies of the individual components (the time for initial dicoloration at 180°C for the organothiotin, organothiosilicon and their mixtures was 120', 60' and 90' respectively). It is highly probable that the organothiosilicon compound may function as an absorber of the organotin chloride liberated.

$$Ph_2Si(SPh)_2 + Bu_2SnCl_2 \rightarrow Ph_2SiCl_2 + Bu_2Sn(SPh)_2$$

Such reactions, which involve Si-S bond cleavage, are well known in model systems[98].

Admixture of di(phenylthio) diphenylsilane with metal soaps (Systems E to H in Table-1) was effective in prolonging the time for onset of the initial discoloration period.

But an overall improvement (particularly the time for complete discoloration) which may be expected, was striking particularly for Zn-Ca soap-DPTDS mixture. For example, the time for blackening for PVC with Zn-Ca laurate was 70 minutes whereas addition of DPTDS as the third component increased it to more than 120 minutes. An overall improvement was also noticed with Ba-Cd soap mixture. It may be considered that di(phenylthio) diphenylsilane, added as the third component, will function as a good acceptor of the formed metal chloride (the prodegrading effect of metal chlorides on PVC is well known). These reactions can be written as:

$$Ph_2Si(SPh)_2 + MCl_2 \rightarrow Ph_2SiCl_2 + M(SPh)_2$$

$$(M = Zn, Cd, Ba, Ca)$$

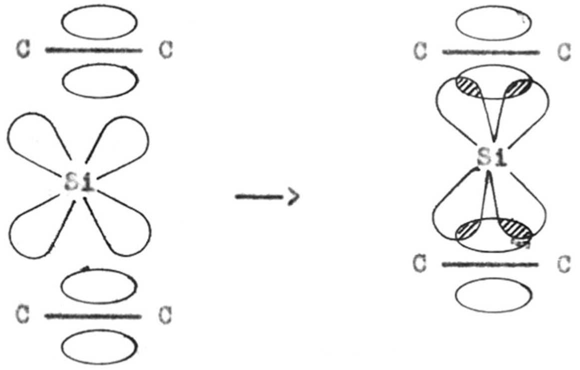
Such types of Si-S bond cleavages in organothiosilicon compounds by metal chlorides have been shown in model systems to result in good yields of metal mercaptides[97,99]. These metal mercaptides may also function as auxillary stabilizers. The effect of formed organosilicon chloride on the stability of PVC is, however, not clear.

Abel et al[100] have shown that alkyl chlorides are also capable of reacting with organothiosilicon compounds involving Si-S bond cleavage. Such reactions are, however, very slow compared to alkyl bromides or iodides.

Minsker et al[64] suggested the formation of d_π-p_π

type complexes between the tin atom in organotin compounds and the double bonds in degrading PVC. Such types of donor-acceptor complexes may be considered to be formed involving the filled π-orbitals of double bonds in PVC and the empty 5d-orbitals of tin atom. Silicon is also capable of forming similar d_π-p_π bonds. Intramolecular d_π-p_π bonding between 3d orbitals of silicon and π-electrons of nucleophiles (S, N, O etc.) has been shown to be possible by bond length-measurement and spectral studies[97,101,102]. Stone and Seyfreth[103] also consider intramolecular d_π-p_π bonding in vinyl silanes involving empty d-orbitals of silicon and π-electrons of the double bond. Based on these evidences, we envisage the probable formation of Minsker-type d_π-p_π complexes which involve π-electrons of the unsaturation sites in the polymer and empty 3d-orbitals of silicon, as shown below.

Using molecular orbital picture, the formation of the complex may be visualized as:



The effect of the formation of such a complex might be to destabilize the extended conjugation in the polymer.

EXPERIMENTAL

Materials

Ether refers to diethyl ether dried over anhydrous calcium chloride, distilled over sodium and stored over sodium wire.

Magnesium used was of Grignard reagent grade. It was washed with several portions of dry ether and after drying at 60-70°C was immediately used.

Silicon tetrachloride (b.p. 55°C) was carefully distilled and the portion boiling between 55-56°C was collected and used.

Bromobenzene, benzene and 2,2,4-trimethyl pentane were purified by known methods in the literature.

Lauric acid, zinc acetate, calcium chloride and dibutyltin oxide were used without further purification. Maleic anhydride was purified as described on page

PVC used was a suspension polymer of K-value 66 and chlorine content of 57.47%.

Methods

Preparation of Phenyl magnesium bromide

In a flame-dried 3-necked flask equipped with a mechanical stirrer, an addition funnel and a reflux condenser were placed magnesium turnings (2.5 g, 0.1 g atom) and ether (10 ml). Bromobenzene (5.0 g) in ether (25 ml) was slowly added into the flask followed by ethyl bromide (1 ml, synthesized from ethyl alcohol and hydrobromic acid). The flask was externally warmed for a short period with warm water to initiate the reaction which, once initiated, proceeded vigorously, and the colour of the reaction mixture turned brown. Another portion of bromobenzene (10.7 g) in ether (50 ml) was added dropwise, with vigorous stirring, to maintain a steady reflux. After the completion of addition, the reaction mixture was gently refluxed for further 2 hours. The resulting solution, which was clear brown, was used as such for further reactions. Yield: 75-80%.

Preparation of Phenyl Trichlorosilane

In a dry 4-necked round bottomed flask, equipped with a stirrer, a thermowell, an addition funnel and a reflux condenser carrying a $CaCl_2$-guard tube, were placed silicon tetrachloride (30 g) and 2,2,4-trimethyl pentane (75 ml). The ethereal solution of phenyl magnesium bromide prepared above was added dropwise with efficient stirring. Immediate discharge of the brown colour of phenyl magnesium bromide and the precipitation of magnesium salts in the flask was observed. The temperature was maintained at 40-45°C throughout the addition to minimize silicon tetrachloride escape. After the addition of the Grignard reagent, the reaction mixture was refluxed for 6 hours, cooled and filtered through a dry Buchner funnel as quickly as possible. The precipitate was washed several times with 2,2,4-trimethyl pentane, and from the filtrate were distilled off excess silicon tetrachloride and 2,2,4-trimethyl pentane under reduced pressure. The residue was transferred to a 50 ml dry flask and was vacuum distilled to yield phenyl trichlorosilane. Yield 55% (about 6-7% of diphenyl dichlorosilane was also obtained as other product).

b.p. 62-65°C/1.5 torr. n_D^{27} 1.524

Anal. $C_6H_5SiCl_3$ Requires: Cl, 50.28%, Si, 11.69%
Found : Cl, 49.43%, Si, 11.58%

IR Spectrum (Liquid Film): 1120 (Si-C); 1430, 1490 and 1590 cm^{-1} (Phenyl ring absorptions).

Diphenyl dichlorosilane

This was prepared from silicon tetrachloride (7.5 g) and phenyl magnesium bromide (prepared from 15.7 g of bromobenzene and 2.5 g magnesium) using the same procedure described for the preparation of phenyl trichlorosilane. Yield: 53%. b.p. 122°C/2 torr. n_D^{27} 1.577

Anal: $C_{12}H_{10}SiCl_2$ Requires: Cl, 28.02%, Si, 11.06%
Found : Cl, 27.90%, Si, 11.02%

Synthesis of tris(phenylthio)phenyl silane

Into a solution of benzenethiol (2.2 g) in ether (50 ml) was added dry pieces of sodium (0.5 to 0.7 g) followed by more ether. After a period of 2-3 hours, ether was distilled off and the white suspension of sodium benzenethiolate was taken up in benzene (50 ml).

Phenyltrichlorosilane (2.02 g) in benzene (10 ml) was added with stirring at room temperature to benzene-sodium benzenethiolate dispersion. The addition was exothermic. After the addition, the reaction mixture was refluxed for 6 hours, cooled and filtered. After removing benzene under reduced pressure, the residue was fractionally vacuum-distilled to yield tris(phenylthio)phenylsilane, a pale-yellow coloured, clear liquid. Absence of hydrolyzable chlorine was confirmed by titration with alkali.

b.p. 280-290°C (bath)/6-7 torr. n_D^{27} 1.643

Anal: $C_{24}H_{20}S_3Si$ Requires: Si, 6.5%

Found : Si, 6.41%

IR Spectrum (Fig.6.1)(Liquid film): 1120(Si-phenyl), 1440, 1490 and 1590 cm^{-1} (phenyl ring absorptions). The bands at 1120 cm^{-1} and 1430-1440 cm^{-1} are characteristic of silicon-phenyl absorptions.

Synthesis of di(phenylthio)diphenyl silane

This was prepared from diphenyl dichlorosilane (2.5 g) and sodium benzenethiolate (prepared from 2.2 g benzenethiol and 0.5 - 0.7 g sodium) using the procedure described for the synthesis of tris(phenylthio)phenyl silane.

b.p. 230°C (bath)/9 torr. n_D^{27} 1.614, d 1.085

Molar Refraction: Calcd: 127.28: Found: 127.6

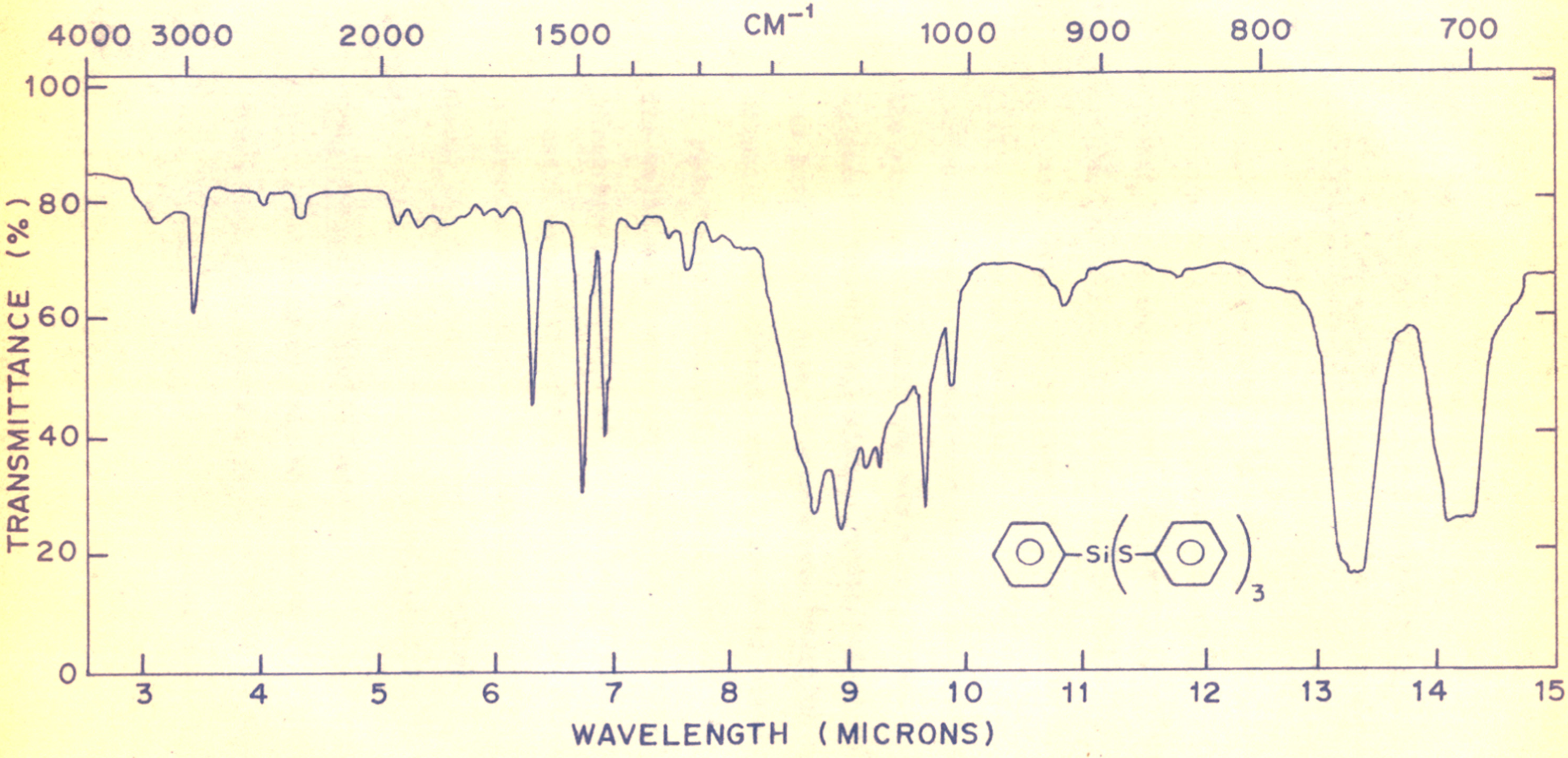


FIG. 6·1 IR SPECTRUM OF TRIS (PHENYLTHIO) PHENYLSILANE

Anal: $C_{24}H_{20}S_2Si$ Requires: Si, 7.02%
Found : Si, 6.91%

Preparation of Zinc Laurate

Into a solution of lauric acid (2.0 g) in alcohol (25 ml) was added from a burette a 0.2 N alcoholic sodium hydroxide to a phenolphthalein end point. Bulk of the alcohol was evaporated and the total volume of the contents was made upto 150 ml with distilled water.

Separately was prepared a solution of zinc acetate (1.1 g) in water (30 ml).

Both the solutions were warmed separately to 60°C and the zinc acetate solution was slowly added with stirring to sodium laurate solution. Precipitation of zinc laurate was immediate. After the complete addition of zinc acetate solution, the contents were allowed to stand for 2 hours at room temperature and filtered through a Buckner funnel. The solid was washed many times with water, then with three small portions of ethyl alcohol and finally once with a small amount of ether, and allowed to air-dry. The product was fluffy, white powder. m.p. 127°C.

Anal: $C_{24}H_{46}O_4Zn$: Requires: Zn, 14.11%
Found : Zn, 14.02%

Preparation of Calcium Laurate

A solution of calcium chloride (0.7 g) in water (25 ml) was added with stirring to a solution of sodium laurate [prepared from lauric acid (2.0 g) as described in the preceding synthesis] in water (150 ml). Precipitation of calcium laurate was immediate. After complete addition, the contents were allowed to stand for 2 hours at room temperature and filtered through a Buchner funnel. The solid was washed several times with water until the washings gave no precipitation or turbidity with silver nitrate solution. Then washed with 2-3 small portions of ethyl alcohol and air-dried. The product was a fluffy, white powder. m.p. 130°C.

Anal: $C_{24}H_{46}O_4Ca$ Requires: C, 64.63%, H, 12.11%
Found : C, 64.87%, H, 11.03%

Preparation of Cadmium bis(mono 2-ethylhexyl maleate)

Into a solution of pure maleic anhydride (9.8 g, 0.102 mole) in benzene (50 ml) in a 100 ml round bottomed flask was added 2-ethyl hexanol (13.0 g, 0.1 mole) and refluxed for 3 hours. At the end of the reaction, benzene was distilled off and the reaction mixture, after being transferred to a 500 ml beaker, was neutralized with saturated aqueous sodium carbonate solution. The aqueous solution of sodium salt of the organic acid was extracted several times with ether to remove starting material impurities. To the aqueous solution of the sodium salt was added with stirring an aqueous solution of cadmium chloride. The cadmium salt of the organic acid (half-ester of maleic acid) separated and started collecting at the bottom. After the complete addition of cadmium chloride the upper aqueous layer was decanted off and the product was dissolved in petroleum ether (60-80°C), dried over anhydrous sodium sulfate and finally the solvent was removed under reduced pressure.

Anal: $C_{24}H_{38}O_8Cd$ Requires: C, 50.85%, H, 6.71%, Cd, 21.68%

Found : C, 50.73%, H, 6.33%, Cd, 21.53%

Preparation of Barium bis(mono 2-ethyl hexylmaleate)

This was prepared from barium chloride and the sodium salt of 2-ethyl hexyl maleate as described in the preceding synthesis.

Anal: $C_{24}H_{38}O_8Ba$ Requires: C, 48.71%, H, 6.43%

Found : C, 48.53%, H, 5.98%

Preparation of Dibutyltin-S,S'-bis(2-ethyl hexyl thioglycolate)

Into a benzene solution of dibutyltinoxide (2.48 g, 0.01 mole) placed in a flask equipped with a Dean-Stark azeotropic apparatus was added 2-ethyl hexyl thioglycolate (4.08 g, 0.02 mole). The reaction mixture was refluxed to remove all water azeotropically, cooled and filtered. From the filtrate, benzene was stripped off under reduced pressure to yield the product, a colourless liquid.

Anal: $C_{28}H_{56}O_4S_2Sn$: Requires: Sn, 18.59%

Found : Sn, 18.48%

IR Spectrum: 1730 cm^{-1} (C=O)

Compounding and Testing: The following compounding recipe was used to evaluate the stabilizers and stabilizer compositions (shown in Table-1) in PVC.

PVC resin	100 g
Dioctyl phthalate (DOP)	50 g
Stabilizer	2 g
Stearic acid	1 g

Stearic acid and a stabilizer (or the stabilizer composition) were added to DOP (plasticizer) and thoroughly blended with PVC. A sheet of thickness 0.01 - 0.02" was taken out on a laboratory 2-roll mixing mill after milling for 8 minutes at 120°C. From this sheet were cut out pieces of size 1" x 2", kept on clean dry glass plates and heat aged in an oven at 180°C. Heat-aged samples were removed at regular time intervals and the colour developed were compared visually. These results have been recorded in Table-2.

Analytical Methods

Estimation of Grignard Reagent[104,105]

An aliquot of phenyl magnesium bromide solution (in a small volume of ether) was transferred to a 100 ml volumetric flask and diluted to the mark with dry tetrahydrofuran. 2 ml aliquots were carefully and quickly pipetted out into 500 ml conical flasks containing distilled water (50 ml). One flask served as control. 0.5 N sulfuric acid (50 ml) was pipetted out into each flask and heated on a water bath at 60-70°C for 30 minutes, cooled and titrated against standard sodium hydroxide solution using phenolphthalein as an indicator.

Estimation of Hydrolyzable Chlorine in Chlorosilanes[106]

Accurately weighed samples were carefully dissolved in dry methyl, ethyl, or isopropylalcohol (20 ml) contained in iodine flasks, and the flasks were immediately securely stoppered. Distilled water (50 ml) was carefully added and titrated against standard sodium hydroxide solution using phenolphthalein as an indicator.

Gravimetric Analysis for Silicon[107]

An accurately weighed amount of the organosilicon compound was digested with A.R sulfuric acid (1-1.5 ml) in a crucible. After evaporating the acid with a low flame, the crucible was heated for further 30-40 minutes with a full flame, cooled and weighed again.

Gravimetric Analysis for Tin[108]

Tin in the organotin compound was determined as tin oxide by digesting the compound with a small amount of a mixture of concentrated nitric acid (3 volumes) and concentrated sulfuric acid (2 volumes).

Analysis for Zn and Cadmium in Organozinc and Organocadmium Compounds respectively[109,110]

Zinc or cadmium were determined as the corresponding oxides by oxidation with nitric acid. The organometallic compound was slowly digested with a few drops of concentrated nitric acid till the brown fumes of the acid evolved no longer. Then heated with a full flame for a constant weight.

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