STUDIES IN POLYMERIZATION OF ACRYLAMIDE; MODIFIED ACRYLAMIDES AND POLYMERS THEREFROM

A THESIS

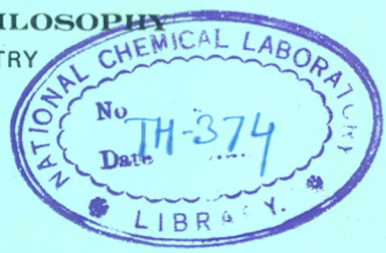
SUBMITTED TO THE

UNIVERSITY OF POONA

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY



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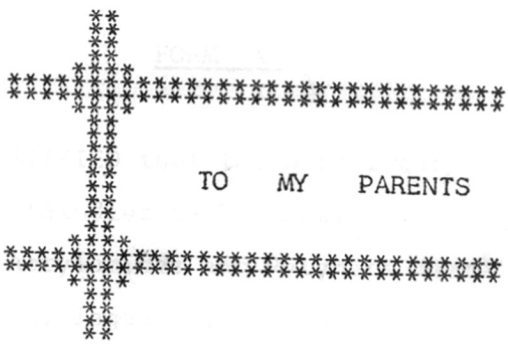
TO MY PARENTS

FORM 'A'

CERTIFIED that the work incorporated in thesis entitled, 'Studies in Polymerization of Acrylamide; Modified Acrylamides and Polymers therefrom' submitted by Shri S.M. Jagadale, was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

[N.D.Ghatge]
Supervisor

C O N T E N T S

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A C K N O W L E D G E M E N T

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Sjagadale 27/4/83

[S.M.Jagadale]

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GENERAL REMARKS

1. All melting points are uncorrected.
2. The NMR spectra are recorded in DMSO-d_6 using TMS as an internal standard on Perkin-Elmer R-32 model.
3. The IR spectra are recorded as nujol mulls on either Perkin-Elmer E 137 or Pye Unicam SP-300 infrared spectrophotometer, with sodium chloride optics.
4. Elemental analysis of compounds is carried out by microanalytical procedures for carbon, hydrogen, nitrogen and sulfur.
5. The list of References pertaining to each part is given at the end of that part.

GENERAL INTRODUCTION

INTRODUCTION

The acrylamide family of monomers is a highly versatile group of chemical intermediates. The major use of these monomers is in the preparation of polymers and copolymers having a highly polar functional groupsattached to the backbone.

Acrylamide, (2-propeneamide, $CH_2=CH-CONH_2$), a white crystalline solid, prepared by Moureu in 1893 from acryloyl chloride and ammonia, became available commercially in 1940.

Linear polyacrylamide is a hard glassy or porous solid, extremely soluble in water and most aqueous solutions of electrolytes, but insoluble in most of the polar organic solvents. By replacing one or both of the hydrogen atoms attached to the nitrogen atom of acrylamide molecule by organic groups, products with increasing solubility in organic solvents and decreasing water solubility are obtained. The polyacrylamide products range from insoluble solids through rubbery and mushy gels to soluble products. Many of the polymers and copolymers of acrylamide may be cured by thermal or chemical methods.

In recent years, acrylamide has gained increasing industrial importance as a monomer and as a chemical intermediate. Polyacrylamide is useful as a flocculant[1], as a thickening agent[2], as a pigment retention aid in paper making[3], hydraulic fracturing of oil well, in secondary oil recovery of oil wells[4] etc.

Preparation of Acrylamide

The methods of preparation for acrylamide are :

A) From Acrylonitrile

(1) Acrylonitrile is the preferred starting material because of its low cost and ready conversion to acrylamide sulfate by the use of sulfuric acid at a concentration corresponding to its monohydrate.

$$CH_2=CH-CN + H_2SO_4 \cdot H_2O \longrightarrow CH_2=CH-CONH_2 \cdot H_2SO_4$$

Acrylamide sulfate

The addition of acrylonitrile to sulfuric acid is strongly exothermic reaction and is complete in about an hour at 90-100°C[5] or in 4-7 min. at 150-200°C[6]. The heat of reaction is 31 Kcal/mole including heats of mixing of reactants[7].

It is necessary to use a polymerization inhibitor that is not affected by the strongly acidic medium. Copper and iron salts are particularly useful for this purpose. The use of resorcinol has also been claimed as effective inhibitor[8].

Several methods have been available for the isolation of pure acrylamide from acrylamide sulfate[9-16].

Aqueous hydrochloric acid can be used as a substitute for sulfuric acid in the reaction with acrylonitrile[17].

$$CH_2=CH-CN + HCl \xrightarrow{H_2O} ClCH_2-CH_2-CONH_2$$

$$ClCH_2-CH_2-CONH_2 + NaOH \xrightarrow{H_2O} CH_2=CH-CONH_2 + NaCl + H_2O$$

Ethylene cyanohydrin may be substituted for acrylonitrile as a starting material. By treatment with 100% sulfuric acid it gives sulfate of 3-hydroxypropionamide, which upon treatment with ammonium sulfate gives acrylamide[18].

$$HOCH_2\text{-}CH_2\text{-}CN + H_2SO_4 \longrightarrow HO_3S\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CONH_2$$

$$HO_3S\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CONH_2 + (NH_4)_2SO_4 \xrightarrow{\Delta} CH_2{=}CH\text{-}CONH_2 + 2NH_4HSO_4$$

Another approach is to isolate 3-hydroxypropionamide and subject it to catalytic dehydration at 155°C[5].

$$HO\text{-}CH_2\text{-}CH_2\text{-}CONH_2 \xrightarrow[155^\circ C]{Na_2CO_3} CH_2{=}CH\text{-}CONH_2 + H_2O$$

(2) Direct Methods

i) Hydrolysis of an aqueous solution of acrylonitrile on Dowex 50 sulfonic acid ion exchange resin yields dilute acrylamide solution[19].

ii) Acrylamide has been prepared by hydration of acrylonitrile over manganese dioxide[20]. Transition metal chromates are also reported as hydration catalysts[21,22].

iii) Acrylamide has been prepared with an increased yield by hydrolysis of acrylonitrile at 80-160°C in the presence of copperoxide-zincoxide-aluminiumtrioxide catalyst[23].

(3) By using Micro-Organism

Acrylamide is produced in an aqueous medium by Corynebacterium or Nacardia strains capable of hydrolyzing

acrylonitrile[24]. Acrylamide obtained contains no unreacted acrylonitrile and no by-products such as acrylic acid.

B). Miscellaneous Methods

(1) The first reported preparation of acrylamide is the reaction of acryloyl chloride with dry ammonia in benzene.

$$CH_2=CH-COCl + 2NH_3 \longrightarrow CH_2=CH-CONH_2 + NH_4Cl$$

Similarly, acrylic anhydride can be used[25].

$$(CH_2=CH-CO)_2O + 2NH_3 \longrightarrow 2CH_2=CH-CONH_2 + H_2O$$

(2) Reaction of acryloyl isocyanate with water gives acrylamide[26].

$$CH_2=CH-CONCO + H_2O \longrightarrow CH_2=CH-CONH_2 + CO_2\uparrow$$

(3) Esters of acrylic acid with ammonia are converted to 3-aminopropionamides, which on pyrolysis yields acrylamide[27].

$$3CH_2=CH-COOCH_3 + 4NH_3 \longrightarrow N(-CH_2-CH_2-CONH_2)_3 + 3CH_3OH.$$

$$N(-CH_2-CH_2-CONH_2)_3 \xrightarrow{\Delta} 3CH_2=CHCONH_2 + NH_3$$

(4) By pyrolysis of 3-alkyloxypropionamides in the presence of catalysts such as lithium phosphate,, titanium dioxide etc.[28,29].

$$R-O-CH_2-CH_2-CONH_2 \xrightarrow{\Delta} CH_2=CH-CONH_2 + ROH$$

(5) Acrylamide may also be prepared from acrylic esters

by interchange with acetamide[30].

$$CH_2{=}CH{-}COOCH_3 + CH_3{-}CONH_2 \longrightarrow CH_2{=}CH{-}CONH_2 + CH_3COOCH_3$$

(6) Acrylic acid with ammonia in presence of dehydration catalyst gives acrylamide[31].

$$CH_2{=}CH{-}COOH + NH_3 \xrightarrow{H_3PO_4} CH_2{=}CH{-}CONH_2 + H_2O$$

(7) The reaction of acetylene with carbon monoxide and ammonia, yields acrylamide[32].

$$CH{\equiv}CH + CO + NH_3 \longrightarrow CH_2{=}CH{-}CONH_2$$

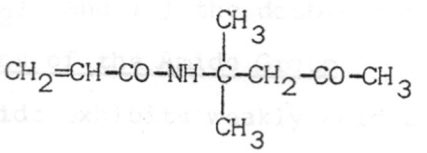
Preparation of N-Substituted Acrylamides

1) Condensation of acrylonitrile with formaldehyde in presence of excess of 85% sulfuric acid gives N,N'-methylene-bisacrylamide[33].

$$2CH_2{=}CH{-}CN + HCHO \xrightarrow{H_2SO_4} (CH_2{=}CH{-}CO{-}NH)_2CH_2$$

2) Diacetone acrylamide is obtained by reaction of acrylonitrile with acetone and sulfuric acid[34].

$$CH_2{=}CH{-}CO{-}NH_2 + 2CH_3{-}CO{-}CH_3 \xrightarrow{H_2SO_4}$$



Diacetone acrylamide

3) By the reaction of appropriate secondary amine with cold acryloyl chloride, N,N'-disubstituted acrylamides are formed[35].

$$CH_2=CH-COCl + R-NH-R' \longrightarrow CH_2=CH-CO-NRR' + HCl$$

4) N-Aryl-N'-acryloylureas are prepared as below :

The reaction of aryl isocyanate with acrylamide in o-dichlorobenzene at 150°C[36];

$$CH_2=CH-CONH_2 + Ar-NCO \xrightarrow{150^{\circ}C} CH_2=CH-CO-NH-CO-NH-Ar$$

or by the reaction[37]

$$CH_2=CH-CO.NCO + Ar-NH_2 \longrightarrow CH_2=CH-CO-NH-CO-NH-Ar$$

5) N,N'-Oxydimethylenebisacrylamide is obtained from N-methylolacrylamide by using p-toluensulfonic acid (p-TSA) as the catalyst in dioxane or in ethyl acetate[38].

$$2CH_2=CH-CONH-CH_2OH \xrightarrow[Dioxane]{p\text{-}TSA} (CH_2=CH-CO-NH-CH_2)_2O+H_2O$$

Physical properties of Acrylamide

The physical properties of acrylamide are listed in Table-1[39].

Chemical Reactions of Acrylamide

Acrylamide contains two reactive centres, i) the amide group ($-CONH_2$) and ii) the double bond.

Reactions of the Amide Group

1) Acrylamide exhibits weakly acidic and basic properties.

Table 1 : Physical properties of acrylamide[39]

1] Molecular weight	71.08
2] Melting point	84.5±0.3°C
3] Vapour pressure	0.007 mm at 25°C
4] Boiling point	125°C at 25 mm
5] Heat of polymerization	19.8 Kcal/mole
6] Density	1.122 g/ml at 30°C
7] Crystal system	monoclinic or triclinic
8] Solubility	g/100 ml solvent at 30°C
Acetone	63.10
Benzene	0.346
Chloroform	2.66
Ethanol	86.20
Ethyl acetate	12.60
n-Heptane	0.0068
Methanol	155.00
Water	215.50

It forms a sulfate salt with sulfuric acid[40] and a potassium salt by reaction with potassium tert-butoxide in tert-butyl alcohol at room temperature[41].

2) By hydrolysis with acidic or basic catalyst acrylamide gives acrylic acid and acrylate ion respectively[40].

$$CH_2=CH-CONH_2 \xrightarrow{H^+ \text{ or } OH^-} CH_2=CH-COOH \text{ (or } CH_2=CH-COO^-) + NH_3$$

3) Acrylamide on treatment with a strong dehydrating agent such as phosphorus pentoxide gives acrylonitrile[42].

$$CH_2=CH-CONH_2 \xrightarrow{P_2O_5} CH_2=CH-CN + H_2O$$

4) Acrylamide reacts with aqueous sodium hypochlorite to form N-chloroacrylamide, a strongly irritating substance[43].

$$CH_2=CH-CONH_2 \xrightarrow{NaOCl} CH_2=CH-CONHCl$$

5) Reaction of acrylamide with formaldehyde under basic condition yields N-methylol derivative[44].

$$CH_2=CH-CONH_2 + HCHO \xrightarrow[\text{aqueous}]{\text{pH 7-9}} CH_2=CH-CONH-CH_2OH$$

This on acidification reacts with additional acrylamide to yield N,N'-methylenebisacrylamide.

$$CH_2=CH-CONH-CH_2OH + CH_2=CH-CONH_2 \downarrow$$

$$(CH_2=CH-CONH)_2CH_2 + H_2O$$

6) Chloral on reaction with acrylamide in carbon tetra chloride gives N-(1-hydroxy-2,2,2-trichloroethyl) acid amide[45].

$$Cl_3C\text{-}CHO + CH_2\text{=}CH\text{-}CONH_2 \longrightarrow CH_2\text{=}CH\text{-}CONH\text{-}CH(OH)\text{-}CCl_3$$

ii) Reactions of the Double Bond

1) Halogens add to the double bond of acrylamide. This reaction is quantitative in the case of bromine and is used as a method of analysis[43].

$$CH_2\text{=}CH\text{-}CONH_2 + Br_2 \longrightarrow CH_2Br\text{-}CHBr\text{-}CONH_2$$

2) Hydroxy compounds add readily to acrylamide in presence of a base[40].

$$CH_2\text{=}CH\text{-}CONH_2 + ROH \xrightarrow{RONa} ROCH_2\text{-}CH_2\text{-}CONH_2$$

3) Acrylamide reacts with amines[40] as follows :

i) Primary amines give mono or bis adduct without catalyst.

$$nCH_2\text{=}CH\text{-}CONH_2 + RNH_2 \longrightarrow RNH_{\overline{2-n}}(CH_2\text{-}CH_2\text{-}CONH_2)_n$$

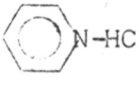
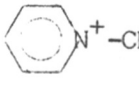
where n = 1 or 2

ii) Secondary amines give only a mono adduct.

iii) Ammonia gives 3,3',3'' -nitrilotrispropionamide.

$$3CH_2\text{=}CH\text{-}CONH_2 + NH_3 \longrightarrow N(\text{-}CH_2\text{-}CH_2\text{-}CONH_2)_3$$

iv) Tertiary amine salts yield quaternary ammonium adducts.

$$CH_2\text{=}CH\text{-}CONH_2 + \text{  } \longrightarrow \text{  } + Cl^-$$

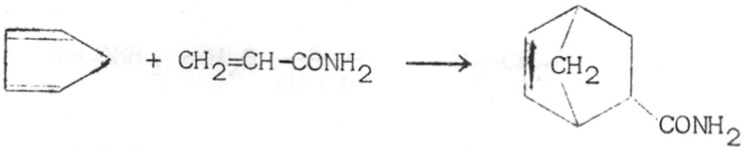
4) By reaction with sodium sulfite or bisulfite, acrylamide yields sodium-β-sulfopropionamide[43].

$$CH_2{=}CH{-}CONH_2 + NaHSO_3 \longrightarrow NaO_3S{-}CH_2{-}CH_2{-}CONH_2$$

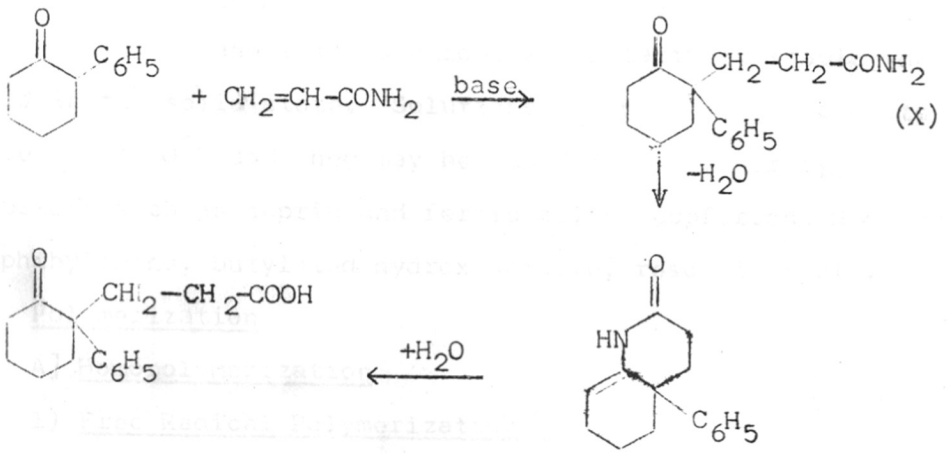
5) Acrylamide with hydrogen halides gives 3-halopropionamide[46].

$$CH_2{=}CH{-}CONH_2 + HX \longrightarrow XCH_2{-}CH_2{-}CONH_2$$

6) Acrylamide reacts with dienes to give the Diels-Alder addition product[43].



7) Activated Ketone reacts with acrylamide to yield adduct 'X' which cyclizes to lactam[47]. The lactam can be hydrolyzed to yield substituted propionic acid.



8) Acrylamide reacts with nitroform in presence of sodium acetate[48].

$$CH_2=CH-CONH_2 + HC(NO_2)_3 \longrightarrow (O_2N)_3C-CH_2-CH_2-CONH_2$$

9) Electrolytic hydrodimerization of acrylamide with adipamide yields a tail-to-tail dimer rather than a polymer[49].

$$2CH_2=CH-CONH_2 + 2H_2O + 2\bar{e} \longrightarrow (H_2N-CO-CH_2-CH_2)_2 + 2OH^-$$

10) Acrylamide reacts with hydrogen sulfide in an aqueous medium to give β,β'-thiobispropionamide[50].

$$2CH_2=CH-CONH_2 + H_2S \xrightarrow[pH < 8]{H_2O} S(CH_2-CH_2-CONH_2)_2$$

Handling and Storage

Because of the neurotoxic nature of acrylamide and its skin-irritating property, precautions must be taken to avoid the contact.

Acrylamide and related amides are relatively stable when stored in the solid state. Solutions of acrylamide are quite stable below 50°C and they may be stabilized further by using inhibitors such as cupric and ferric salts, cupferron, N-phenyl-2-naphthylamine, butylated hydroxyanisole, resorcinol, etc.

Polymerization

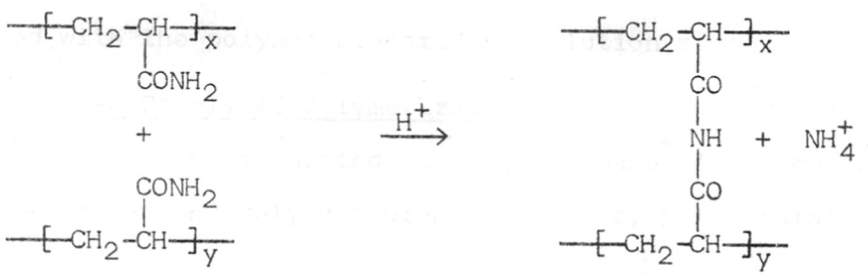
A] Homopolymerization

1) Free Radical Polymerization

Acrylamide polymerizes rapidly by free radicals to high molecular weight polymers. The common initiators used are

peroxides, azo compounds, redox pairs, photochemical system, X-rays and ultrasonic energy[51]. Aqueous polymerization is generally the preferred method.

Polymerization may be carried out in 10-30% aqueous solution at 30-60°C using catalyst concentrations 0.01-1.0% at pH 3-6. The polymer may be recovered by precipitation and extraction with methanol or acetone. The molecular weight of the polymer may be reduced by the addition of a chain transfer agent such as alcohol, mercaptan or some inorganic salts. At pH 9 or above the hydrolysis of the amide group is accomplished while at pH 2.5 or below, imidization may occurs, which forms crosslinking as shown below :



Organic solvents may be used as polymerization media. The polymer precipitation in solvent limits the maximum molecular weight build-up.

2) Solid-State Polymerization

There are reports on the mechanism of solid-state polymerization of acrylamide initiated by ionization radiation[52,53].

If the monomer is irradiated with gamma rays and is then removed from the source, the polymerization continues for many months. Microscopical and x-ray studies showed that both crystalline and amorphous phases are present until all of the monomer has been converted. X-ray studies showed no crystallinity in the polymer, but the morphology of the original monomer crystal may be retained and the polymer may be birefringent.

This polymerization is free radical in nature but is quite different from liquid state reactions. Initiation occurs at crystal imperfections. Propogation may continue at polymer-monomer interface. Termination is prevented by unfavourable disposition of growing polymer chains in the relatively immobile matrix.

Polymer obtained have relatively low molecular weight as compared with the polymer prepared by solution method.

3) Base Catalyzed Polymerization

If acrylamide is heated with strong base[54,55], the polymer obtained has an entirely different structure, poly-β-alanine (nylon-3).

$$n CH_2=CH-CONH_2 \xrightarrow{\text{Base}} -\left[-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH-\right]_n$$

This polyamide is clearly distinguishable from ordinary polyacrylamide by its general physical properties, its infrared spectrum and by the formation on hydrolysis of the amino acid-β-alanine[54,56]. The molecular weights obtained are 50,000 to 1,00,000, but not millions as with free radical initiated polymers.

Anionic polymerization through the double bond, as distinct from poly-β-alanine formation, yields a series of crystallizable polyacrylamides when N,N'-disubstituted monomers are used[34]. Preferred catalysts are metal alkyls dispersed in hydrocarbons. The polymers are distinguished from their free radical-initiated counterparts by their X-ray diffraction patterns, by their infrared spectra, by high melting or softening points and by reduced solubility. The configuration of these polymers is thought to be isotatic[34].

B] Copolymerization

The copolymerization of acrylamide occurs readily with acrylates, methacrylates and most of the styrene derivatives; but acrylamide does not copolymerize readily with vinyl halides.

The amide group is electron withdrawing and activates the double bond. In copolymerization N-substituted derivatives[57] are less reactive than acrylamide itself due to substitution on nitrogen atom which causes, the reactivity of the amide radical to decrease and the polarity of the double bond to become less positive.

Copolymerization of acrylamide in aqueous solution gives the highest molecular weight copolymers and the molecular weight of the copolymer is lower than can be achieved with acrylamide alone.

Co-polymerization of acrylamide with N,N'-methylenebis-acrylamide produces a polymer gel with a nearly uniform distribution of pendent methyleneacrylamide groups. The pendent

double bonds have the same reactivity as the first double bond of the monomer except for the restriction of mobility[58].

C] Graft and Block Polymerization

Acrylamide and its derivatives have been grafted onto numerous substrates for the purpose of increasing hydrophilicity, altering crystallinity or providing a reactive site. Grafts are initiated by chemical free radical sources, ultraviolet light or x-rays. Substrates include starch, cellulose, polyolefins, polyvinyl chloride, polyvinyl alcohol, acrylics, polyesters, polysaccharides, polyamides, urethanes, etc.

Block polymers of acrylamides are rare. They may be prepared by mechanical or ultrasonic degradation of polymer in the presence of acrylamide monomer[59] or by incorporating a reactive end group in the base polymer[60].

Monomers such as styrene, acrylic acid, acrylonitrile, vinylchloride or ethylene oxide may be grafted onto polyacrylamide containing substrate. The vinyl-type monomers are grafted using free radical catalysts[61] and ethylene oxide with acidic or basic catalysts[62].

Applications of Polyacrylamide

Acrylamide and its polymers are building blocks for industries because of their reactivity and versatility. The vinyl group offers ease of polymerization or copolymerization to a variety of products and molecular weights. The amide group offers a reactive site to change the ionic character or

to crosslink the polymer. Theoretically, polyacrylamide should be nonionic; however, in practice, aqueous polymerization or polymer solutions provide a small degree of hydrolysis and result in a mildly ionic polymer.

Polymers of acrylamide are water soluble over a broad range of conditions, making them adaptable to many processes. There are several end uses ; the largest application is liquid-solid separation, where the polymer is flocculant and aids in processing minerals in mining, waste treatment and water treatment for municipalities or industry. Flocculation is the agglomerization of particles into larger units called flocs, which normally settle and filter easily due to their increased size. Flocculation can occur because of polymer adsorption by ionic bonding, charge neutralization or inter-particle bridging. Polyacrylamides are extensively used as chemical additives or processing aids in the manufacturing of paper and paperboard products.

Another major use of polyacrylamide, which is increasing in importance because of the energy crisis, is enhanced oil recovery. An anionic polymer solution is pumped into an oil well and the high viscosity solution pushes the oil from the rock formation or reservoir to another well where the oil can be recovered. The ability of polyacrylamide to gel or thicken is a unique characteristic. The crosslinking can be accomplished by methylolation or ionic bridging to give a curable coating, an adhesive or a water-holding gel.

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PART - I

REDOX SYSTEM - ACRYLAMIDE POLYMERS

INTRODUCTION

Free Radical

Free radical is an unsaturated molecular fragment that can be formed by the homolytic fission of covalent bond or by transfer process. Free radicals are usually highly reactive species.

A] Fission of covalent bond

Fission of covalent bond is caused due to thermal or photochemical reactions. High energy irradiation causes the fission of the weak bond in the molecule and for free radical formation at temperature convenient for polymerization, the molecule must contain the weak covalent bond like -O-O- bond in a peroxide

$$R\text{-}O\text{-}O\text{-}R' \xrightarrow{\Delta} RO^{\bullet} + R'O^{\bullet}$$

Dissociation of compound into free radicals may be accompanied by the elimination of stable molecule; e.g. azo compounds

$$R\text{-}N{=}N\text{-}R' \xrightarrow{\Delta} R^{\bullet} + R'^{\bullet} + N_2\uparrow$$

Photochemical activation of weak bond may also cause a molecule to dissociate into free radicals and a compound which decomposes thermally is also susceptible to photodissociation, often with the formation of same radical species. Many organic compounds, which are not readily susceptible to thermal or photolytic decomposition will dessociate into radicals on

bombardment with high energy radiation (e.g. Gamma rays or x-rays).

B] Transfer Process

Radicals can be produced by electron transfer process in redox (oxidation - reduction) reactions, which are the main source of free radicals. Redox process involves the transfer of one electron to or from an ion or molecule with the formation of radical[1].

Ferrous ions are oxidized into ferric ions by H_2O_2 with the formation of hydroxyl radical[2].

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \bar{O}H + \dot{O}H$$

H_2O_2 also reduces ferric ions to ferrous ions

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

$$Fe^{3+} + HO_2^- \longrightarrow Fe^{2+} + \dot{H}O_2$$

Peroxydisulfate ion oxidizes ferrous ion with the formation of sulfate radical ion[3].

$$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot -}$$

Free Radical Polymerization

It is convenient to divide the vinyl polymerization by free radicals into initiation, propagation and termination steps.

A] The Initiation Reaction

Certain monomers are known to polymerize (without any

initiator which produces free radicals) either by heat or by radiation alone, eventhough it is known that such uncatalyzed polymerization also proceeds by free radical mechanism.

Initiation of polymerization generally is effected by substances which are known to generate free radicals, either by thermal or photochemical decomposition. Organic peroxides and azo compounds are widely used as single initiators and the mixture such as hydrogen peroxide and ferrous ion forms a redox system.

It has been presumed that the free radicals which are produced[4-6] attack the monomer by pairing with one of the π electrons of the double bond, leaving the other unpaired, e.g.

$$R^{\bullet} + R'-CH=CH_2 \longrightarrow R'\dot{C}H-CH_2R$$

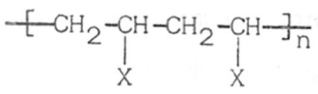
B] The Propagation Reaction

The propagation process involves essentially the addition of a free radical to a molecule of monomer to produce a new radical. The various isomeric structures of the polymer chain are formed by the addition of a monomer unit in different ways to the growing chain.

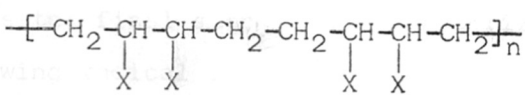
1) Head-to-Head, Tail-to-Tail or Head-to-Tail

The structure of the products obtained by polymerization of various vinyl compounds of the type $CH_2=CHX$, have been considered by many investigators. There are three ways, in which units of the vinyl type may combine to form a long chain molecule. The units may join in a 'head-to-tail' fashion to produce

a linear polymer of type I;



(I)



(II)

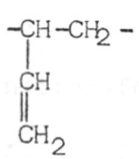
in a 'head-to-head' or 'tail-to-tail' fashion to give a linear polymer of type II; or in a random fashion to give a linear polymer in which some of the substituents are on adjacent carbons and some are in the 1,3-positions with respect to each other.

Marvel and his coworkers[7] have investigated the structure of number of vinyl monomers by chemical means. Most of the polymers appeared to have a 'head-to-tail' structure.

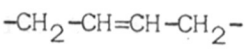
2) Optical Isomerism

In case of monomers of the type giving asymmetric carbon atoms in the chain, XY = CH_2 (e.g. styrene, vinyl acetate and methyl methacrylate) the addition of monomer to the growing chain may take place so as to give a polymer structure in which the groups are regularly or irregularly arranged.

If the monomer is a diene, such as butadiene, propagation may take place either by 1,2 or by 1,4-addition



1,2-Addition



1,4-Addition

C] The Termination Reaction

The termination is the final step in the polymerization reaction by which a growing radical loses its activity and a dead polymer is formed. The termination step can take place by combination of the two radicals or by disproportionation. Evidence for both the mechanisms is strong and it has been assumed that one or the other of the two reactions, ingeneral predominates in the polymerization reaction.

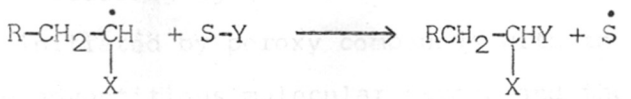
Chain Transfer

It is recognised[8] that the reactivity of a radical can be transferred to another species which will usually be capable of continuing the chain reaction. The reaction involves the transfer of an atom between the radical and the molecule.

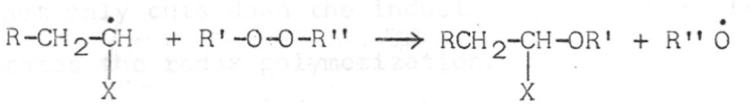
Typical chain transfer processes are :

(1) Chain transfer with monomer :

(2) Chain transfer with solvent :



(3) Chain transfer with initiator :



The transfer with the initiator may also be considered as the secondary decomposition of the initiator by the polymer radical.

The chain transfer with solvent in particular, has been studied by a number of workers[9-13] using a large number of solvents with different structures.

Redox Polymerization

The outstanding recent development in the field of initiators has been the use of redox system in which an oxidizing and reducing agent (each thermally stable by itself) react to form free radicals at low or moderate temperature. It is rapid production of free radicals from stable compounds, which accounts for the present technical importance. Redox initiation in contrast to the production of free radicals by thermal dissociation of the initiator, which must either be unstable at room temperature (such as diazo thio ethers) or else be used at elevated temperature.

First in Germany[14] and later in United States[15] and in England[16] reducing agents were added to the polymerization systems initiated by peroxy compounds with the objective of removing adventitious molecular oxygen and thus eliminating the induction period caused by the latter. The addition of reducing agent not only cuts down the induction period but also markedly accelerates the redox polymerization.

The method of polymerization provides direct experimental evidence of the existance of transient radical intermediates

generated in redox reaction and identification of these radical end groups in the polymer obtained throws new light on reaction mechanism of redox system.

Helogens

Halogen as a component of redox systems has been studied. Uri[1] in 1952, reported Fe^{2+}—Br_2 initiator system and Saha et al[17] have demonstrated the initiating efficiencies of metal salt-halogen, amine-halogen and ammonia-halogen redox system. It was observed by Sengupta et al[18] that halogen (Cl_2 and Br_2) form redox initiating system with thiourea and urea in aqueous and in t-butyl alcohol media. Iodine as expected, from its known inhibiting power, fails to initiate. Guanidine-halogen initiating system is highly interesting, since guanidine is known to be inhibitor. Though guanidine and iodine are both inhibitors, they together form a somewhat weak initiating system[18].

Sulfur Compounds

Organic sulfur compounds such as thiourea[19-28], thio-acetamide[29-31], 2-mercaptoethanol[32], 2-mercaptoethylamine[33], glycolic acid[34] and thioglycolic acid[35-38] coupled with suitable catalyst forms useful redox pair for the vinyl polymerization in aqueous medium. The generation of complex thio-free radicals by the above redox systems have been observed to initiate the vinyl polymerization quite smoothly and effectively.

Metal Ions

Certain transition metals in their higher valence states

alone or coupled with easily reducible organic substrates act as potential initiator for redox polymerization of vinyl monomers[39]. The metal ions which have been used for initiating vinyl polymerization are (1) Permangnate, (2) Ceric ion (IV), (3) Vanadium (V), (4) Manganese (III), (5) Ferric ion, (6) Cobalt ion, and (7) Cuprous ion.

Permanganate - Organic Substrate Redox System

Permanganate ion is one of the most versatile oxidizing agents, reacting with all types of organic substrates[40]. Its reactions are most interesting because of the several oxidation states to which it can be reduced, the fate of the manganese ion being largely determined by the reaction conditions, in particular, the acidity of the medium. Permanganate ion coupled with water soluble organic compounds can produce free radicals which can initiate the vinyl polymerization.

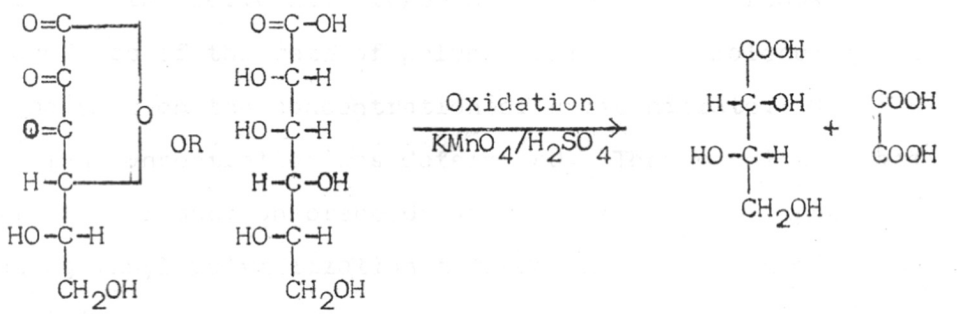
Potassium permangnate has been used with various reducing agents such as thiourea[25], glycolic acid[34], thioglycolic acid[38], oxalic acid[41], lactic acid[42], tartaric acid[43], ascorbic acid[44], malic acid[45], mercaptosuccinic acid[46] and citric acid[47] for acrylamide polymerization.

Mishra and coworkers have reported the homogeneous redox polymerization of acrylamide initiated by the permanganate-tartaric acid[43]/citric acid[47] redox systems. The rate of polymerization increases with increasing catalyst and monomer concentration. The initial rate increases with increasing

temperature but the maximum conversion shows a decrease as the temperature is increased beyond 35°C. Addition of neutral salts, organic solvents and complexing agents reduces the rate and percentage conversion. An addition of manganese sulfate or the injection of more catalyst at intermediate stage increases both initial rate and the maximum conversion. NaF decreases the rate but increases the conversion.

The distinguishing feature of the permanganate system is that there are two consecutive redox systems operative in the presence of the monomer i.e. permanganate (oxidant) and monomer (reductant); and manganese dioxide (oxidant) and the added reducing agent (reductant).

In potassium permagnate - ascorbic acid[44] redox system, the optimum amount of sulfuric acid is essential to initiate the polymerization but its presence in excess produced no effect on the rate of reaction and maximum conversion. In the initial stages permanganate oxidizes ascorbic acid to form threonic acid and oxalic acid as presented below :



Ascorbic acid
Keto form Hydrated form

Dehydroascorbic acid

Threonic acid Oxalic acid

In second step, permanganate reacts with oxalic acid to produce the $\dot{C}OO^-$ radical which initiates polymerization at room temperature with very short induction period.

Husain and Gupta[48] have reported the effect of some additives on aqueous polymerization of acrylamide initiated by permanganate-oxalic acid redox system. The rate of polymerization increases in the presence of alkali metal chlorides. Cupric chloride and ferric chloride were found to be retarders for the system. Anionic and cationic detergents showed a marked influence on the rate of polymerization.

Ceric Ion

Ceric salts (such as per chlorate, nitrate and sulfate) form very effective redox system in the presence of organic agents such as alcohols[49-52], aldehydes[53,54], amines[55,56], glycerols[57,58] and thiols[59,60]. The oxidation-reduction produces cerous ions and the free radical species capable of initiating vinyl polymerization.

Mino et al[61] investigated the polymerization of acrylamide initiated by the ceric nitrate/3-chloro-1-propanol redox system. The dependence of the rate of polymerization and molecular weight of the polymer on the concentration of ceric nitrate, pH and nitrate ion concentration was determined. They predicted that the the oxidation-reduction proceeds via free radicals, capable of initiating vinyl polymerization through the formation of complex intermediate.

$$Ce^{4+} + \text{Alcohol} \underset{}{\overset{K}{\rightleftharpoons}} \underset{\text{complex}}{(\text{ceric-alcohol})} \xrightarrow{K'} \dot{R} + Ce^{3+} + H^+$$

The initiation of polymerization is due to the free radical $\dot{R}$, and termination takes place by the ceric ion.

Machida et al[62-66] investigated the use of ceric ion alone or coupled with organic substrates for the aqueous polymerization of acrylamide. Narita and Machida[66] have reported the mechanism of acrylamide polymerization initiated by ceric ion.

The mechanism of aqueous polymerization of acrylamide by Ce (IV)/glycerol redox system was studied by Santappa and coworkers[58]. Misra and Dubey[67] have studied the aqueous polymerization of acrylamide by Ce (IV)/thiomalic acid in which ceric ammonium sulfate reacts with thiomalic acid to form a complex that decomposes slowly in acid medium producing H^+ ion, Ce^{3+} ion and a free radical which initiates the polymerization.

Various studies by different investigators revealed that the rate of initiation of vinyl monomers of various ceric salts were in the order: Ceric perchlorate > ceric nitrate > ceric sulfate and the chain lengths of polymers initiated by the above salts were in reverse order.

Vanadium (V) - Organic Substrate Redox System

Vanadium (V) in the presence of various organic reducing agents has been used as an effective initiator in the polymerization of vinyl monomers. In a qualitative survey of the reduction of V^{5+} by a multitude of organic substrates, Littler and Waters[68] have shown that, most of the such reactions proceed via a free radical mechanism which can initiate vinyl polymerization.

Nayak and coworkers[69] reported the homogeneous polymerization

of acrylamide using V^{5+}-cyclohexanone redox system. They also studied the effect of certain salts such as KCl, Na_2SO_4 and $CuSO_4$ and organic solvents on the rate of polymerization.

Manganese (III) - Organic Substrate Redox System

Waters and colleagues[70-72] have studied the oxidation of a multitude of organic substrates using trivalent manganese either in the form of sulfate or pyrophosphate.

Nayak et al have reported the vinyl polymerization using multitude of Mn^{3+}-organic substrates such as thioacetamide[29], thioglycolic acid[35], fructose[73], citric acid[74], cyclohexanol[75], thiourea[28,76], glycerol[77] and ascorbic acid[78].

Santappa et al[79] have studied the kinetics and mechanism of acrylamide polymerization by Mn (III) acetate - diglycolic acid redox system. The polymerization reaction is initiated by the organic free radical arising from the Mn^{3+}-diglycolic acid reaction and the termination is by the metal ions. They also studied the acrylamide polymerization using Mn (III) acetate alone at high temperature[80].

Ferric Ion

The effect of ferric salt on vinyl polymerization has been reported in recent years.

Carvell and coworkers[81] showed that the rate of acrylamide polymerization is proportional to the reciprocal of the concentration of ferric salt.

Machida et al[82] have reported the aqueous polymerization

of acrylamide initiated by ferric nitrate. A complex formed with monomer and ferric salt generates an active monomer radical capable of initiating polymerization. The ferric ion was found to initiate as well as to terminate the polymerization. The initiating capability of ferric ion is smaller than the termination capability. Therefore, the polymerization proceeds at lower concentration of ferric ion, where as it is inhibited by higher concentration.

The role of ferric salt in the polymerization of acrylamide initiated by ceric ion has been studied by Machida et al[63].

Cobaltic Ion

A wide variety of organic compounds - aromatic as well as aliphatic aldehydes, alcohols, ketones, olefins, and hydrocarbons have been found to be susceptible to oxidation by cobaltic ions. Baxendale and Wells[83] have studied the reduction of Co (III) by hydrogen peroxide and mentioned that Co^{3+} would initiate vinyl polymerization.

Polymerization of acrylamide initiated by cobaltic ions in aqueous solution in perchloric acid and sulfuric acid media have been studied by Santappa and coworkers[84]. Besides the polymerization reaction, it was observed that side reactions like water oxidation and monomer oxidation also contribute to the rate of cobaltic ion disappearance.

Recently Sur and Choi[85] studied the aqueous polymerization of acrylamide initiated by cobaltous chloride/N,N-dimethylaniline.

Copper Ion

The role of Cu^{2+} ion in various capacities has been studied for the polymerization of vinyl monomers[86-88]. Mostly it has been used to promote the activity of the catalyst. In three component systems, it has been found to act as an oxidant and reductant.

Misra and Dubey[89] studied the polymerization of acrylamide in an aqueous medium with Cu (II) - metabisulfite redox pairs in which Cu^{2+} has been used as an oxidant with metabisulfite.

Peroxydisulfate

The peroxydisulfate is an oxidizing agent in aqueous solution. The standard oxidation - reduction potential for the reaction

$$2\ SO_4^{2-}{}_{(aq.)} \longrightarrow S_2O_8^{2-}{}_{(aq.)} + 2\bar{e}$$

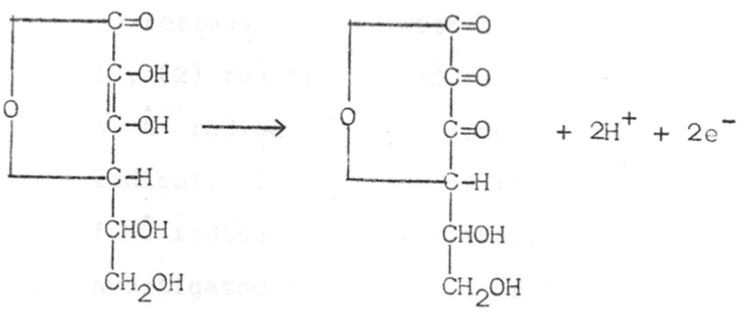
is - 2.01 volts[90].

House[91], Wilmarth and Haim[92] have reviewed the oxidation of various organic and inorganic substrate by peroxydisulfate.

Many workers have studied the aqueous polymerization of acrylamide by using peroxydisulfate with various reducing substrates such as 2-mercaptoethanol[32], 2-mercaptoethylamine-hydrochloride[33], thioglycolic acid[37], sodium thiosulfate[93], hydrogen peroxide[94], sodium sulfite[95], triethanolamine[96], silver amino acetatechelate[97], 2-piperidinoethanol[98] and thiomalic acid[99].

PRESENT INVESTIGATION, RESULTS AND DISCUSSION

The use of ascorbic acid as an analytical reagent depends principally on its reducing properties. On oxidation by moderate oxidants, it yields dehydroascorbic acid.



Strong oxidants may oxidize this product further, ultimately to carbondioxide and water. Ascorbic acid is a weak acid, hence the redox potential of the dehydroascorbic - ascorbic acid system depends on the hydrogen ion concentration.

The reducing action of ascorbic acid has been described by earlier workers[100,101] in the titrimetric determination of several inorganic and organic substances. Several publications have described the reduction of ascorbic acid from the kinetic point of view, some of which have been directed towards the catalytic reduction[102]. Grinstead[103] have studied the kinetics of the oxidation of ascorbic acid by hydrogen peroxide in the presence of the iron chelate of ethylenediaminetetraacetic acid (EDTA) in the pH range 3.4-4.5. The direct reduction of the

ferric chelate by ascorbic acid involves a one-electron oxidation of the ascorbic acid to a radical intermediate, the ascorbate ($\dot{A}H$) radical. This species reacts with a second ferric chelate molecule to complete the process. The hydrogen peroxide oxidation involves a chain process being initiated by the above reduction step. The chain itself consists of three steps : (1) reaction of the ferrous chelate with hydrogen peroxide to produce $H\dot{O}$ radicals, (2) reaction of $H\dot{O}$ radical with ascorbic acid to produce the $\dot{A}H$ radical and (3) reduction of ferric chelate by the ascorbate radical. Termination of the chain occurs mainly by the reaction of $H\dot{O}$ radicals with ascorbate radicals. Khan and Martell[104] have investigated the kinetics of the uncatalyzed and copper (II) and iron (III) ion catalyzed oxidation of ascorbic acid in the pH range 2-5.5 and found that the monoionic ascorbic acid as the main reacting species. The catalyzed oxidation were explained on the basis of the formation of complex between catalyst and ascorbic acid. Mattok[105] has studied the mechanism of the reduction of Adrenochrome by ascorbic acid and reported that the dehydroascorbic acid is formed as an intermediate. The reduction of Palladium[106] and hexacyanoferrate (III)[107] by ascorbic acid has also been studied and supported the concept of the formation of an ascorbate radical intermediate.

Ascorbic acid has been used as reducing component with hydrogen peroxide[108], t-butyl peroxybenzoate[109], potassium permangnate[42] and Mn (III)[78]. The kinetics of the redox system ascorbic acid-Peroxydisulfate was studied by Mushran and

Mehrotra[110] and a mechanism involving $\dot{SO}_4^-$, $\dot{O}H$ and ascorbate radical intermediate was proposed[110,111]. This redox system has been used for aqueous polymerization of methacrylamide[112] and methyl methacrylate[113].

The present work explains the aqueous polymerization of acrylamide by an ascorbic acid - peroxydisulfate system as a redox initiator at 35±0.2°C in the presence of atmospheric oxygen.

REACTION MECHANISM

Weissberger and coworkers[114] have observed that the reaction between oxygen and ascorbic acid is autocatalytic, accelerated by dehydroascorbic acid. The reaction scheme is as follows :

$$AH_2 \xrightarrow[\text{slow}]{O_2} \dot{A}H + H\dot{O}_2 \xrightarrow[\text{very fast}]{O_2} A + H_2O_2 \qquad (1)$$

$$AH_2 + A \underset{\text{very fast}}{\rightleftharpoons} 2\,\dot{A}H \qquad (2)$$

$$H_2O_2 \longrightarrow 2\dot{O}H \xrightarrow{\text{deactivation}} H_2O + {}^1/_2\ O_2 \qquad (3)$$

where AH_2, $\dot{A}H$ and A represents the ascorbic acid, ascorbate radical and dehydroascorbic acid respectively. In aqueous solution ascorbic acid dissociates into ionic fragments and the monohydroascorbate ion is mainly responsible for the strong

reducing action of ascorbic acid in aqueous media :

$$AH_2 \rightleftharpoons AH^- + H^+ \qquad (4)$$

The primary steps in all oxidation involving peroxydisulfate is its symmetrical decomposition into two sulfate radical ions followed by several consecutive reactions following a chain. The redox reaction between ascorbic acid and peroxydisulfate involves the chain reactions[110] shown in eqs. (5) - (10) for the generation of primary radicals:

$$S_2O_8 \xrightarrow{Kd} 2\ \dot{SO}_4^- \qquad (5)$$

$$\dot{SO}_4^- + H\text{-}OH \xrightarrow{K_1} SO_4^{2-} + H^+ + \dot{O}H \qquad (6)$$

$$\dot{O}H + AH^- \xrightarrow{K_2} \dot{A}H + \bar{O}H \qquad (7)$$

$$\dot{A}H + S_2O_8^{2-} \xrightarrow{K_3} A + SO_4^{2-} + \dot{SO}_4^- + H^+ \qquad (8)$$

$$\dot{A}H + \dot{SO}_4^- \xrightarrow{K_4} A + SO_4^{2-} + H^+ \qquad (9)$$

$$\dot{A}H + \dot{O}H \xrightarrow{K_5} A + H^+ + \bar{O}H \longrightarrow A + H_2O \qquad (10)$$

Initiation :

$$M + \dot{SO}_4^- \text{ or } \dot{A}H \xrightarrow{K_i} \dot{M} \qquad (11)$$

Propagation :

$$\dot{M} + M \xrightarrow{K_p} \dot{M}_i \qquad (12)$$

$$\dot{M}_{n-1} + M \xrightarrow{K_p} \dot{M}_n \qquad (13)$$

Termination :

$$\dot{M}_x + \dot{M}_y \xrightarrow{K_t} P \text{ (Polymer)} \qquad (14)$$

$$\dot{M}_x + \dot{A}H \xrightarrow{K_{dt}} A + M_xH \text{ (Polymer)} \qquad (15)$$

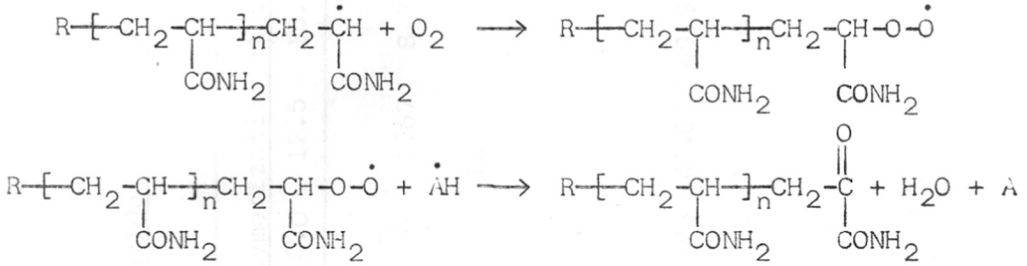
Role of Atmospheric Oxygen

The peroxydisulfate initiated polymerization of acrylamide[115,116] was carried out in the absence of atmospheric oxygen after thoroughly deaerating the reaction mixture because the molecular oxygen generally tends to inhibit the polymerization reaction and increases the induction period (IP). The peroxydisulfate-ascorbic acid system, however, acts as an efficient initiator in an aqueous medium even in the presence of atmospheric oxygen. It has been observed[117] that in the absence of oxygen the reaction starts after a prolonged induction period at room temperature. It, therefore, appears that oxygen acts as a co-catalyst and helps to reduce rather than increase IP. Infact, oxygen facilitates the possibility of ascorbic acid undergoing autoxidation like other hydroxy ketones or enediols[114] and thus participates in the reaction. The catalyzing action of molecular oxygen with autoxidizable substrates like hydrazine hydrate[118] and sulfite ion[119] in different systems of catalyzed polymerization of vinyl monomers has also been observed by others.

The role of molecular oxygen in minimizing the IP in

such systems is of greater importance industrially. In other words, this is a novel system in which oxygen is used favourably in decomposing the ascorbic acid, whereas in other redox systems like hydrogen peroxide - ascorbic acid[120] and permaganate-ascorbic acid[44] the initiation of vinyl polymerization showed a marked inhibition in the presence of atmospheric oxygen from air.

The low molecular weight of the polymer obtained by using this redox initiating system may be due to oxygen acting as chain terminator, as reported by Baxendal and coworkers[121].



Dependence of Rate (R_i) and Induction Period (IP) on Ascorbic Acid Concentration

The observations in Table-2 at various concentrations of ascorbic acid show that, the initial rate (R_i) and limiting conversion increases with increasing concentration of ascorbic acid in the range [(2.84 - 11.36) x 10^{-4} mole/litre]. At relatively high concentration of ascorbic acid [(11.36 - 28.4) x 10^{-4} mole/litre] an appreciable decrease in the initial rate and limiting conversion has been observed (Fig.1).

Table-2 : Polymerization of acrylamide with varying ascorbic acid concentration

No.	Ascorbic acid conc. M x 10^4	Extent of Polymerization at various time t (min), %									
		2.5	5.0	7.5	10.0	12.5	15.0	20.0	25.0	30.0	40.0
1.	2.84	-	-	1.85	4.92	6.67	8.79	10.75	14.93	14.42	19.34
2.	4.26	-	-	2.72	10.39	12.84	16.64	22.62	28.59	30.75	35.92
3.	5.68	4.14	10.55	13.87	20.14	23.26	29.26	40.72	46.32	53.38	61.65
4.	8.52	7.18	14.42	22.29	31.41	35.12	42.85	53.43	59.68	66.83	72.10
5.	11.36	10.28	17.93	26.46	36.83	43.07	49.34	58.38	66.83	74.12	78.78
6.	14.20	6.94	14.08	20.66	28.10	34.56	39.62	48.27	55.87	60.62	68.58
7.	22.72	6.35	12.69	19.34	26.38	32.84	37.34	44.74	53.78	58.28	62.54
8.	28.40	5.10	10.94	16.12	22.36	26.37	34.07	42.61	47.13	52.80	56.68

[Monomer] = 4.0 x 10^{-2} mole/litre; [Peroxydisulfate] = 5.0 x 10^{-3} mole/litre
Temperature = 35±0.2°C

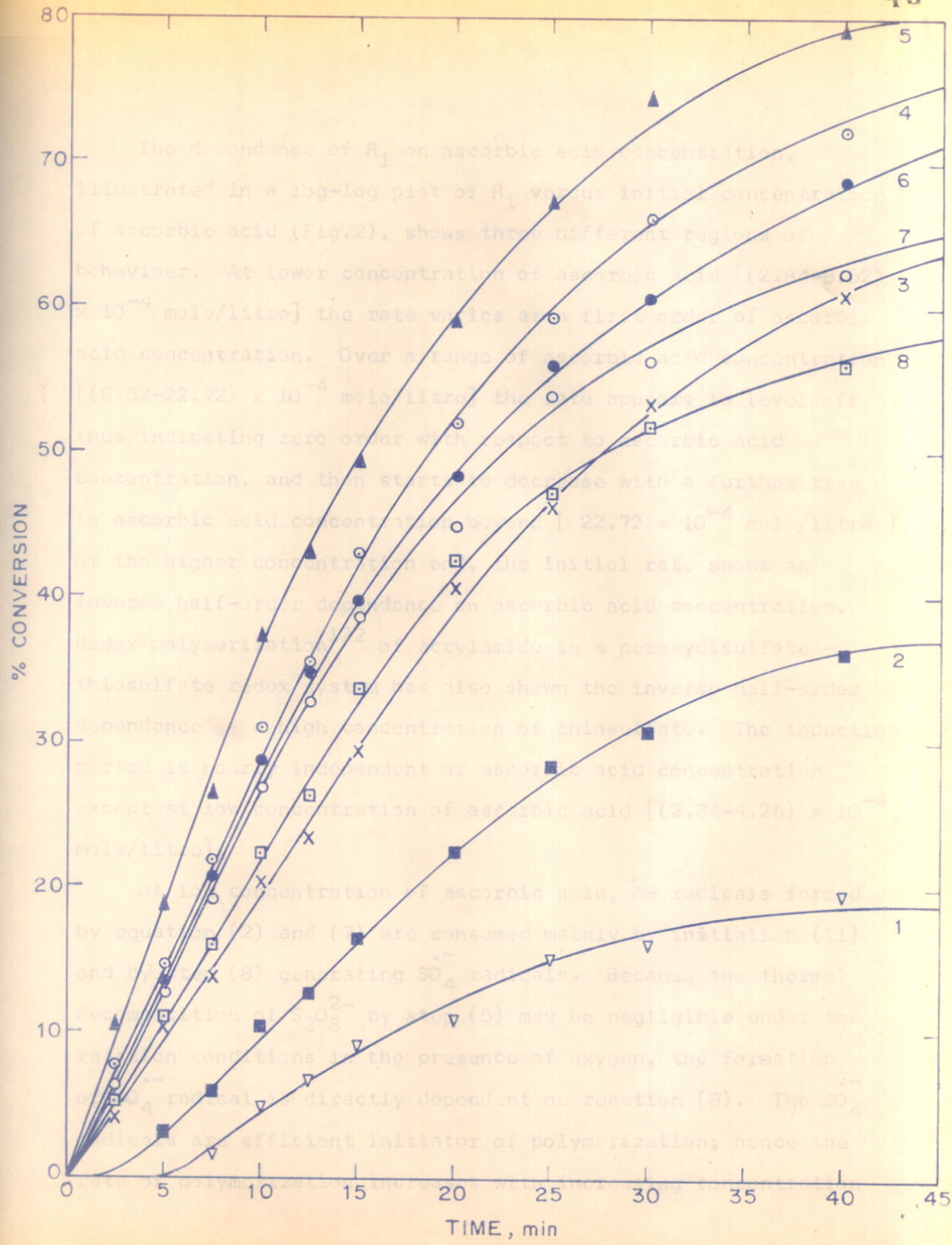


FIG. 1. POLYMERIZATION OF ACRYLAMIDE WITH VARYING ASCORBIC ACID CONCENTRATION, (TABLE-2)

The dependence of R_i on ascorbic acid concentration, illustrated in a log-log plot of R_i versus initial concentration of ascorbic acid (Fig.2), shows three different regions of behaviour. At lower concentration of ascorbic acid [(2.84-8.52) x 10^{-4} mole/litre] the rate varies as a first order of ascorbic acid concentration. Over a range of ascorbic acid concentration [(8.52-22.72) x 10^{-4} mole/litre] the rate appears to level off, thus, indicating zero order with respect to ascorbic acid concentration, and then starts to decrease with a further rise in ascorbic acid concentration beyond [22.72 x 10^{-4} mole/litre]. At the higher concentration end, the initial rate shows an inverse half-order dependence on ascorbic acid concentration. Redox polymerization[122] of acrylamide in a peroxydisulfate - thiosulfate redox system has also shown the inverse half-order dependence at a high concentration of thiosulfate. The induction period is nearly independent of ascorbic acid concentration except at low concentration of ascorbic acid [(2.84-4.26) x 10^{-4} mole/litre].

At low concentration of ascorbic acid, $\dot{A}H$ radicals formed by equation (2) and (7) are consumed mainly by initiation (11) and by step (8) generating $\dot{SO}_4^-$ radicals. Because the thermal decomposition of $S_2O_8^{2-}$ by step (5) may be negligible under the reaction conditions in the presence of oxygen, the formation of $\dot{SO}_4^-$ radical is directly dependent on reaction (8). The $\dot{SO}_4^-$ radicals are efficient initiator of polymerization; hence the rate of polymerization increases with increasing concentration

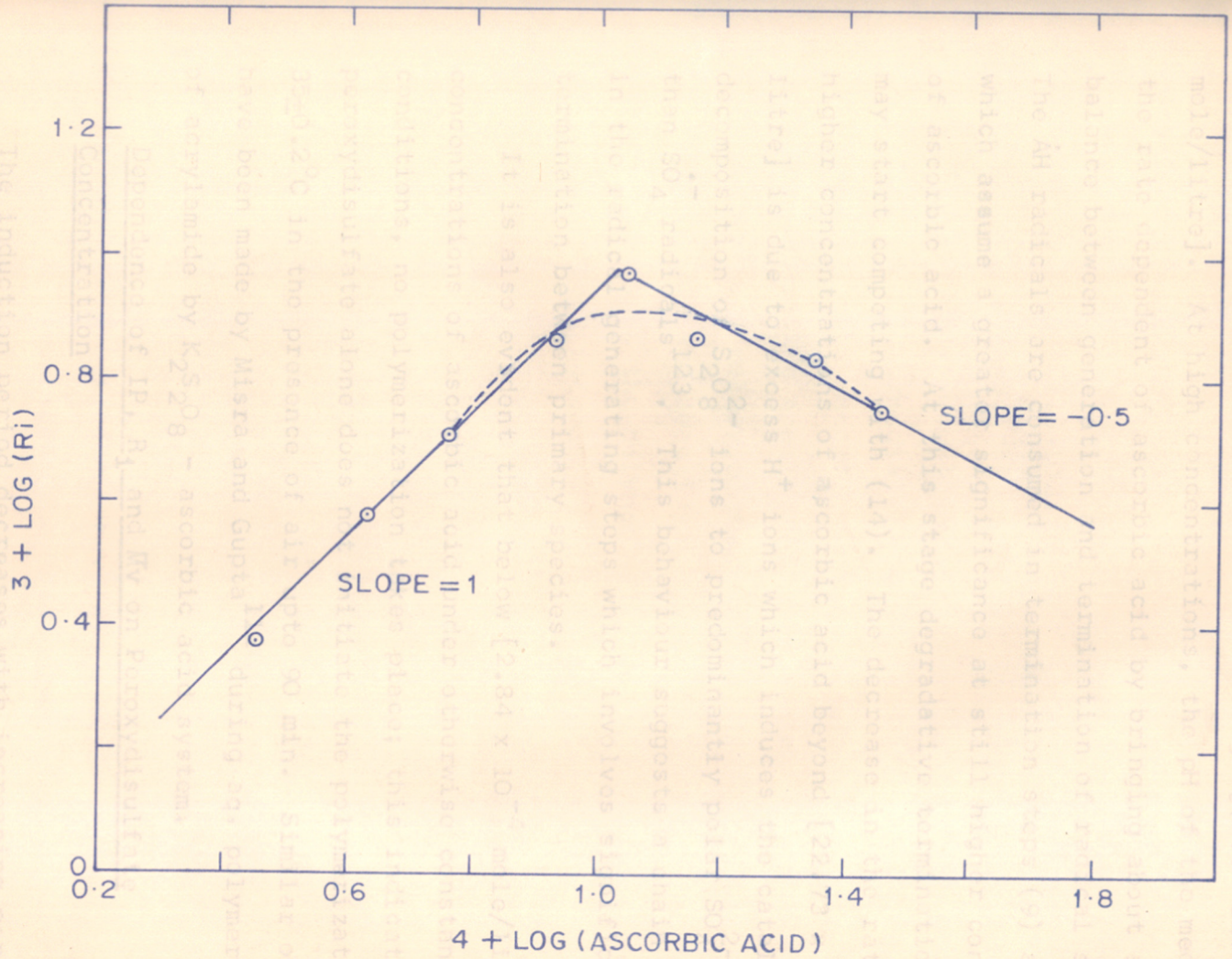


FIG. 2. DOUBLE LOGARITHMIC PLOT OF INITIAL RATE OF POLYMERIZATION (Ri IN mole / lit/sec) VERSUS CONCENTRATION OF ASCORBIC ACID

of ascorbic acid in low concentration range [(2.84-11.36) x 10^{-4} mole/litre]. At high concentrations, the pH of the medium makes the rate dependent of ascorbic acid by bringing about a sort of balance between generation and termination of radical species. The $\dot{A}H$ radicals are consumed in termination steps (9) and (10) which assume a greater significance at still higher concentration of ascorbic acid. At this stage degradative termination by (15) may start competing with (14). The decrease in the rate at higher concentrations of ascorbic acid beyond [22.73 x 10^{-4} mole/litre] is due to excess H^+ ions which induces the catalyzed decomposition of $S_2O_8^{2-}$ ions to predominantly polar SO_4^{2-} rather than $SO_4^{\cdot-}$ radicals[123]. This behaviour suggests a chain process in the radical generating steps which involves significant termination between primary species.

It is also evident that below [2.84 x 10^{-4} mole/litre] concentrations of ascorbic acid under otherwise constant conditions, no polymerization takes place; this indicates that peroxydisulfate alone does not initiate the polymerization at 35±0.2°C in the presence of air upto 90 min. Similar observation have been made by Misra and Gupta[112] during aq. polymerization of acrylamide by $K_2S_2O_8$ - ascorbic acid system.

Dependence of IP, R_i and $\bar{M}v$ on Peroxydisulfate Concentration

The induction period decreases with increasing peroxydisulfate concentration and to a negligible extent reaches to

[10.0 x 10^{-3} mole/litre] under otherwise constant conditions.

The observations in Table-3 at various concentrations of peroxydisulfate show that, the initial rate (R_i) and limiting conversion tend to increase with increasing concentration of peroxydisulfate [(1.5-10.0) x 10^{-3} mole/litre] at a fixed concentration of ascorbic acid and monomer (Fig.3). Because ascorbic acid alone is incapable of initiating the polymerization, the transient intermediates ($SO_4^{\bullet -}$ and $\dot{A}H$) of chain reactions between $S_2O_8^{2-}$ and ascorbic acid, shown in the reaction mechanism, are the initiating species. The $\dot{O}H$ radical generated by steps (3) and (6) are mainly consumed in step (7) or radical termination step (10) and deactivation step (3) and are not detectable as end groups in the polymer[112,113]. An increasing amount of $S_2O_8^{2-}$, however, increases the formation of the initiating $SO_4^{\bullet -}$ radicals at any fixed concentration of ascorbic acid; hence the observed rise in the initial rate.

The order of reaction with respect to peroxydisulfate concentration can be obtained from the log-log plot of R_i versus peroxydisulfate concentration (Fig.4). The slope of 0.5 for the linear plot indicates the normal half-power dependence on peroxydisulfate concentration, which generally means a mutual termination of the growing polymer chains. Suen and coworkers[124] and Riggs and Rodriguez[115] have also obtained similar results with the redox-initiated aqueous polymerization of acrylamide.

The viscosity-average molecular weight decreases with increasing concentration of peroxydisulfate and log-log plot of

Table-3 : Polymerization of acrylamide with varying peroxydisulfate concentration

No.	Peroxydisulfate conc. $M \times 10^3$	Extent of polymerization at various time t (min), %									
		2.5	5.0	7.5	10.0	12.5	15.0	20.0	25.0	30.0	40.0
1.	1.5	-	-	1.18	3.10	11.16	19.94	37.15	42.88	45.52	54.77
2.	2.5	-	3.54	14.02	25.36	34.75	42.86	55.28	63.08	66.69	71.68
3.	4.0	2.10	6.95	17.81	32.06	41.93	53.25	68.21	73.86	77.40	83.97
4.	5.0	5.22	16.32	33.26	49.51	59.39	63.54	72.83	78.31	83.10	88.10
5.	7.5	9.46	19.57	36.75	53.90	63.64	70.12	75.29	80.18	85.35	90.61
6.	10.0	15.35	31.84	48.98	59.95	68.13	74.84	80.05	84.78	88.10	87.74

[Monomer] = 5.0×10^{-2} mole/litre; [Ascorbic acid] = 14.20×10^{-3} mole/litre;
Temperature = $35 \pm 0.2^{\circ}C$

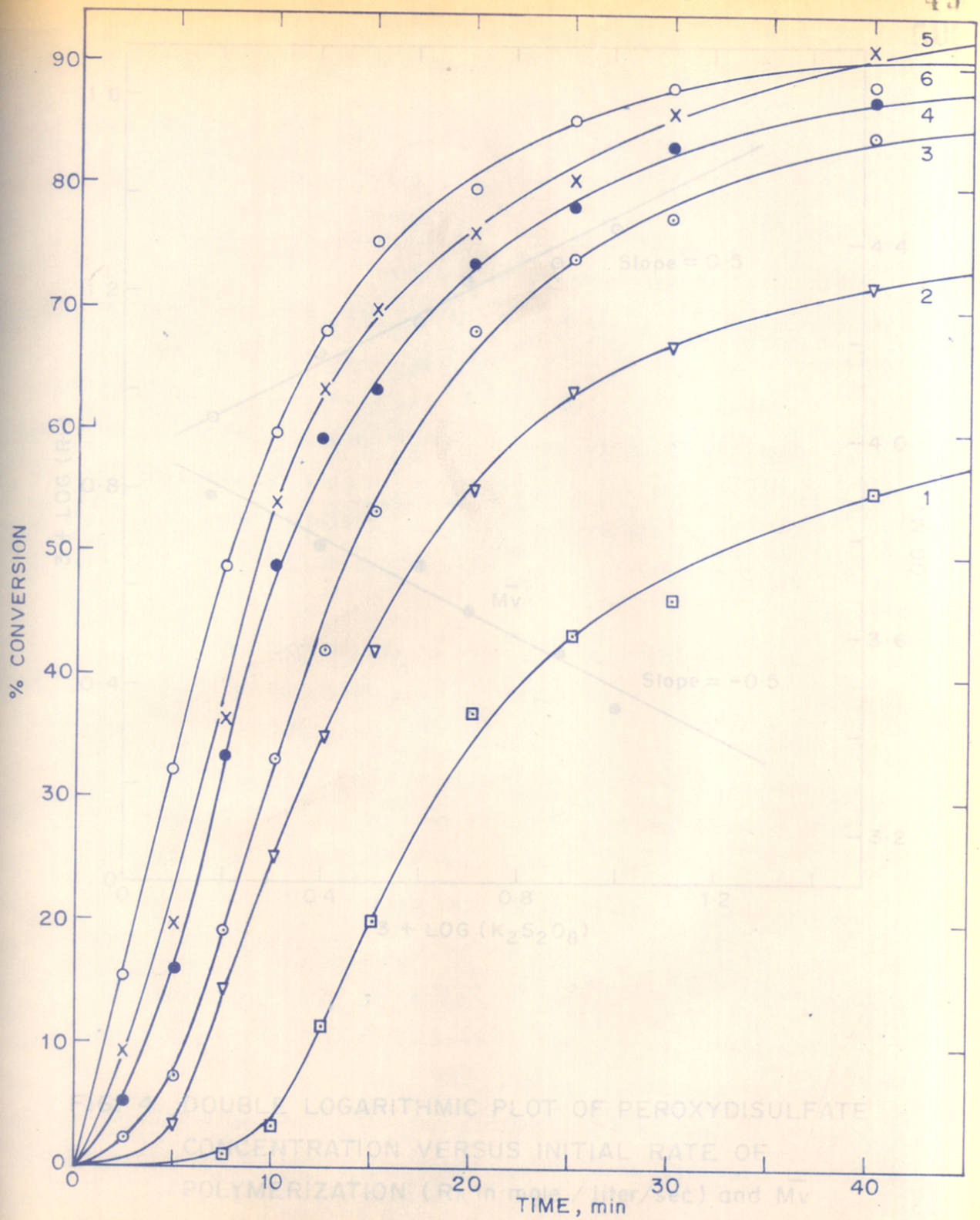


FIG. 3. POLYMERIZATION OF ACRYLAMIDE WITH VARING PEROXYDISULFATE CONCENTRATION, (TABLE-3)

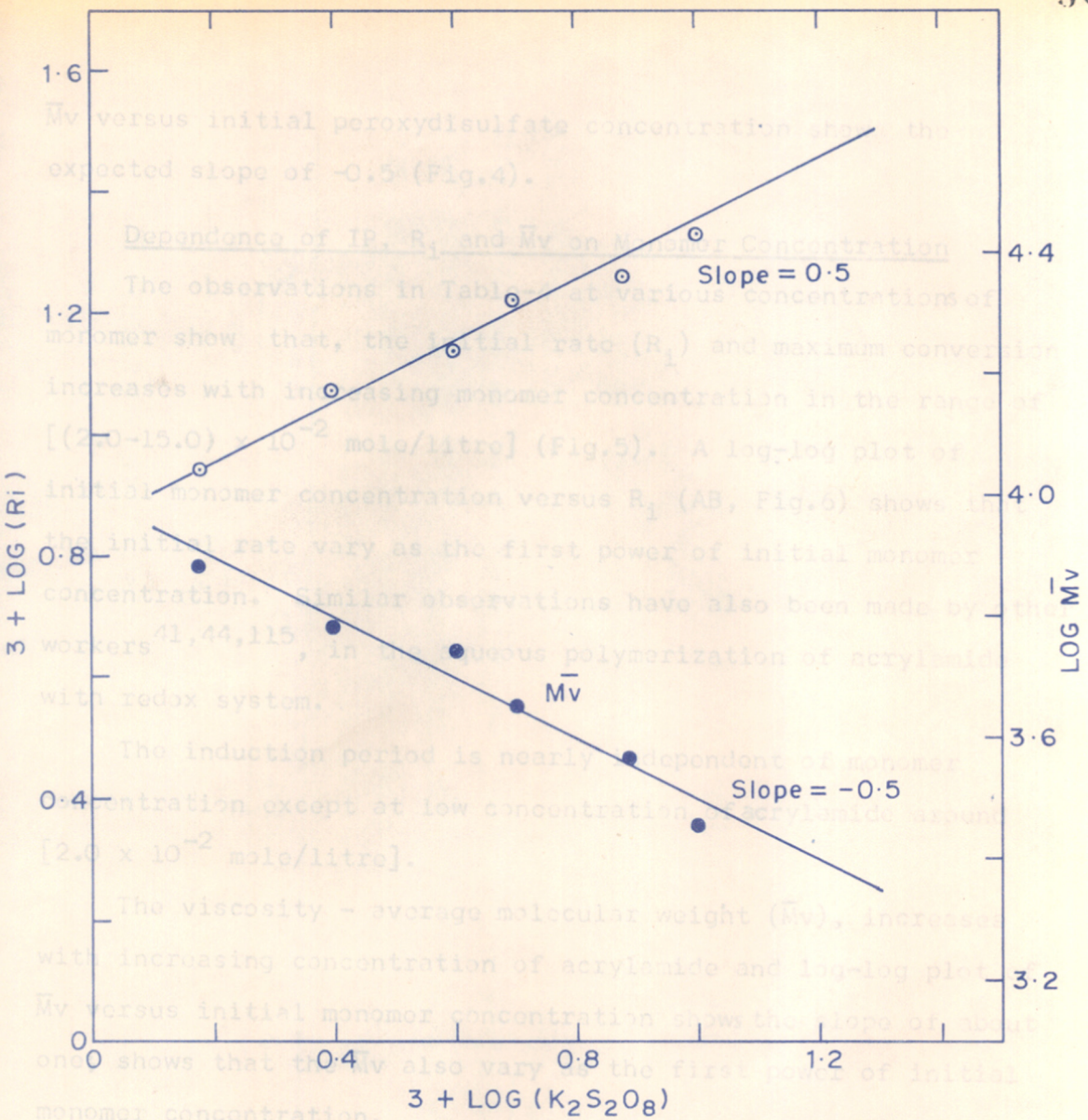


FIG. 4. DOUBLE LOGARITHMIC PLOT OF PEROXYDISULFATE CONCENTRATION VERSUS INITIAL RATE OF POLYMERIZATION (Ri in mole / liter/sec) and $\bar{M}v$

$\bar{M}v$ versus initial peroxydisulfate concentration show the expected slope of -0.5 (Fig.4).

Dependence of IP, R_i and $\bar{M}v$ on Monomer Concentration

The observations in Table-4 at various concentrations of monomer show that, the initial rate (R_i) and maximum conversion increases with increasing monomer concentration in the range of [(2.0-15.0) x 10^{-2} mole/litre] (Fig.5). A log-log plot of initial monomer concentration versus R_i (AB, Fig.6) shows that the initial rate vary as the first power of initial monomer concentration. Similar observations have also been made by other workers[41,44,115], in the aqueous polymerization of acrylamide with redox system.

The induction period is nearly independent of monomer concentration except at low concentration of acrylamide around [2.0 x 10^{-2} mole/litre].

The viscosity - average molecular weight ($\bar{M}v$), increases with increasing concentration of acrylamide and log-log plot of $\bar{M}v$ versus initial monomer concentration shows the slope of about one; shows that the $\bar{M}v$ also vary as the first power of initial monomer concentration.

Dependence of R_i, IP and $\bar{M}v$ on Temperature

The observations in Table-5 at various temperatures show that, the initial rate (R_i) and limiting conversion increases with rising polymerization temperature from 25 to 50°C (Fig.7) according to the Arrhenius theory. The induction period decreases

Table-4 : Polymerization of acrylamide with varying monomer concentration

No.	Monomer conc. $M \times 10^2$	Extent of polymerization at various time t (min), %									
		2.5	5.0	7.5	10.0	12.5	15.0	20.0	25.0	30.0	40.0
1.	2.0	-	-	-	1.86	6.28	8.12	12.66	19.66	33.82	38.34
2.	3.5	2.10	6.58	12.34	14.66	20.50	26.32	36.08	40.29	48.52	59.44
3.	6.0	4.08	11.42	17.12	26.00	31.76	39.46	45.96	51.84	61.43	69.20
4.	8.0	5.80	14.23	21.68	31.34	38.46	42.91	51.38	61.82	66.00	74.84
5.	10.0	7.12	16.10	27.84	35.12	41.72	48.28	68.26	66.08	73.30	82.48
6.	13.0	11.48	23.85	35.10	45.56	51.91	61.40	70.88	75.95	80.52	86.42
7.	15.0	17.22	34.96	49.20	57.90	65.78	67.77	76.00	82.32	85.10	91.52

[Peroxydisulfate] = 5.0×10^{-2} mole/litre; [Ascorbic acid] = 14.20×10^{-4} mole/lt.,

[Temperature = $35 \pm 0.2^{\circ}C$

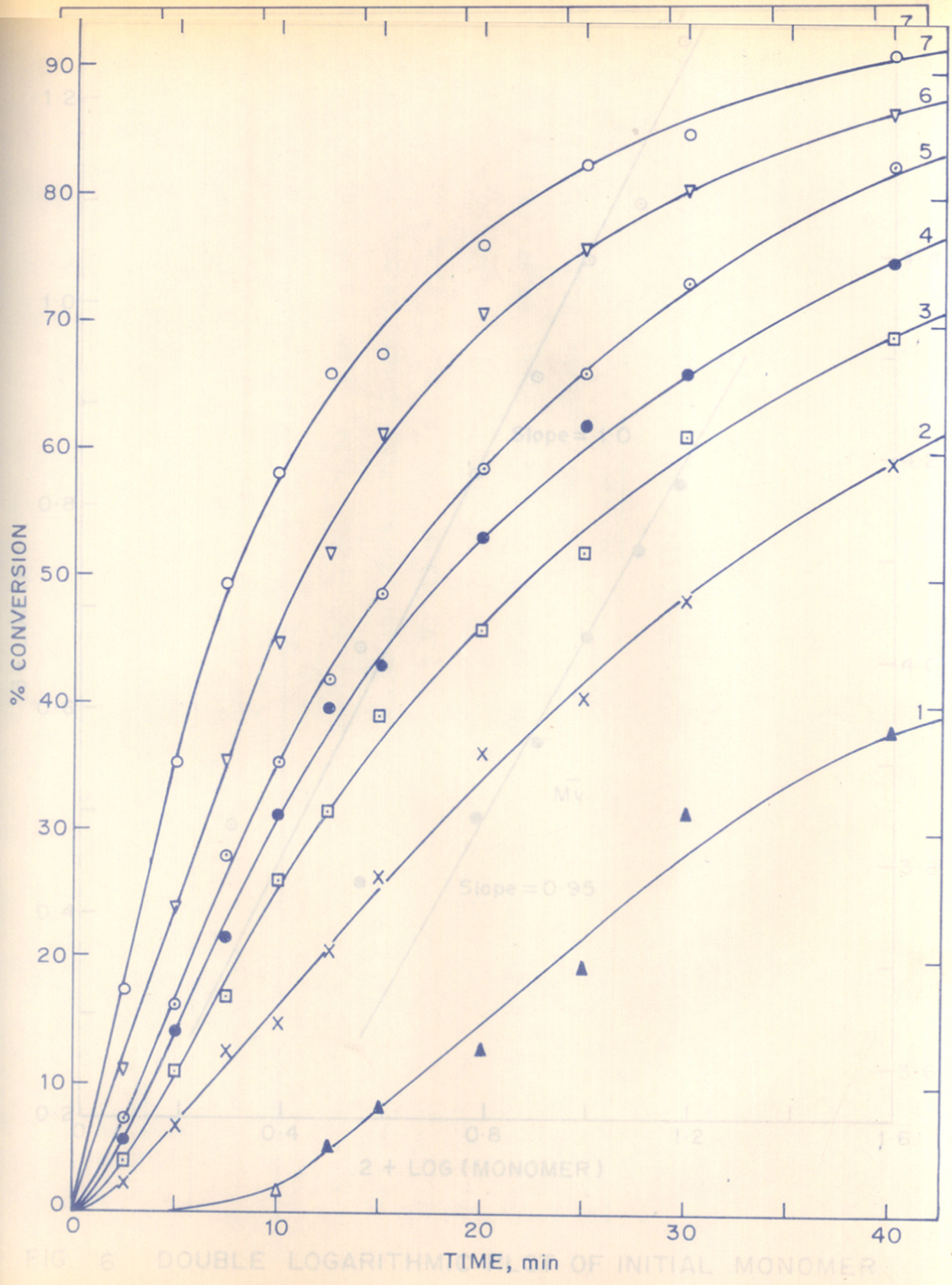


FIG. 5. POLYMERIZATION OF ACRYLAMIDE WITH VARYING MONOMER CONCENTRATION, (TABLE - 4)

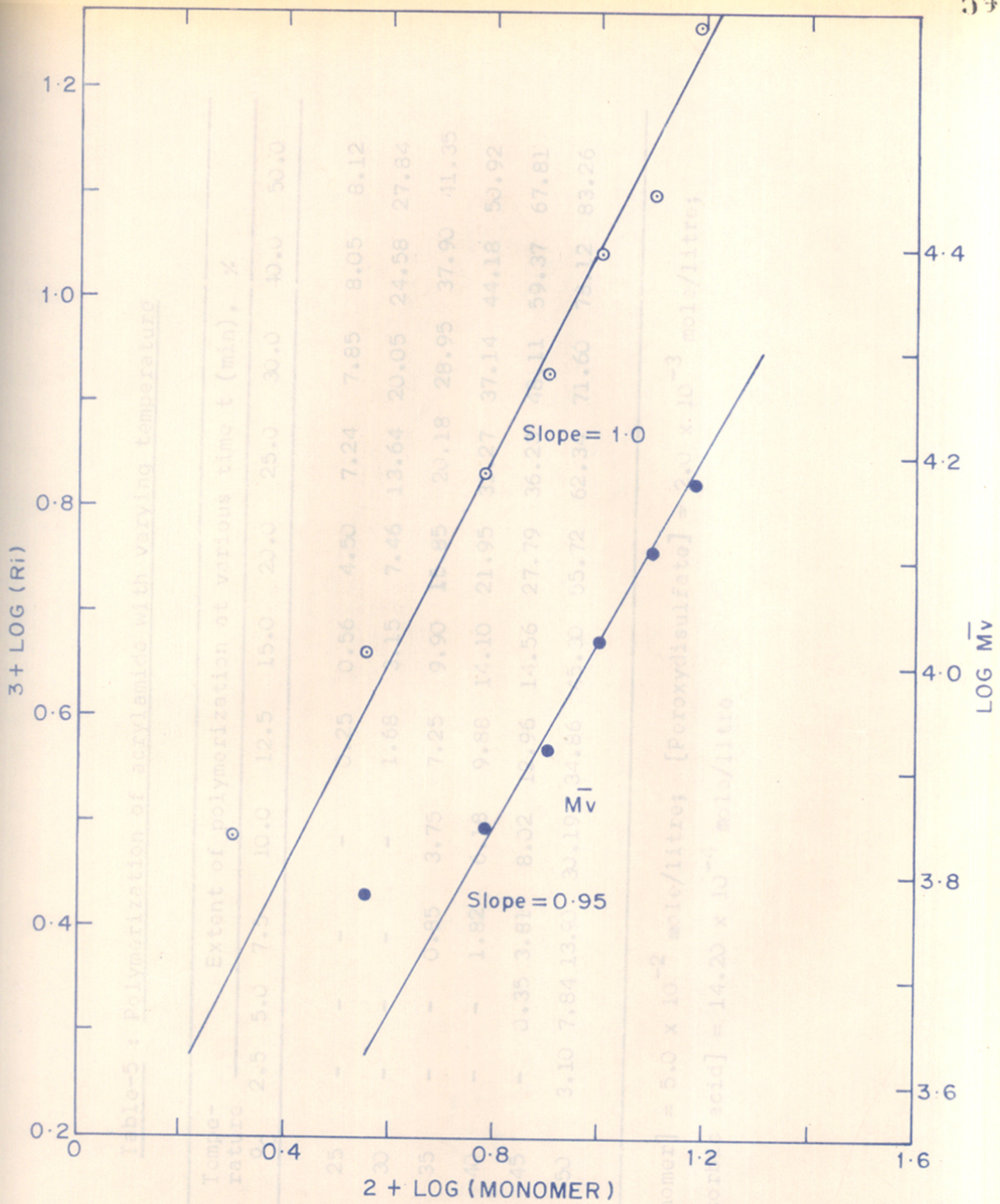


FIG. 6. DOUBLE LOGARITHMIC PLOT OF INITIAL MONOMER CONCENTRATION VERSUS Ri (mole/liter/sec) and $\bar{M}v$

Table-5 : Polymerization of acrylamide with varying temperature

No.	Temperature °C	Extent of polymerization at various time t (min), %										
		2.5	5.0	7.5	10.0	12.5	15.0	20.0	25.0	30.0	40.0	50.0
1.	25	-	-	-	-	0.25	0.56	4.50	7.24	7.85	8.05	8.12
2.	30	-	-	-	-	1.68	3.15	7.46	13.64	20.05	24.58	27.84
3.	35	-	-	0.85	3.75	7.25	9.90	15.85	20.18	28.95	37.90	41.35
4.	40	-	-	1.82	6.18	9.88	14.10	21.95	31.27	37.14	44.18	50.92
5.	45	-	0.35	3.81	8.02	12.96	14.56	27.79	36.23	48.11	59.37	67.81
6.	50	3.10	7.84	13.90	30.19	34.86	45.30	55.72	62.34	71.60	78.12	83.26

[Monomer] = 5.0×10^{-2} mole/litre; [Peroxydisulfate] = 2.0×10^{-3} mole/litre;
[Ascorbic acid] = 14.20×10^{-4} mole/litre

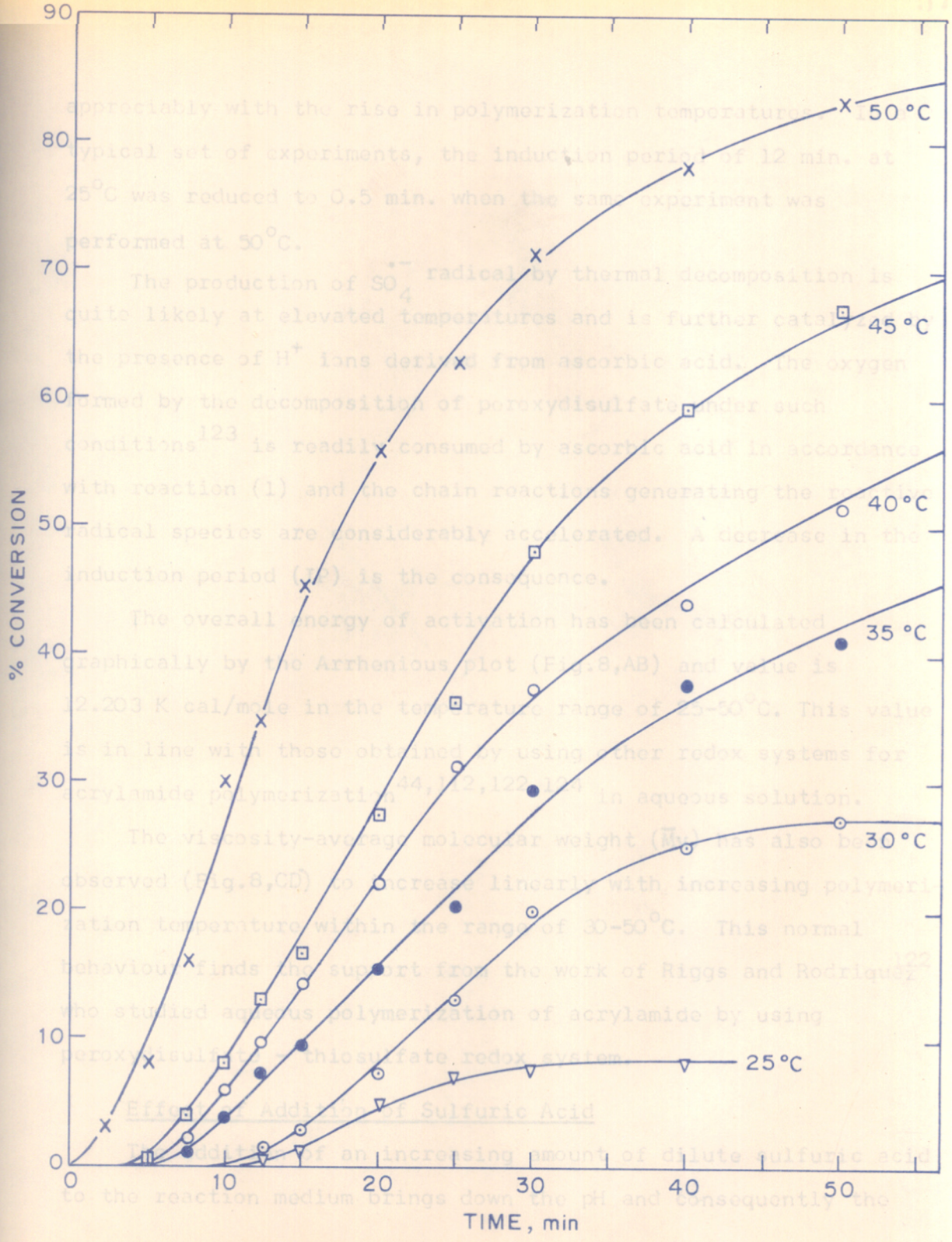


FIG. 7. POLYMERIZATION OF ACRYLAMIDE WITH VARYING TEMPERATURE, (TABLE-5)

appreciably with the rise in polymerization temperatures. In a typical set of experiments, the induction period of 12 min. at 25°C was reduced to 0.5 min. when the same experiment was performed at 50°C.

The production of $SO_4^{\cdot -}$ radical by thermal decomposition is quite likely at elevated temperatures and is further catalyzed by the presence of H^+ ions derived from ascorbic acid. The oxygen formed by the decomposition of peroxydisulfate under such conditions[123] is readily consumed by ascorbic acid in accordance with reaction (1) and the chain reactions generating the reactive radical species are considerably accelerated. A decrease in the induction period (IP) is the consequence.

The overall energy of activation has been calculated graphically by the Arrhenious plot (Fig.8,AB) and value is 12.203 K cal/mole in the temperature range of 25-50°C. This value is in line with those obtained by using other redox systems for acrylamide polymerization[44,112,122,124] in aqueous solution.

The viscosity-average molecular weight ($\bar{M}v$) has also been observed (Fig.8,CD) to increase linearly with increasing polymerization temperature within the range of 30-50°C. This normal behaviour finds the support from the work of Riggs and Rodriquez[122] who studied aqueous polymerization of acrylamide by using peroxydisulfate - thiosulfate redox system.

Effect of Addition of Sulfuric Acid

The addition of an increasing amount of dilute sulfuric acid to the reaction medium brings down the pH and consequently the

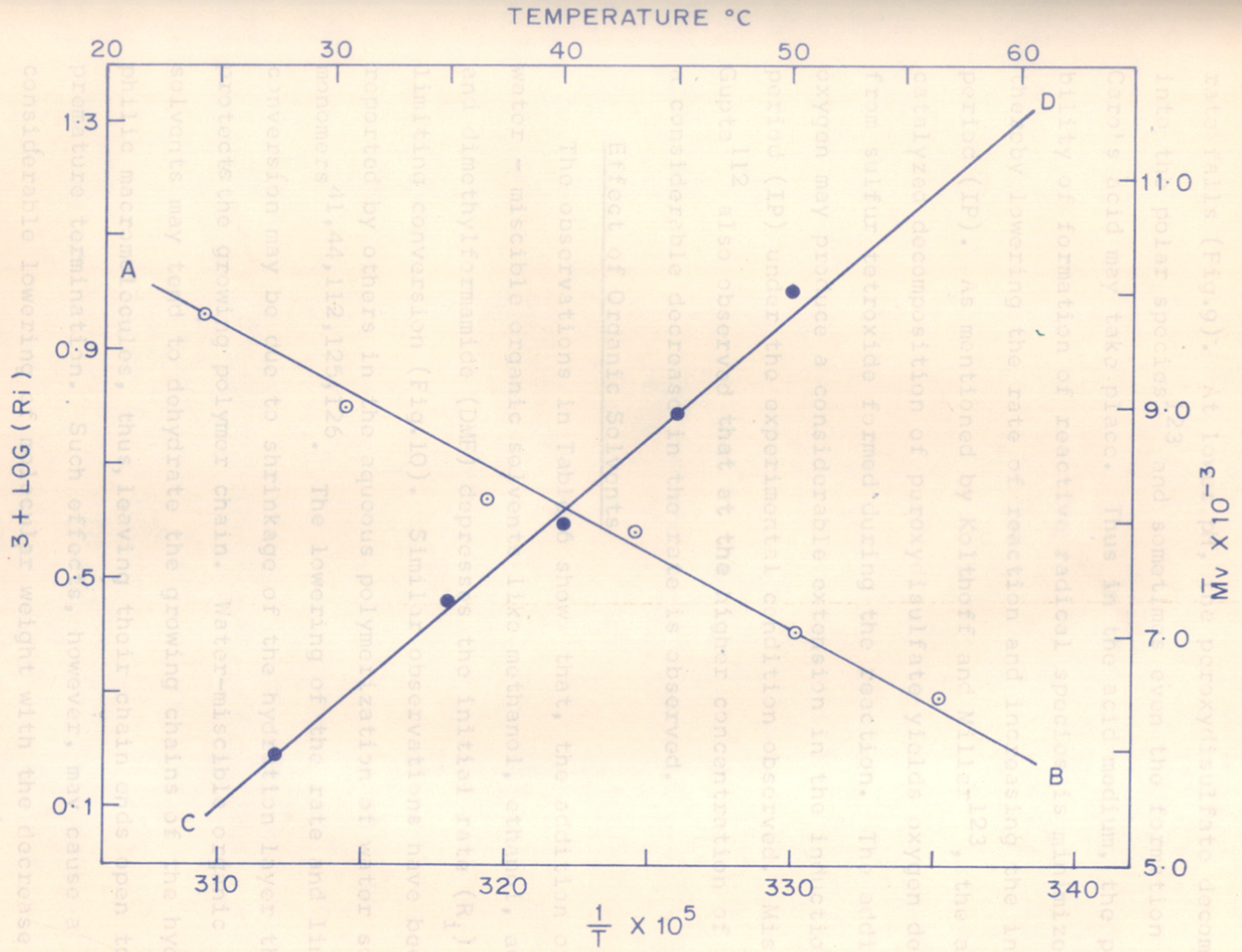


FIG. 8. AB ⟶ ARRHENIUS PLOT OF THE INITIAL RATE OF POLYMERIZATION (Ri mole/liter/sec); CD ⟶ DEPENDENCE OF MOLECULAR WEIGHT ON TEMPERATURE (Concentrations taken are similar to Fig. 7.)

rate falls (Fig.9). At lower pH, the peroxydisulfate decomposes into the polar species[123] and sometimes even the formation of Caro's acid may take place. Thus in the acid medium, the possibility of formation of reactive radical species is minimized, thereby lowering the rate of reaction and increasing the induction period (IP). As mentioned by Kolthoff and Miller[123], the acid-catalyzed decomposition of peroxydisulfate yields oxygen derived from sulfur tetroxide formed during the reaction. The additional oxygen may produce a considerable extension in the induction period (IP) under the experimental condition observed. Misra and Gupta[112] also observed that at the higher concentration of acid, a considerable decrease in the rate is observed.

Effect of Organic Solvents

The observations in Table-6 show that, the addition of water - miscible organic solvents like methanol, ethanol, acetone and dimethylformamide (DMF) depresses the initial rate (R_i) and limiting conversion (Fig.10). Similar observations have been reported by others in the aqueous polymerization of water soluble monomers[41,44,112,125,126]. The lowering of the rate and limiting conversion may be due to shrinkage of the hydration layer that protects the growing polymer chain. Water-miscible organic solvents may tend to dehydrate the growing chains of the hydrophilic macromolecules, thus, leaving their chain ends open to premature termination. Such effects, however, may cause a considerable lowering of molecular weight with the decrease in

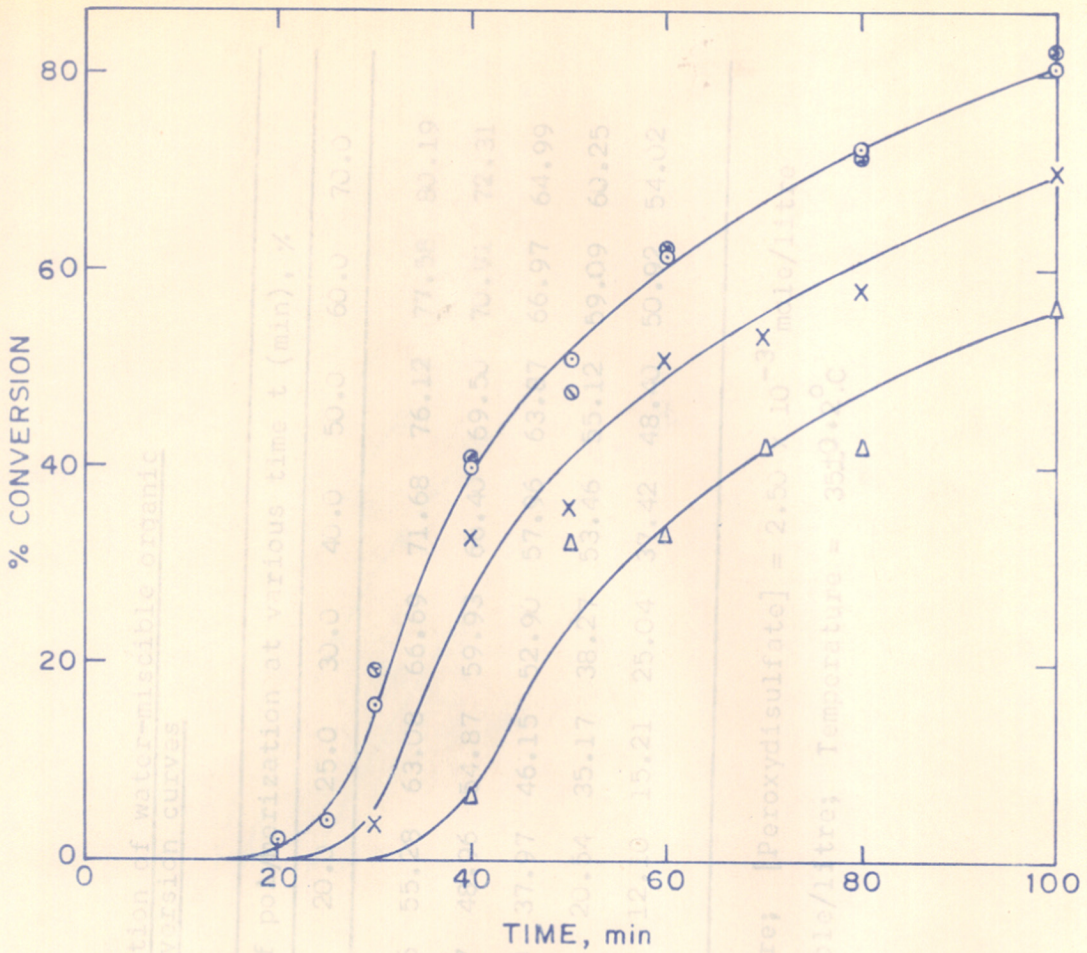


FIG. 9. EFFECT OF ADDITION OF SULFURIC ACID ON THE CONVERSION CURVES

$[\text{Monomer}] = 7{\cdot}0 \times 10^{-2}$ mole/liter; $[\text{peroxydisulfate}] = 10{\cdot}0 \times 10^{-3}$ mole/liter; $[\text{Ascorbic acid}] = 11{\cdot}36 \times 10^{-4}$ mole/liter and Temperature = 30 ± 0·2 °C

⊙ Control, ● $[H_2SO_4] = 5{\cdot}0 \times 10^{-4}$ mole/litre,

× $[H_2SO_4] = 10{\cdot}0 \times 10^{-4}$ mole/liter and Δ $[H_2SO_4] = 30{\cdot}0 \times 10^{-4}$ mole/liter

Table-6 : Effect of addition of water-miscible organic solvents on conversion curves

No.	Solvent 5% v/v	Extent of polymerization at various time t (min), %									
		5.0	10.0	15.0	20.0	25.0	30.0	40.0	50.0	60.0	70.0
1.	Controll	3.54	25.36	42.86	55.28	63.08	66.69	71.68	76.12	77.58	80.19
2.	Methanol	3.10	18.29	35.17	48.96	54.87	59.93	66.40	69.50	70.91	72.31
3.	Ethanol	2.81	12.66	28.98	37.97	46.15	52.90	57.96	63.87	66.97	64.99
4.	DMF	1.97	7.03	14.91	20.54	35.17	38.27	53.46	55.12	59.09	60.25
5.	Acetone	-	2.25	5.07	12.10	15.21	25.04	37.42	48.40	50.92	54.02

[Monomer] = 5.00×10^{-2} mole/litre; [Peroxydisulfate] = 2.50×10^{-3} mole/litre
[Ascorbic acid] = 14.20×10^{-4} mole/litre; Temperature = $35 \pm 0.2^{\circ}C$

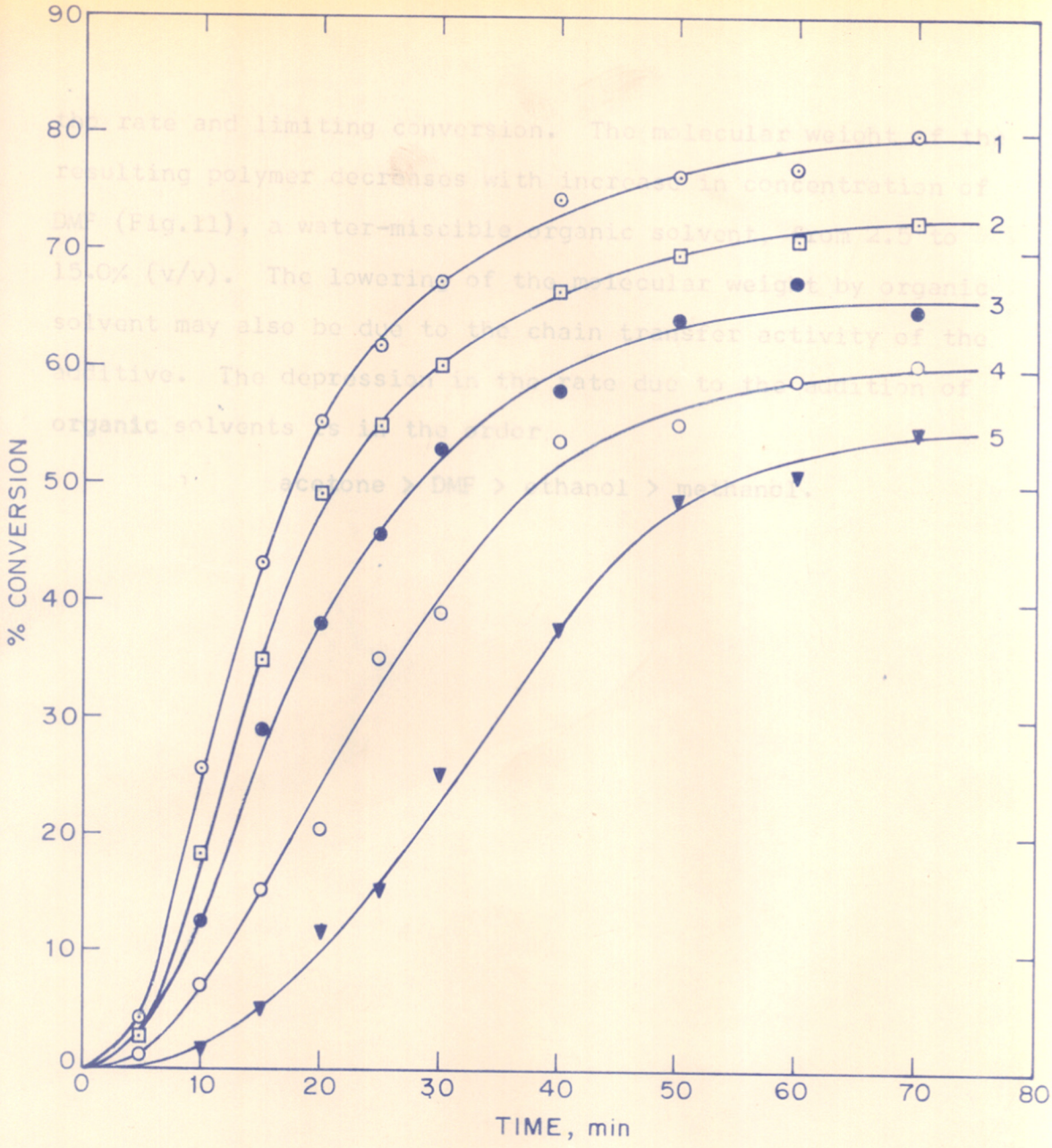


FIG. 10. EFFECT OF ADDITION OF WATER-MISCIBLE ORGANIC SOLVENTS ON THE CONVERSION CURVES:

$[\text{Monomer}] = 5{\cdot}0 \times 10^{-2}$ mole/liter; $[\text{peroxydisulfate}] = 2{\cdot}5 \times 10^{-3}$ mole/liter; $[AH_2] = 14{\cdot}2 \times 10^{-4}$ mole/liter and temperature $= 35 \pm 0{\cdot}2$ °C

(1) Control, (2) Methanol (5% v/v), (3) Ethanol (5% v/v), (4) DMF (5% v/v), (5) Acetone (5% v/v)

the rate and limiting conversion. The molecular weight of the resulting polymer decreases with increase in concentration of DMF (Fig.11), a water-miscible organic solvent, from 2.5 to 15.0% (v/v). The lowering of the molecular weight by organic solvent may also be due to the chain transfer activity of the additive. The depression in the rate due to the addition of organic solvents is in the order:

acetone > DMF > ethanol > methanol.

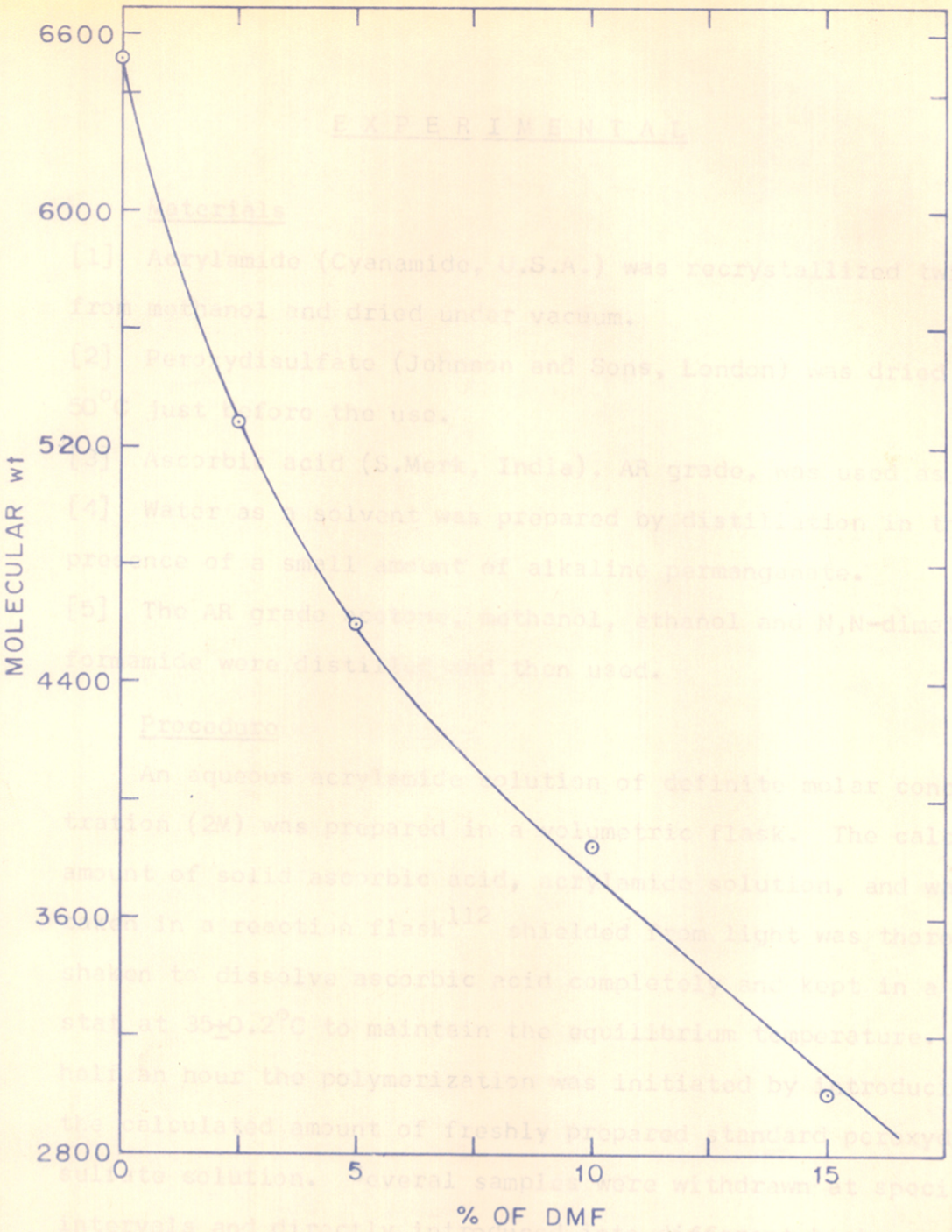


FIG. 11. EFFECT OF ADDITION OF DMF ON MOLECULAR WEIGHT: $[\text{Monomer}] = 5{\cdot}0 \times 10^{-2}$ mole/liter; $[\text{peroxydisulfate}] = 2{\cdot}5 \times 10^{-3}$ mole/liter; $[AH_2] = 14{\cdot}2 \times 10^{-4}$ mole/liter and temperature $= 35 \pm 0{\cdot}2$ °C

EXPERIMENTAL

Materials

[1] Acrylamide (Cyanamide, U.S.A.) was recrystallized twice from methanol and dried under vacuum.

[2] Peroxydisulfate (Johnson and Sons, London) was dried at 50°C just before the use.

[3] Ascorbic acid (S.Merk, India), AR grade, was used as such.

[4] Water as a solvent was prepared by distillation in the presence of a small amount of alkaline permanganate.

[5] The AR grade acetone, methanol, ethanol and N,N-dimethylformamide were distilled and then used.

Procedure

An aqueous acrylamide solution of definite molar concentration (2M) was prepared in a volumetric flask. The calculated amount of solid ascorbic acid, acrylamide solution, and water taken in a reaction flask[112] shielded from light was thoroughly shaken to dissolve ascorbic acid completely and kept in a thermostat at 35±0.2°C to maintain the equilibrium temperature. After half an hour the polymerization was initiated by introducing the calculated amount of freshly prepared standard peroxydisulfate solution. Several samples were withdrawn at specified intervals and directly introduced into different beakers, each containing 10 ml of ice cold 1% hydroquinone in 2N of sulfuric acid to short-stop the polymerization reaction and decompose

the remaining peroxydisulfate ions in the samples to sulfate ions. Peroxydisulfate, which is insoluble in alcohol, causes interference in the gravimetric procedure for estimating the extent of polymerization, whereas, sulfate ions are miscible in alcohol. After about half an hour the polymer was isolated by precipitation with an excess of ethanol (methanol or acetone). A few drops of 1% aluminium sulfate solution[116] were added before isolation of the polymer to obtain the complete precipitation of lower-molecular-weight polymer. The beakers that contained polymer were kept cold overnight to obtain complete precipitation of the polymer, which was then filtered in a sintered glass crucible under vacuum, dried in vacuum at 50°C, and weighed until a constant weight was achieved.

For molecular weight determination polymerization was stopped at the desired level, as mentioned above, and purified by a two-fold solution and precipitation procedure with water and alcohol. After drying under vacuum at 50°C the viscosity of the series of aqueous solutions of polyacrylamide was measured at 25°C with an Ubbelhode viscometer and the viscometric average molecular weight ($\bar{M}v$) was calculated from the equation[127]

$$[\eta] = K\bar{M}v^{a}$$

where $K = 6.84 \times 10^{-4}$

$a = 0.66 \pm 0.05$

and concentration is in g/100 ml.

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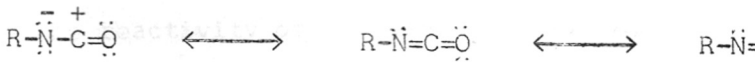
PART - II

MODIFIED NEW ACRYLAMIDE MONOMERS & POLYMERS

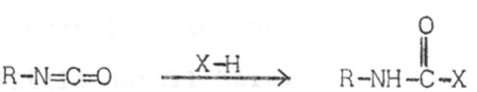
INTRODUCTION

Isocyanates, the esters of isocyanic acid, are very versatile compounds and are known since middle of nineteenth century. They have a number of applications in organic, as well as, polymer chemical industries. The significant industrial importance of isocyanates was however realised only after second World-War. The progress in the development of isocyanate chemistry has been well reviewed[1-6].

Isocyanates are characterized by the heterocumulene double bond system (-N=C=O). The electronic structure of the isocyanate group indicates that it should have the following resonance possibilities :



The presence of high unsaturation in -N=C=O group is responsible for the high reactivity of isocyanates. Isocyanates react with a broad spectrum of compounds containing 'active hydrogen'. The reaction can be described as the attack of a nucleophile on the electrophilic carbon atom in the -N=C=O group. The hydrogen atom gets attached to the nitrogen of the isocyanate group while the remainder of the reactant to the carbonyl carbon atom.



The addition product, in many cases, is stable. In those where it is unstable, it either dissociates to form the initial reactants or decomposes to some other products. Other types of reactions, which do not involve active hydrogen atom, usually proceed through an opening of the carbon - nitrogen double bond.

In most of the reactions, aromatic isocyanates are relatively more reactive than the aliphatic isocyanates[7]. This may be due to the fact that the partial negative charge on the nitrogen of the isocyanate (-NCO) group is shared by the unsaturation in the aromatic ring making the carbonyl carbon atom more positive and hence susceptible to be attacked by nucleophiles. This suggests that the presence of electron withdrawing groups in the ring enhance the reactivity, while electron donating groups reduce the reactivity of the isocyanates. Acids as well as bases catalyze these reactions of isocyanates. Certain metal compounds serve as catalysts. Steric factor also plays a considerable role in all these isocyanate reactions.Reaction medium too affects the course of the reaction if the reaction is carried out in solvent.

Some of the important reactions of the isocyanates are given in Table-7.

The present work deals with the reaction of the isocyanate with the -NH of the amide group and O-H group. Therefore, the reaction of isocyanate with the -NH and -O-H groups only described in little detail here.

Table-7 : Reactions of Isocyanates with various functional groups and products obtained therefrom.

No.	Group reacting with isocyanate R-NCO	Product obtained		References
1.	Water	Disubstituted urea	R-NH-CO-NH-R	8,9
2.	Alcohol Primary, Secondary	Urethane	R-NH-CO-O-R	1,10,11
	Alcohol tertiary	Disubstituted ureas and olefins	R-NH-CO-NH-R $CH_2-C(CH_3)=CH_2$ type	
3.	Phenol	Urethane	R-NH-CO-O-R	12
4.	Carboxylic acid	Amide	R-NH-CO-R	13,14
5.	Amine (Primary, secondary, aliphatic or aromatic)	Disubstituted urea	R-NH-CO-NH-R'	15,16
6.	Ammonia	Monosubstituted urea	$R-NH-CO-NH_2$	16
7.	Amides	Acyl ureas	R-NH-CO-NH-CO-R'	17-20
8.	Urea	Biuret	R-N(CO-NH-R')-CO-NH-R	21,22

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Table-7 : (contd

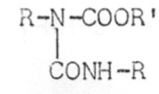
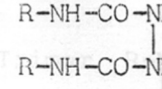
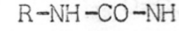
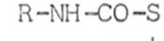
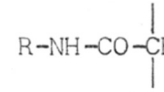
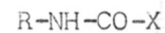
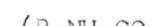
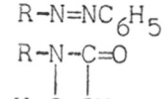
No.	Group reacting with isocyanate R-NCO	Product obtained		References
9.	Urethane	Allophanate		22
10.	Hydrazines	Substituted diurea		21
11.	Hydroxylamine			23
12.	R'-SH	Thiourethanes		15,24-27
13.	$-CH_2-$	N-Substituted amides		15,28,29
14.	Aromatic hydrocarbon	Amide		30,31
15.	Halogen acids	Carbamoyl halides		32,33
16.	Cl or Br	Dihalide		34,35
17.	Aqueous sodium, potassium or ammonium bisulfites.	Water soluble adducts		15
18.	Nitrobenzene			36
19.	Diazomethane	β-Lactam		37

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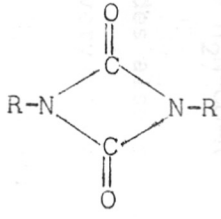
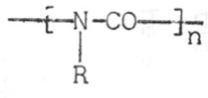
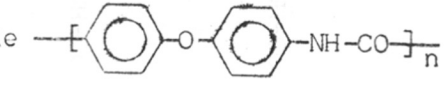
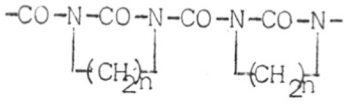
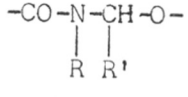
Table-7 : (contd)

No.	Group reacting with isocyanate R-NCO	Product obtained	References
20.	Grignard reagent	Amide 	38
21.	R-NCO	a) Dimer  b) Trimer	39-42
22.	Self polymerization, aromatic isocyanate	a) N-Substituted-1-nylons 	43
		b) Polyamide 	44
23.	Aliphatic diisocyanate	Copolymers 	45-48
24.	Aldehyde	Copolymers 	49,50

Reaction with compounds containing the N-H group

All compounds containing N-H groups react with isocyanates. Generally, amines react with isocyanates with the formation of substituted ureas. Primary aliphatic amines are more reactive towards isocyanates as compared to the secondary aliphatic amines and primary aromatic amines[9,51]. The secondary aromatic amines are still less reactive.

$$R\text{-}NCO + H_2N\text{-}R' \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R'$$

The isocyanates react with amide at a moderate rate to give aryl ureas[15,17].

$$R\text{-}NCO + H_2N\text{-}CO\text{-}R' \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}CO\text{-}R'$$

Sulfonamides also react with isocyanate, but their rate of reaction is very slow.

$$R\text{-}NCO + H_2N\text{-}SO_2\text{-}Ar \xrightarrow{NaOH} R\text{-}NH\text{-}CO\text{-}NH\text{-}SO_2\text{-}Ar$$

Reaction with compounds containing the -OH group

[i] Alcohols

When a alcohol reacts with an isocyanate, a urethane, also called as 'carbamate' is formed.

$$R\text{-}NCO + HO\text{-}R' \longrightarrow R\text{-}NH\text{-}CO\text{-}O\text{-}R'$$

Reactions of isocyanates with primary and secondary alcohols give quantitative yields of the urethanes, which are quite stable. In contrast, reaction with tertiary alcohol is normally

accompanied by olefin formation[1].

[ii] Water

The reactivity of isocyanate with water is usually similar to that of secondary alcohols if both are soluble in the reaction medium. The first addition product (R-NH-COOH) is unstable.

$$R\text{-}NCO + H_2O \longrightarrow [R\text{-}NH\text{-}COOH] \longrightarrow R\text{-}NH_2 + CO_2 \uparrow$$

The amine thus formed reacts more rapidly with isocyanate than the water molecule, forming the disubstituted urea.

$$R\text{-}NCO + H_2N\text{-}R \longrightarrow R\text{-}NH\text{-}CO\text{-}NH\text{-}R$$

The reaction of isocyanate with water can proceed differently in the presence of hydrochloric acid and sodium hydroxide[8]. In the presence of hydrochloric acid the amine hydrochloride is formed and in presence of sodium hydroxide, the amine and sodium carbonate are formed.

$$R\text{-}NCO + H_2O + HCl \longrightarrow R\text{-}NH_2.HCl + CO_2 \uparrow$$

$$R\text{-}NCO + H_2O + NaOH \longrightarrow R\text{-}NH\text{-}COONa$$

$$R\text{-}NH\text{-}COONa + H_2O + NaOH \longrightarrow R\text{-}NH_2 + Na_2CO_3.$$

PRESENT INVESTIGATION, RESULTS AND DISCUSSION

Polymers containing reactive groups along the chain are of great interest, mainly because they provide means for further reactions to give modified polymers. Such polymers are prepared by polymerizing the monomers containing functional groups or by copolymerizing such monomers with other monomers to give copolymers with randomly located reactive groups. For example, to introduce carboxyl groups into polystyrene; styrene and acrylic acid are copolymerized by a free radical initiator.

Homopolymers and copolymers of number of vinyl monomers containing various reactive groups such as hydroxyl, carboxylic, isocyanate, epoxide, etc. are well known.

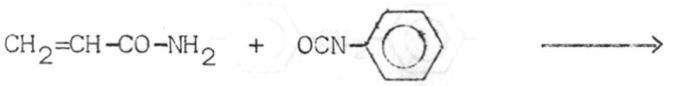
Due to the high reactivity of the isocyanate groups with compounds containing an active hydrogen atom such as alcohols, amines, acids, etc., it is of great interest to synthesize polymers laterally substituted with an isocyanate group. These polymers can be easily modified, crosslinked, grafted, etc. by means of isocyanate groups.

Hart[52], Schulz and Hartmann[53], Overberger et al[54], and Butler and Monroe[55] have studied the vinyl homopolymerization of vinyl isocyanate. Iwakura et al[56] and Welzel and Greber[57] have determined the various reactivity ratios for its copolymerization with styrene, methyl methacrylate, methylacrylate, acrylonitrile and vinylidene chloride. Kropa and Nyquist[58] claim for the copolymer of methyl acrylate with propenyl isocyanate to impair

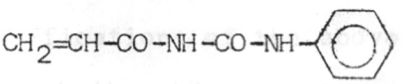
special properties to textiles made of cotton, wool and silk and also its use as binder for various fillers. Hart et al[59] determined the reactivity ratios for the copolymers of isopropenyl isocyanate with methyl acrylate and with styrene. Fujisaki et al[60] claim for its copolymer with acrylonitrile better dying properties in comparison to homopolyacrylonitrile. Butler and Monroe[61] prepared copolymers of both, β-allyloxyethyl isocyanate and of 9-decenyl isocyanate with methyl acrylate, styrene and methyl methacrylate. Graham[62] made graft copolymers from amine-terminated polystyrene with copolymers of β-isocyanatoethyl methacrylate. Vollonert[63] prepared impact-resistant polystyrene by joining a copolymer of styrene - isocyanatohexylacrylamide with a polyacrylate containing free carboxylic groups through the reaction of these carboxylic groups with the isocyanate groups of the styrene copolymer . Liebersohn and Kohn[64] prepared copolymer, poly(styrene-co-styryl isocyanate) by copolymerization of styrene either with cinnamoyl azide or with styryl isocyanate. The poly(styrene-co-styryl isocyanate) can be grafted or cross-linked through the lateral isocyanate groups and coloured copolymers can be obtained by internal dying. The copolymers could be used as matrix to attach enzymes and as carriers for slow release pharmaceuticals, insecticides, etc.

It has been reported in the literature[65] that phenyl isocyanate reacts with the amide group of the acrylamide in the presence of diluent and an organic polymer retarder to yield

acryloylurea, which can be readily polymerized.



Acrylamide Phenyl isocyanate



The present investigation was undertaken with a view to synthesize new acryloylurea monomers and to polymerize them into new polymers.

Acrylamide was reacted with the following diisocyanates in the presence of organic polymer retarder :

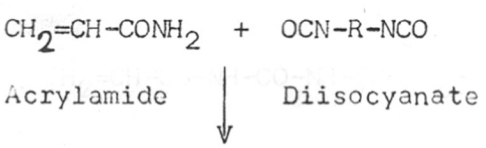
1] 2,4-Toluene diisocyanate (TDI),

2] 4,4'-Methylene bis(phenyl isocyanate)(MDI) and

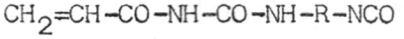
3] 1,6-Hexamethylene diisocyanate (HDI)

Thus, the acryloylurea monomers having one free isocyanate group were obtained.

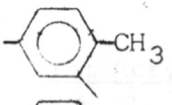
The scheme for the synthesis of isocyanato acryloylurea monomers is as shown below :

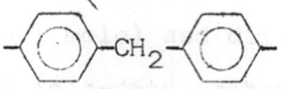


Acrylamide Diisocyanate



Acryloylurea

where, R = i) 

ii) 

iii) $-(CH_2)_6-$

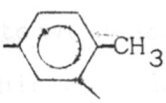
Further modifications of the above acryloylurea monomers were undertaken with the objective to prepare water soluble monomers and the polymers therefrom. The free isocyanate group was reacted with water, ethyl alcohol, ethylene glycol and glycerin as follows :

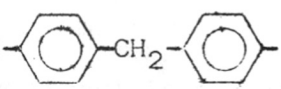
$$R'\text{-}NCO + H_2O \xrightarrow{HCl} R'\text{-}NH_2 + CO_2\uparrow$$

$$R'\text{-}NCO + CH_3\text{-}CH_2\text{-}OH \longrightarrow R'\text{-}NH\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_3$$

$$R'\text{-}NCO + HO\text{-}CH_2\text{-}CH_2\text{-}OH \longrightarrow R'\text{-}NH\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$$

$$R'\text{-}NCO + HO\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}OH \longrightarrow R'\text{-}NH\text{-}CO\text{-}O\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}OH$$

where R' = i] $CH_2=CH\text{-}CO\text{-}NH\text{-}CO\text{-}NH$- 

ii] $CH_2=CH\text{-}CO\text{-}NH\text{-}CO\text{-}NH$- 

iii] $CH_2=CH\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}(CH_2)_6-$

Acryloylureas from Acrylamide and Diisocyanates

Acrylamide (0.1 mole) and diisocyanate (0.11 mole) were heated at 100-110°C in o-dichlorobenzene using hydroquinone as polymer retarder. The reaction mixture was cooled, the product was filtered at suction and washed with carbon tetra chloride (to remove excess diisocyanate). In case of acrylamide-HDI reaction, the product which remained in the solution was precipitated using nonsolvent, carbon tetra chloride.

Hydroquinone, which was added as polymer retarder, was removed by soxhlet extraction with ether. All monomers were dried under reduced pressure.

Characterization of Isocyanato Acryloylurea Monomers

The monomers were characterized by the elemental analysis and spectral data such as IR and NMR. The physical characteristics of all these monomers synthesized are recorded in Table-8.

To confirm the structures of acryloylurea monomers, the model reaction of phenyl isocyanate with acrylamide was carried out. The IR and NMR spectra of this compound is studied.

Infrared Spectra

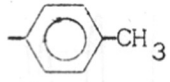
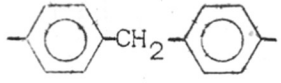
Spectra of acryloylurea from phenyl isocyanate

The IR spectrum is shown in Fig.12.

The spectrum showed a doublet at 1710 and 1700 cm^{-1}. This absorption is amide I band. The two bands at 3120 and 3240 cm^{-1} were assigned to the two N-H groups. The absorptions at 1310 cm^{-1} and 1565 cm^{-1} were attributed to amide III and amide II bands.

Table-8 : Physical characteristics of acryloylureas

$CH_2=CH-CO-NH-CO-NH-R-NCO$

No.	R	Abbre.	M.P. °C	Yield %	Elemental Analysis*% C	H	N
1.		Ia	256	90.0	58.79 58.69	4.49 4.22	17.14 17.35
2.		IIa	>300	85.0	67.28 67.02	4.71 4.62	13.08 12.86
3.	$-(CH_2)_6-$	IIIa	180	65.0	55.24 54.99	7.11 7.35	17.57 17.19

* For each monomer the upper value represents the theoretical analysis and the lower value shows the results obtained experimentally.

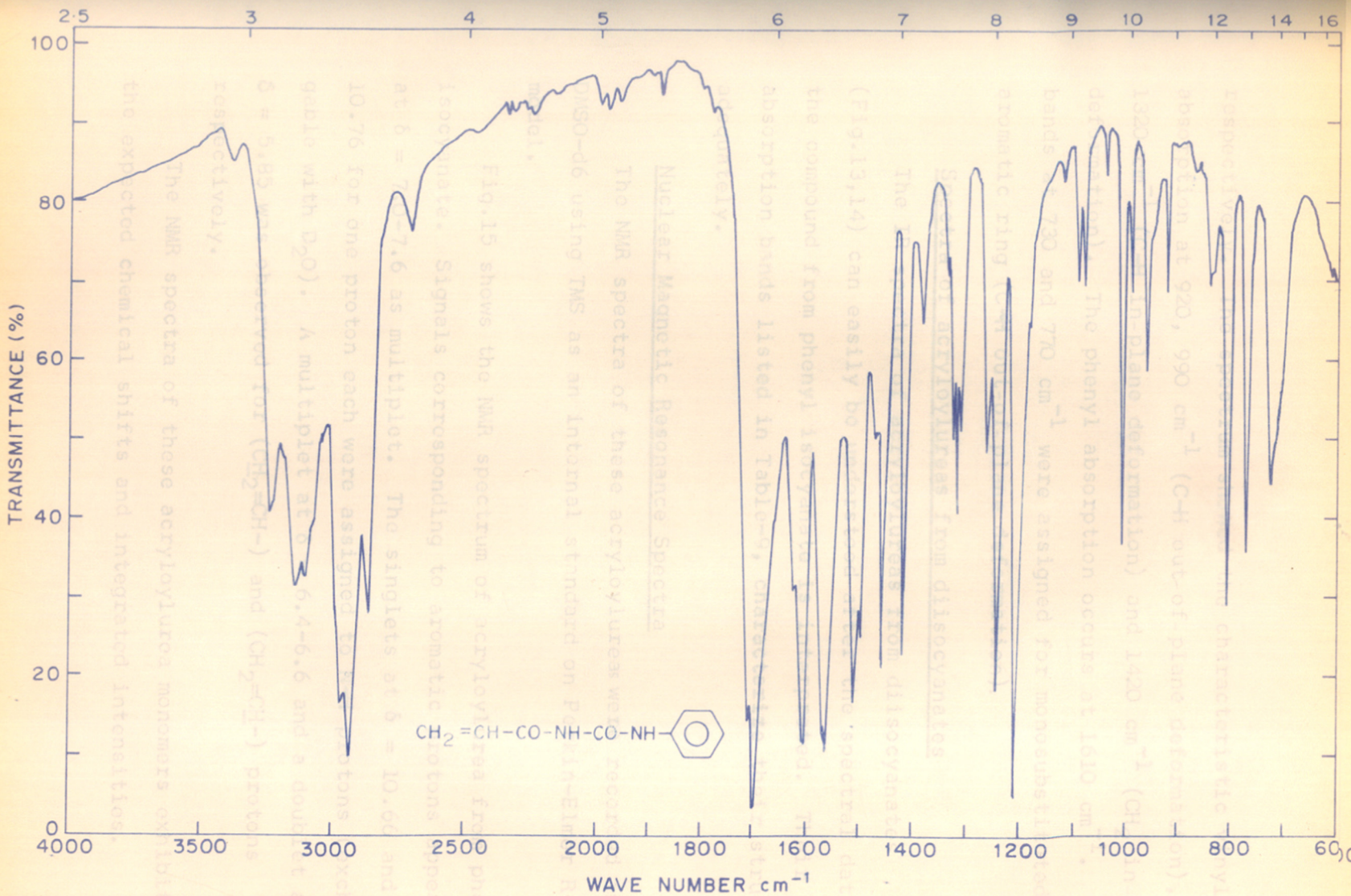


FIG. 12. IR SPECTRUM OF ACRYLOYLUREA FROM PHENYL ISOCYANATE

respectively. The spectrum showed the characteristic vinyl absorption at 920, 990 cm^{-1} (C-H out-of-plane deformation), 1320 cm^{-1} (C-H in-plane deformation) and 1420 cm^{-1} (CH_2 in-plane deformation). The phenyl absorption occurs at 1610 cm^{-1}. The bands at 730 and 770 cm^{-1} were assigned for monosubstituted aromatic ring (C-H out-of-plane deformation).

Spectra of acryloylureas from diisocyanates

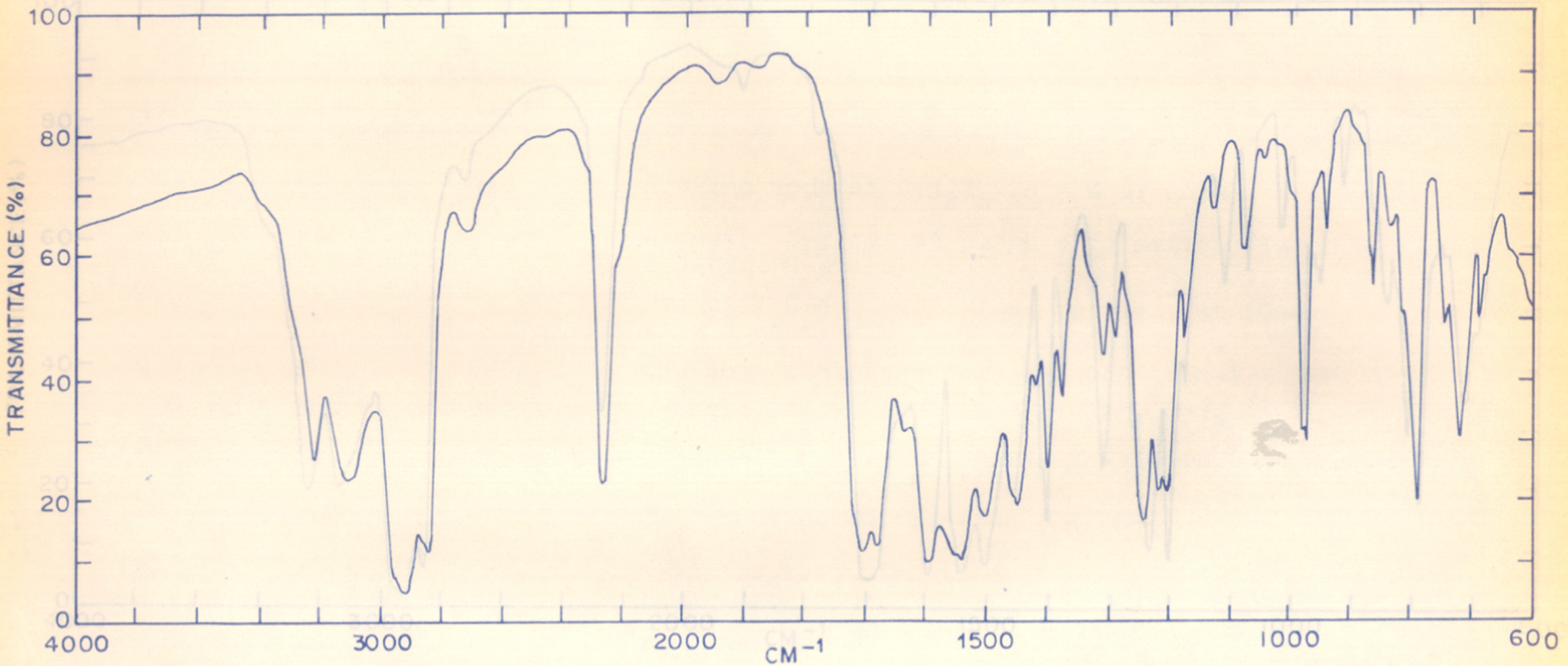
The IR spectra of acryloylureas from diisocyanates (Fig.13,14) can easily be understood after the spectral data of the compound from phenyl isocyanate is interpreted. Their absorption bands listed in Table-9, characterize their structure adequately.

Nuclear Magnetic Resonance Spectra

The NMR spectra of these acryloylureas were recorded in DMSO-d6 using TMS as an internal standard on Perkin-Elmer R-32 model.

Fig.15 shows the NMR spectrum of acryloylurea from phenyl isocyanate. Signals corresponding to aromatic protons appear at δ = 7.0-7.6 as multiplet. The singlets at δ = 10.66 and 10.76 for one proton each were assigned to N-H protons (exchangable with D_2O). A multiplet at δ = 6.4-6.6 and a doublet at δ = 5.85 was observed for (CH_2=CH-) and (CH_2=CH-) protons respectively.

The NMR spectra of these acryloylurea monomers exhibit the expected chemical shifts and integrated intensities.



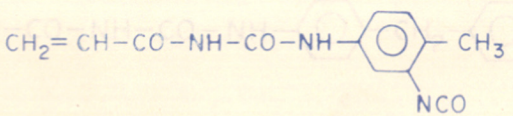
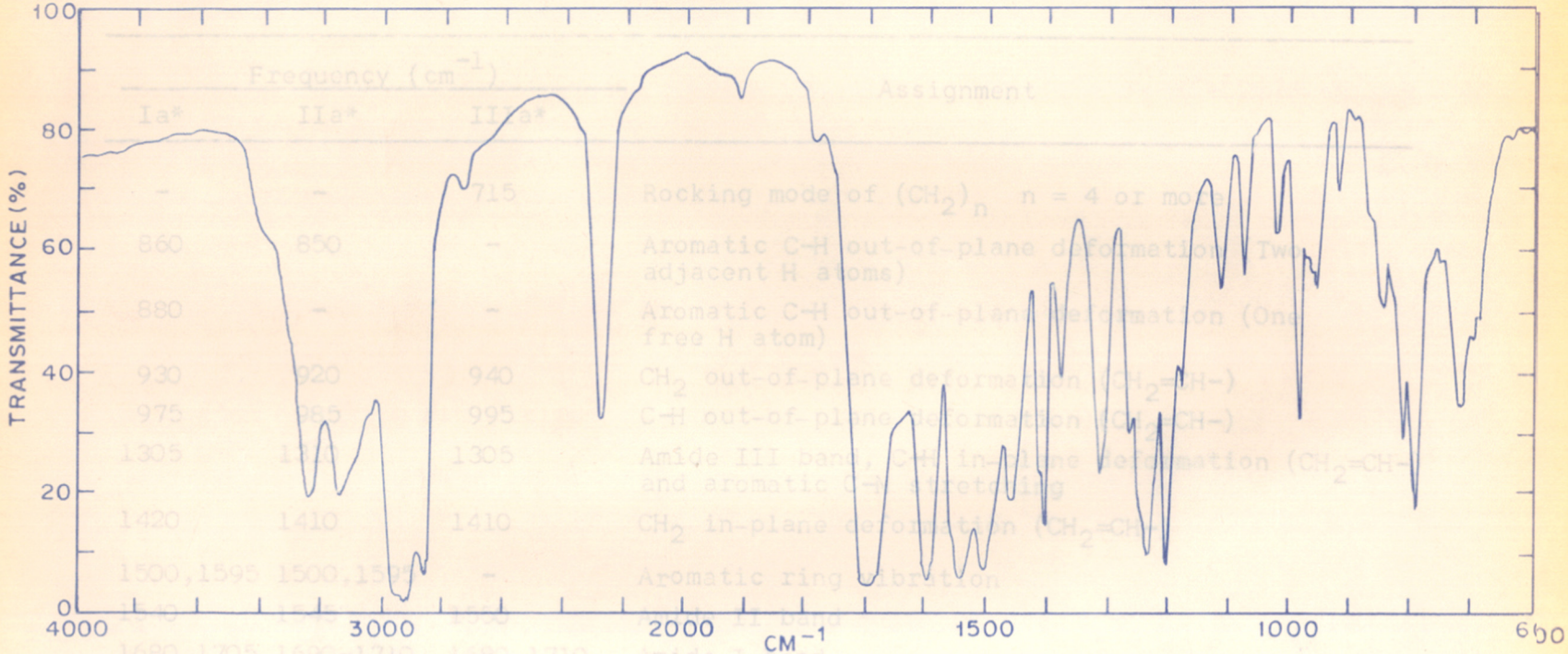


FIG. 13. IR SPECTRUM OF ACRYLOYLUREA FROM TDI



$CH_2=CH-CO-NH-CO-NH-\langle\bigcirc\rangle-CH_2-\langle\bigcirc\rangle-NCO$

FIG. 14. IR SPECTRUM OF ACRYLOYLUREA FROM MDI

Table-9 : Infrared frequencies for absorption bands of acryloylurea monomers

Frequency (cm^{-1})			Assignment
Ia*	IIa*	IIIa*	
-	-	715	Rocking mode of $(CH_2)_n$ n = 4 or more
860	850	-	Aromatic C-H out-of-plane deformation (Two adjacent H atoms)
880	-	-	Aromatic C-H out-of-plane deformation (One free H atom)
930	920	940	CH_2 out-of-plane deformation (CH_2=CH-)
975	985	995	C-H out-of-plane deformation (CH_2=CH-)
1305	1310	1305	Amide III band, C-H in-plane deformation (CH_2=CH-) and aromatic C-N stretching
1420	1410	1410	CH_2 in-plane deformation (CH_2=CH-)
1500,1595	1500,1595	-	Aromatic ring vibration
1540	1545	1550	Amide II band
1680,1705	1690-1710	1680,1710	Amide I band
2260	2270	2270	Asymmetric -N=C=O stretching
3100,3220	3130,3225	3160,3240	N-H stretching

* Ia, IIa and IIa ——→ Abbre. taken from Table 8.

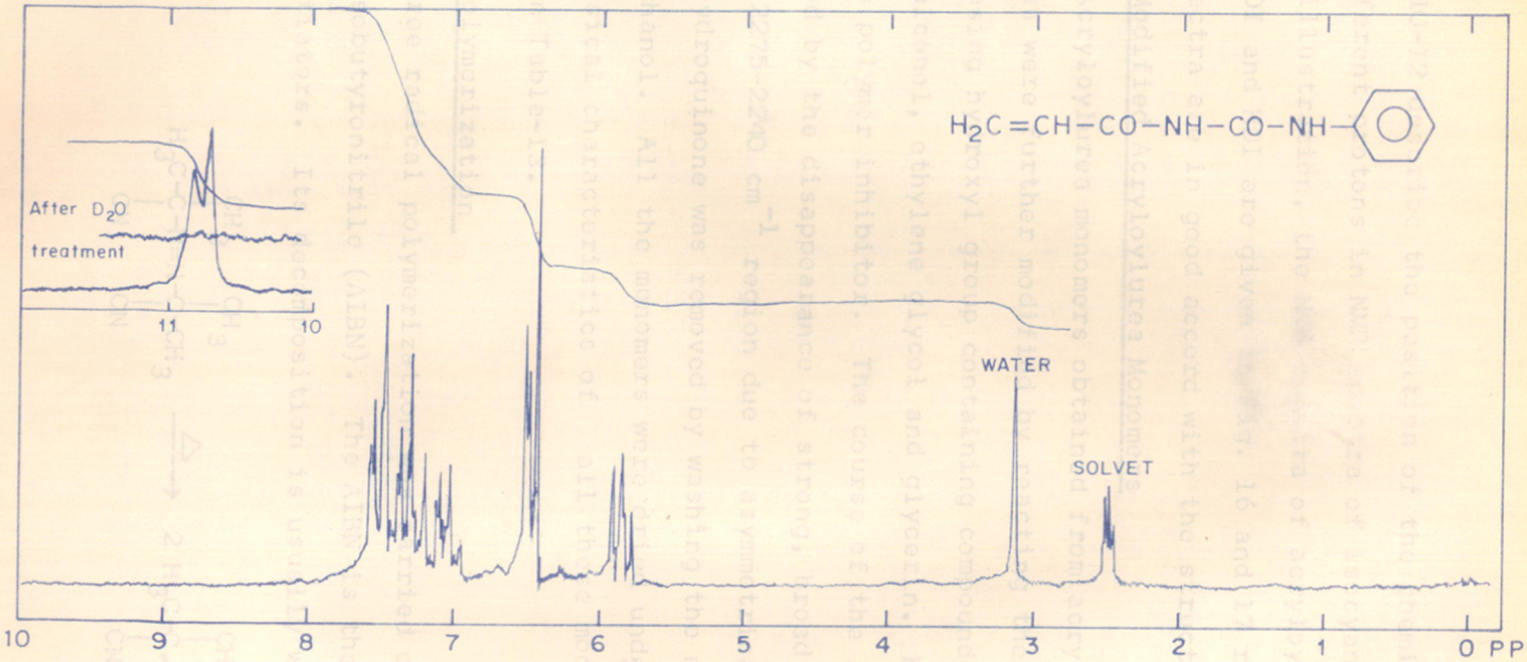


FIG. 15. NMR SPECTRUM OF ACRYLOYLUREA FROM PHENYL ISOCYANATE

Tables10-12 describe the position of the chemical shifts caused by different protons in NMR spectra of isocyanato acryloylureas. As an illustration, the NMR spectra of acryloylureas obtained from MDI and HDI are given in Fig. 16 and 17 respectively. The NMR spectra are in good accord with the structures assigned.

Modified Acryloylurea Monomers

Acryloylurea monomers obtained from acrylamide and diisocyanates were further modified by reacting the free isocyanate group using hydroxyl group containing compounds such as water, ethyl alcohol, ethylene glycol and glycerin. Hydroquinone was used as polymer inhibitor. The course of the reaction was followed by the disappearance of strong, broad absorption band in the 2275-2240 cm^{-1} region due to asymmetrical -N=C=O stretching.

Hydroquinone was removed by washing the modified monomers with ethanol. All the monomers were dried under reduced pressure. The physical characteristics of all these modified monomers are given in Table-13.

Polymerization

Free radical polymerization was carried out by using 2,2'-azobisisobutyronitrile (AIBN). The AIBN is the best known of the azo initiators. Its decomposition is usually written as :

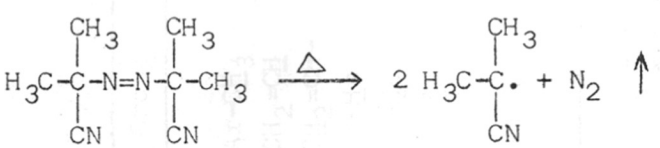
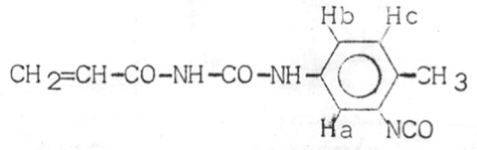


Table-10 : NMR spectral data of acryloylurea Ia

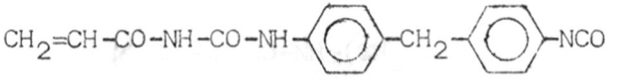


Group	δ ppm	No.of proton/s	Multiplicity
Ar-CH_3	2.14	3H	s
CH_2=CH	5.7-6.0	1H	m
CH_2=CH-	6.3-6.6	2H	m
Ar-Hc	7.10	1H	d (J=8.5 Hz)
Ar-Hb	7.2-7.45	1H	dd (J=8.5, 2 Hz)
Ar-Ha	8.07	1H	d (j=2.0 Hz)
-	8.17	-	s* (Exchanges with D_2O)
-NH	10.70	2H	br.s. (Exchanges with D_2O)

s = singlet, d = doublet, m = multiplet, br. = broad

* Integration shows the presence of slight impurity which might arise due to reaction of -NCO group with H_2O present in DMSO-d_6.

Table-11 : NMR spectral data of acryloylurea IIa



Group	δ ppm	No.of proton/s	Multiplicity
Ar-CH_2-Ar	3.86	2H	br.s.
CH_2=CH-	5.86	1H	dd (J=6.0, 5.5 Hz)
CH_2=CH-	6.3-6.6	2H	m
Aromatic	7.05	2H	d (J=9.0 Hz)
Aromatic	7.14	2H	d (J=9.0 Hz)
Aromatic	7.35	2H	d (J=9.0 Hz)
Aromatic	7.43	2H	d (J=9.0 Hz)
--	8.3-8.5	-	s* (Exchanges with D_2O)
-NH-	10.6	1H	s (Exchanges with D_2O)
-NH-	10.73	1H	s (Exchanges with D_2O)

s = singlet, d = doublet, m = multiplet, br. = broad

* Integration shows the presence of slight impurity which might arise due to reaction of -NCO group with H_2O present in DMSO-d_6.

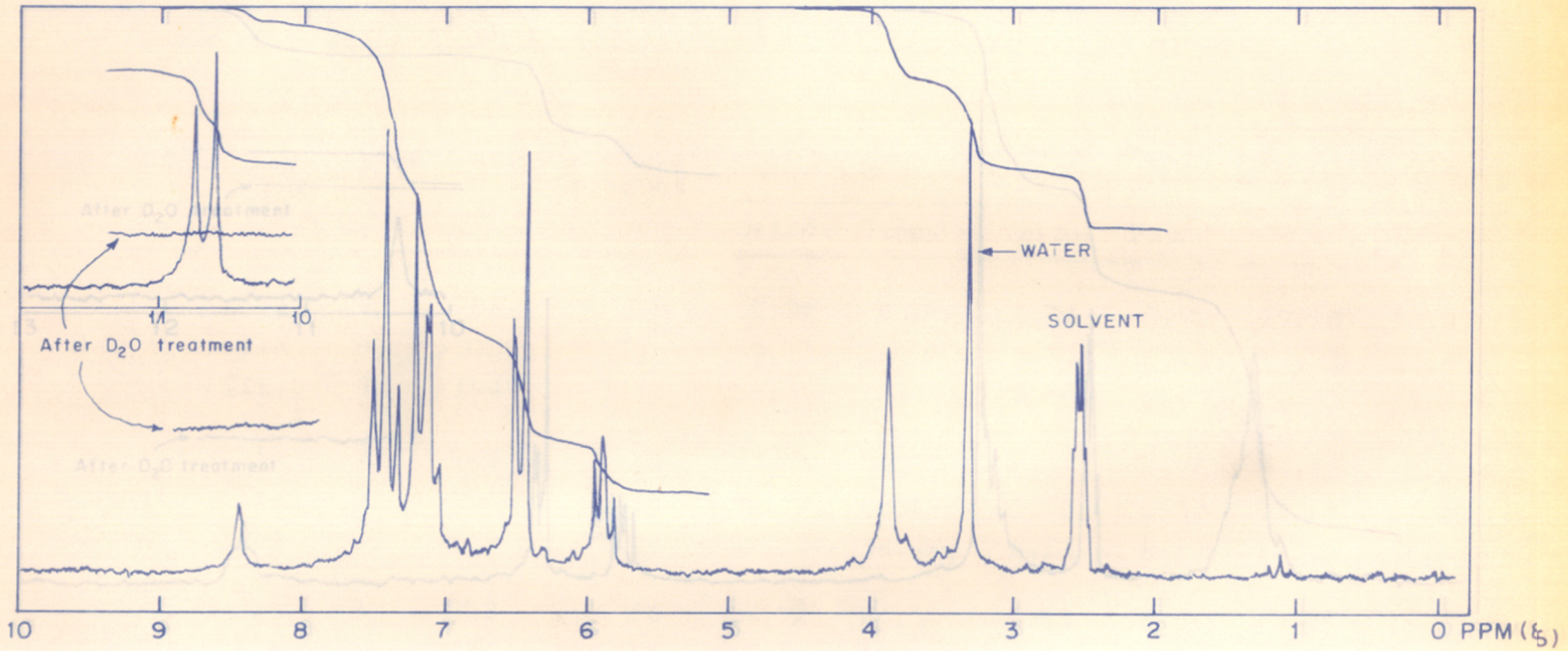
Table-12 : NMR spectral data of acryloylurea IIIa

$CH_2=CH-CO-NH-CO-NH-(CH_2)_6-NCO$

Group	δ ppm	No.of proton/s	Multiplicity
$-(C\underline{H}_2)_4-$	1.0-1.7	8H	m
$-NH-C\underline{H}_2-CH_2$	2.4-2.6	2H	m
$-CH_2-C\underline{H}_2-NCO$	2.9-3.4	2H	m
$CH_2=C\underline{H}-$	5.78	1H	dd (J=7.0, 5.0 Hz)
$C\underline{H}_2=CH-$	6.3-6.5	2H	m
$-N\underline{H}-$	8.3-8.6	1H	br.s* (Exchanges with D_2O)
$-N\underline{H}-$	10.36	1H	br.s (Exchanges with D_2O)

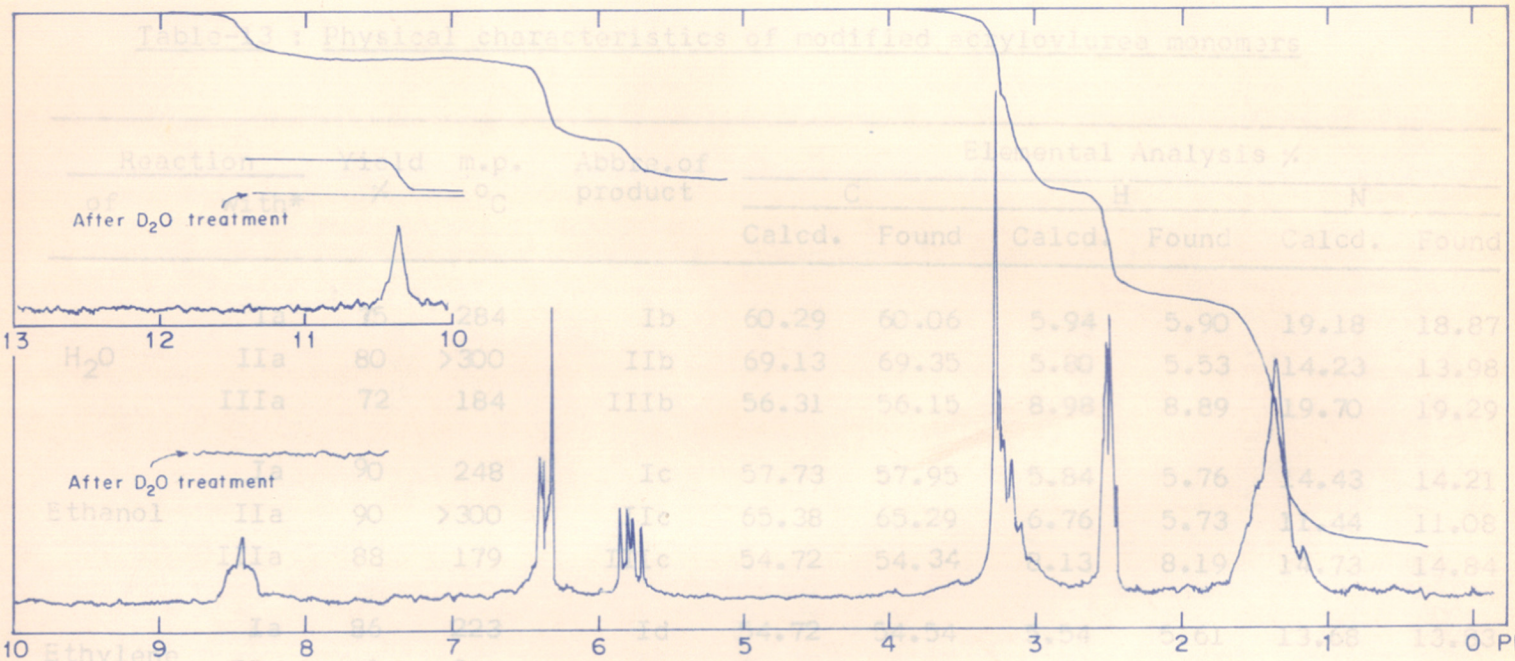
s = singlet, d = doublet, m = multiplet, br. = broad

* Integration shows the presence of slight impurity which might arise due to reaction of -NCO group with H_2O present in DMSO-d_6.



$H_2C=CH-CO-NH-CO-NH-C_6H_4-CH_2-C_6H_4-NCO$

FIG. 16. NMR SPECTRUM OF ACRYLOYLUREA II a.



$CH_2=CHCONH-CO-NH-(CH_2)_6-NCO$

FIG. 17. NMR SPECTRUM OF ACRYLOYLUREA III a.

Table-13 : Physical characteristics of modified acryloylurea monomers

Reaction of	Reaction with*	Yield %	m.p. °C	Abbre.of product	Elemental Analysis % C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
H_2O	Ia	75	284	Ib	60.29	60.06	5.94	5.90	19.18	18.87
	IIa	80	>300	IIb	69.13	69.35	5.80	5.53	14.23	13.98
	IIIa	72	184	IIIb	56.31	56.15	8.98	8.89	19.70	19.29
Ethanol	Ia	90	248	Ic	57.73	57.95	5.84	5.76	14.43	14.21
	IIa	90	>300	IIc	65.38	65.29	6.76	5.73	11.44	11.08
	IIIa	88	179	IIIc	54.72	54.34	8.13	8.19	14.73	14.84
Ethylene glycol	Ia	86	223	Id	54.72	54.54	5.54	5.61	13.68	13.83
	IIa	82	>300	IId	62.65	62.52	5.52	5.50	10.96	10.36
	IIIa	83	188	IIId	51.81	51.67	7.69	7.78	13.95	13.48
Glycerin	Ia	82	250	Ie	53.42	53.68	5.64	5.95	12.46	12.16
	IIa	85	>300	IIe	61.01	60.92	5.57	5.40	10.16	9.85
	IIIa	80	175	IIIe	50.76	50.62	7.55	7.51	12.69	12.34

* Ia, IIa and IIIa ⟶ Abbre. taken from Table 8.

Its thermal decomposition in solution is first order with a small difference between the rates in various solvents. AIBN is not susceptible to attack by radicals so that induced decomposition and transfer reactions are unimportant. It also dissociates into free radicals under the influence of near u.v. light and can be used as photosensitizer of polymerization.

The acryloylurea monomers and modified acryloylurea monomers are insoluble in H_2O, however, they are soluble only in N-methyl-2-pyrrolidone (NMP). Therefore, the polymerization of these monomers were carried out in NMP.

The polymerization was initiated by addition of 100 mg of AIBN to dilute solution (2%) of the monomer (0.1 mole) in NMP. The solution was stirred for 20 hr at 60°C, in nitrogen atmosphere. Finally, the polymer was isolated by precipitation with ethanol or carbon tetra chloride. It was filtered, washed and dried under reduced pressure.

The polymers were characterized by IR spectra and inherent viscosity.

Polymer Characterization

IR spectra

IR spectra of these polymers exhibited no evidence of vinyl unsaturation in the region of 1000-800 cm^{-1}, thus indicating the polymerization through vinyl group. As an illustration, the IR spectra of the polymers obtained from the monomers Ia, IIIa are given in Fig.18,19.

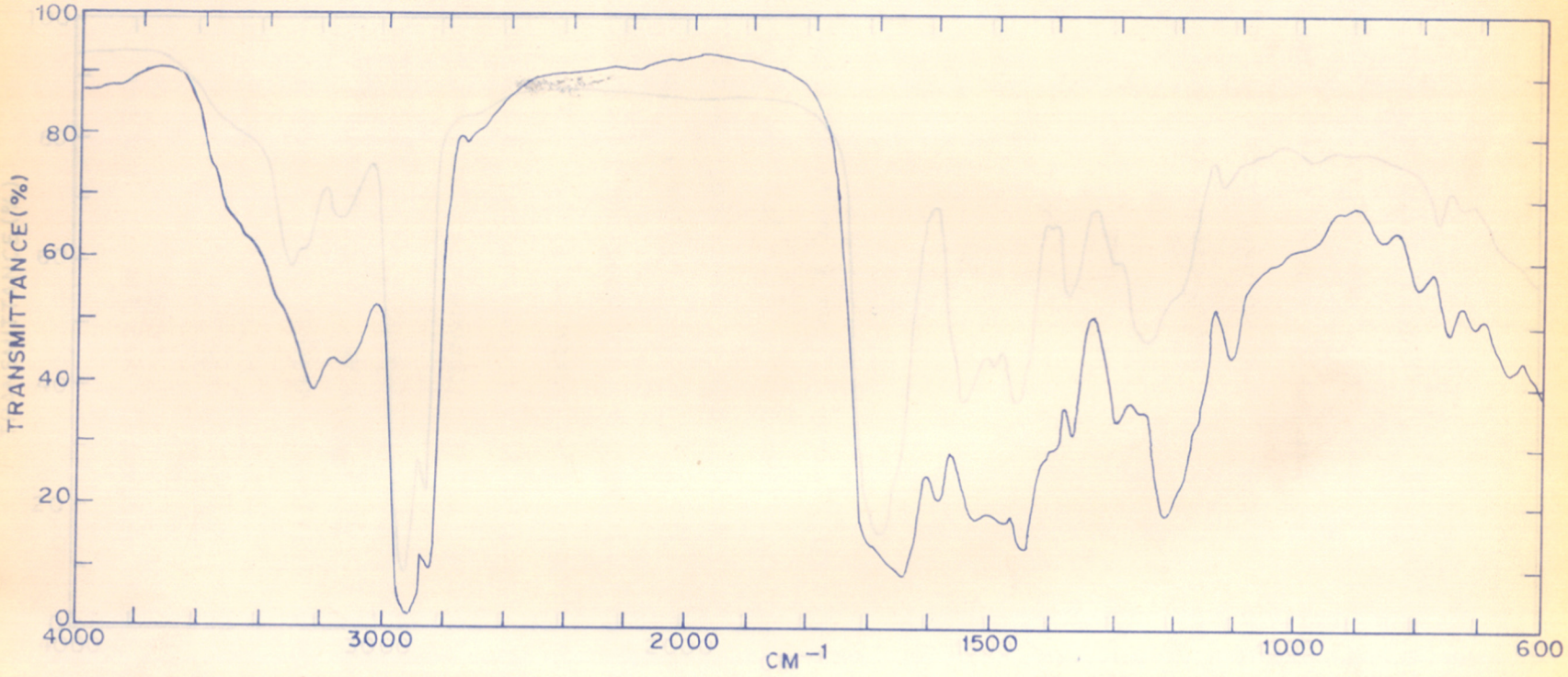


FIG. 18. IR SPECTRUM OF POLYMER FROM Ia

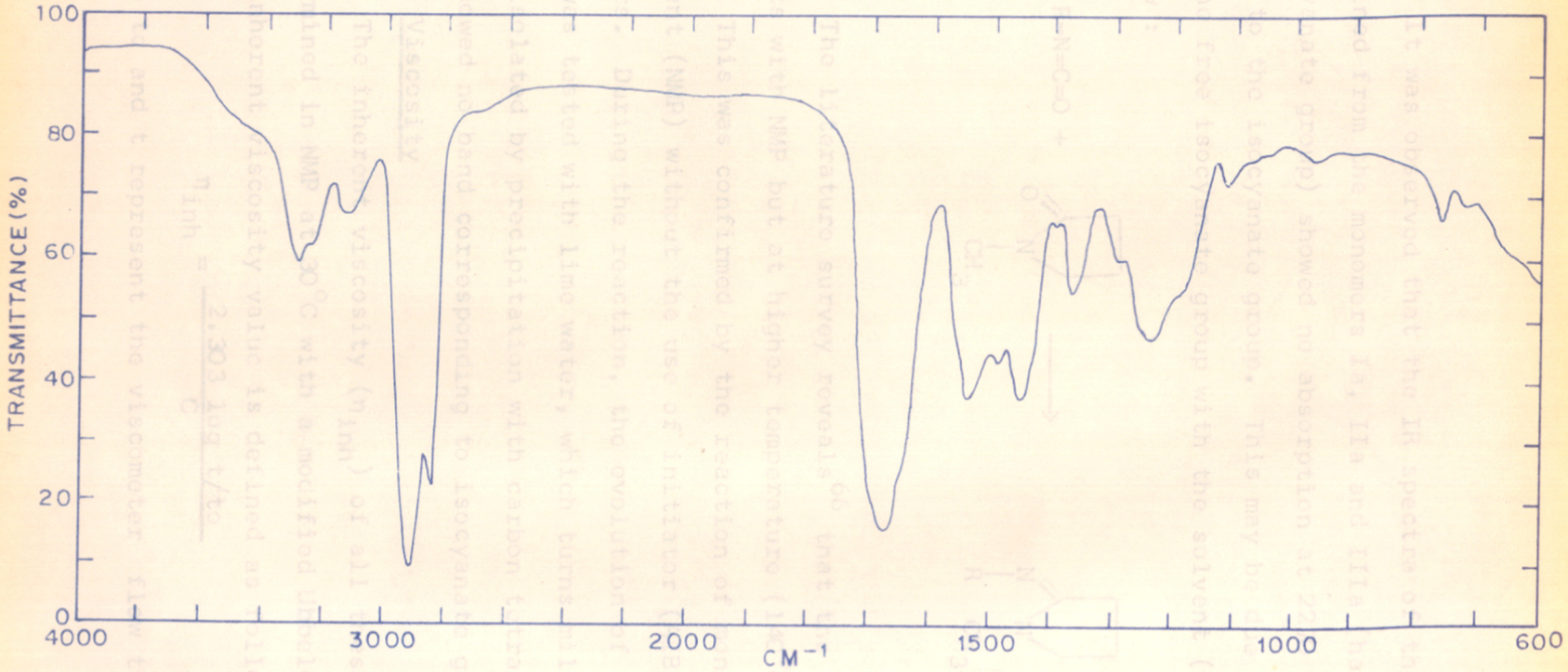
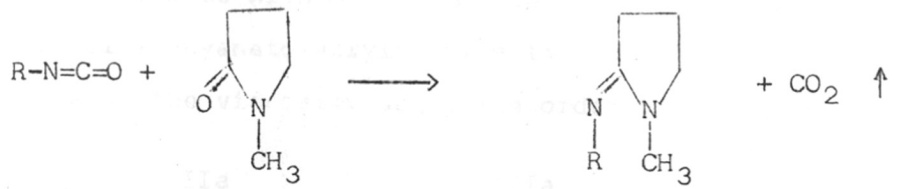


FIG. 19. IR SPECTRUM OF POLYMER FROM III a

It was observed that the IR spectra of the polymers obtained from the monomers Ia, IIa and IIIa (having free isocyanate group) showed no absorption at 2270 cm^{-1} corresponding to the isocyanate group. This may be due to the reaction of the free isocyanate group with the solvent (NMP) as shown below :



The literature survey reveals[66] that the isocyanate group reacts with NMP but at higher temperature (140°C).

This was confirmed by the reaction of monomer Ia with solvent (NMP) without the use of initiator (AIBN) at 60°C for 20 hrs. During the reaction, the evolution of carbon dioxide gas was tested with lime water, which turns milky. The product was isolated by precipitation with carbon tetra chloride. Its IR showed no band corresponding to isocyanate group.

Viscosity

The inherent viscosity (η_{inh}) of all these polymers were determined in NMP at 30°C with a modified Ubbelohde viscometer. The inherent viscosity value is defined as follows :

$$\eta_{inh} = \frac{2.303 \log t/to}{C}$$

where to and t represent the viscometer flow time for NMP

and polymer solution. C is expressed in g/100 ml.

Table-14 describes the inherent viscosities of the polymers obtained by polymerization of isocyanato acryloylurea and modified acryloylurea monomers.

On comparing the viscosity data (Table-14), it was observed that the polymer obtained from IIa (obtained by reaction of acrylamide with MDI) has higher viscosity value than from other isocyanato acryloylurea Ia and IIIa (from IDT and HDI). Using the viscosity data, the order of viscosity is

IIa > Ia > IIIa

The viscosities of the polymers obtained by polymerization of modified isocyanato acryloylurea monomers of IIa are in the following order :

IIb > IIc > IId > IIe

This can be attributed to the increase in the bulkiness of the pendant group (IIb to IIe) which decreases the reactivity of the vinyl group of the monomers.

The same above pattern was also observed for the viscosities of the polymers obtained from Ia and IIIa modified acryloylurea monomers.

Table-14 : Inherent viscosities of the polymers*

Monomer	η_{inh} dl/g	Monomer	η_{inh} dl/g	Monomer	η_{inh} dl/g
Ia	0.429	IIa	1.121	IIIa	0.221
Ib	0.376	IIb	0.813	IIIb	0.201
Ic	0.299	IIc	0.691	IIIc	0.176
Id	0.262	IId	0.640	IIId	0.167
Ie	0.232	IIe	0.610	IIIe	0.157

* 0.2% solution in NMP

EXPERIMENTAL

Materials

1] Acrylamide (Cyanamide, USA) was recrystallized twice from methanol.

2] 4,4'-Methylene bis(phenyl isocyanate)(MDI), 2,4-toluene diisocyanate (TDI) and 1,6-hexamethylene diisocyanate (HDI) were obtained from Bayer AG (West Germany) and purified by distillation under reduced pressure.

3] Hydroquinone was obtained from Sarabhai M.Chem.Ltd.(India) and used without further purification.

4] o-Dichlorobenzene was dried over calcium chloride and distilled.

5] N-Methyl-2-pyrrolidone (NMP) was received from M/s. Fluka AG (Switzerland), was dried over phosphorus pentoxide and distilled.

6] 2,2'-Azobisisobutyronitrile (AIBN) was obtained from SISCO (India) and recrystallized from methanol.

7] Carbon tetra chloride, ethyl alcohol, ethylene glycol and glycerin were purified by standerd procedure[67].

Acryloylurea from Acrylamide and TDI (Ia)

Into a 250 ml, three neck round bottom flask, equipped with a mechanical stirrer, a reflux condenser and a thermowell were placed 7.1 g (0.1 mole) of acrylamide, 17.58 g (0.11 mole) of TDI and 0.1 g hydroquinone in 100 ml o-dichlorobenzene. The

reaction mixture was heated at 100-110°C with stirring. After 15-20 minutes of heating, a white solid started separating out. The heating was further continued for half an hour. Then the reaction mixture was cooled. The solid obtained was filtered, washed several times with carbon tetra chloride (to ensure complete removal of the excess diisocyanate added) and dried under reduced pressure.

The reaction conditions described for acrylamide - TDI were followed to prepare acryloylurea from MDI and HDI. However, in case of HDI, the product remained in solution even after heating at 110°C for 4 hour. The product was recovered by precipitation with carbon tetra chloride.

Reaction of Ia with Water (Ib)

Into a 100 ml round bottom flask were placed 5.0 g of Ia, 0.1 g hydroquinone and 50 ml dilute hydrochloric acid (1%) solution. The reaction mixture was refluxed with stirring, till the IR spectrum of the product showed no absorption at 2270 cm^{-1} corresponding to the isocyanate group. After completion of the reaction, it was neutralized with dilute sodium hydroxide solution. The solid obtained was filtered, washed with several times with water and ethyl alcohol to remove hydroquinone. It was dried under vacuum.

Similar procedure was used to obtain IIb and IIIb from IIa and IIIa respectively.

Reaction of Ia with ethanol (Ic)

Into a 100 ml round bottom flask were placed 5.0 g of Ia, 0.1 g hydroquinone and 50 ml dry ethanol. It was refluxed with stirring till IR spectrum of the product showed no absorption corresponding to isocyanate group. It was cooled, filtered, washed with alcohol and dried under vacuum.

Similar experiments were carried out with IIa and IIIa to obtain IIc and IIIc respectively.

Reaction of Ia with glycol (Id)

Into a 250 ml three neck round bottom flask equipped with a mechanical stirrer, a reflux condenser and a thermowell were placed 4.9 g (0.02 mole) of Ia, 0.1 g hydroquinone, 100 ml o-dichlorobenzene and 2.48 g (0.04 mole) of ethylene glycol. The reaction mixture was heated at 110°C with stirring, till the IR spectrum of the product showed no absorption at 2270 cm^{-1}. Then it was filtered, washed with alcohol and dried under vacuum.

The reaction conditions described for the preparation of Id were followed to obtain IId and IIId from IIa and IIIa respectively.

Reaction of Ia with glycerin (Ie)

Into a 250 ml three neck round bottom flask equipped with a mechanical stirrer, a reflux condenser and a thermowell were placed 4.9 g (0.02 mole) of Ia, 0.1 g hydroquinone, 100 ml o-dichlorobenzene and 3.68 g (0.04 mole) of glycerin. It was heated at 110°C, till the IR spectrum of the product showed no

absorption band corresponding to isocyanate group. It was filtered, washed with ethanol and dried under vacuum.

Similar procedure was adopted to prepare IIe and IIIe from IIa and IIIa respectively.

Polymerization

Into a 100 ml, three neck round bottom flask equipped with a nitrogen gas inlet, a thermowell and a reflux condenser were placed 2% solution of monomer Ia (2.45 g, 0.01 mole) in NMP. It was heated at 50°C then 10.0 mg of initiator (AIBN) was added. The reaction mixture was stirred at 60°C for 20 hr. The polymer was precipitated with ethanol. The polymer obtained was filtered. It was washed with pet. ether and dried under reduced pressure at 50°C.

Similar experiments were carried out with other monomers.

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PART – III

NEW POLY (AMIDE – AMINE) POLYMERS

INTRODUCTION

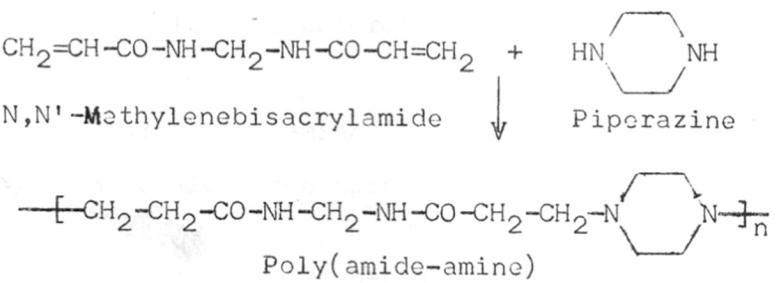
Amino polymers have been described, particularly in the patent literature. Such polymers are, however, extensively used in industry. Some tertiary polyamines and their N-oxides may also be used in pharmacology. For example, a number of these polymers have preventive properties against Silicosis[1-3] and others are anti-heparinic[4]. Due to their basicity and chemical reactivity, amino polymers may interact with a number of biological macromolecular substances present in living organism.

The addition of primary or secondary amines to vinyl double bonds activated by electron attracting groups is well known[5]. For example,

$$\overset{\beta}{CH_2}=\overset{\alpha}{CH}-CO-R + R'-NH_2 \longrightarrow R'-NH-CH_2-CH_2-CO-R$$

In this reaction, nitrogen is always bound to the carbon β to the activating group whereas hydrogen migrates to the α-carbon atom.

Hulse[6] obtained a water soluble poly(amide-amine) by the reaction of N,N'-methylenebisacrylamide and piperazine in water.

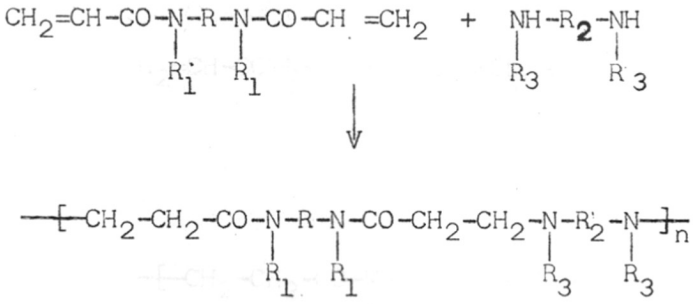


Poly(amide-amine)

Danusso et al[7] have obtained linear poly(amide amines) by polyaddition of primary monoamines or bis(secondary) diamines (aliphatic or cycloaliphatic) to bisacrylamides.

Polymers from bis(secondary) diamines and bisacrylamides

The polymers prepared by this method have the following general structure:



Poly(amide-amine)

Danusso et al[8,9] confirmed that this polymerization is a nucleophilic polyaddition with an ionic mechanism. It is not influenced by the presence of the typical inhibitors of radical polymerization and it does not require acidic or basic catalysts. The polyaddition takes place easily in water or alcohol.

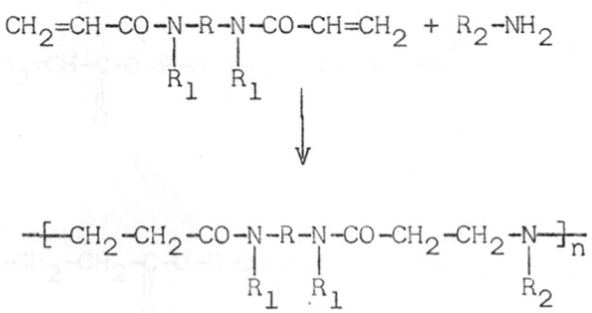
The poly(amide-amines) are often very hygroscopic and are soluble in water, alcohol, chloroform and insoluble in aliphatic hydrocarbons.

In the polymer, the amine (a) and the amide (b) groups are regularly arranged along the main chain according to the repeating sequence.

a-a-b-b-a-a-b-b-

Polymers from primary amines and bisacrylamides

In this case, the product obtained from the first addition of a primary amine to an activated double bond is a secondary amine, which may be further added to a second double bond. Therefore, the primary amine must be considered as a bifunctional monomer, useful for the formation of linear high molecular weight polymers, if cyclization reaction can be avoided.



Poly(amide-amine)

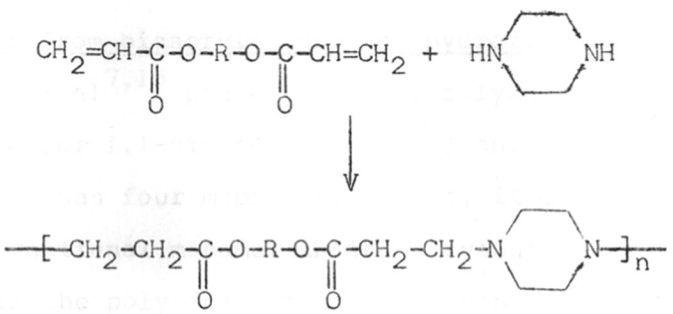
The polymer has amine (a) and amide (b) groups in the following repeating sequence along the main chain.

- -b-b-a-b-b-a-b-b-

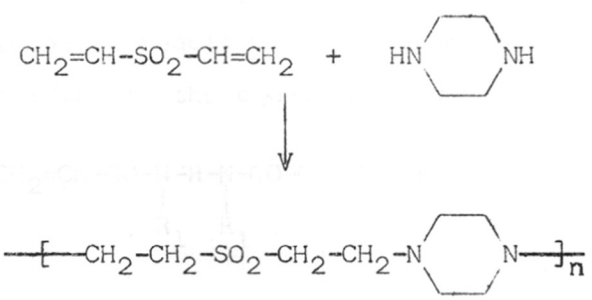
Several properties, including solubility and thermal stability of the poly(amide-amines) obtained from primary amines are substantially similar to those from bis(secondary) diamines.

Polymers from bis(secondary) diamines and acrylic diesters or divinyl sulfone

The polyaddition reaction of bisacrylamide with bis(secondary) diamine or primary amine leading to poly(amide-amines) may be accomplished with acrylic diesters or divinyl sulfone instead of bisacrylamide[10]. Primary amines do not yield well defined products with acrylic diesters, whereas, with divinyl sulfone, they yield cyclic dimeric products[11].



Poly(ester-amine)



Poly(sulfone-amine)

These polymers show a different solubility behaviour from the poly(amide-amines) obtained from bisacrylamide. However, other properties including thermal stability are similar. Yoda

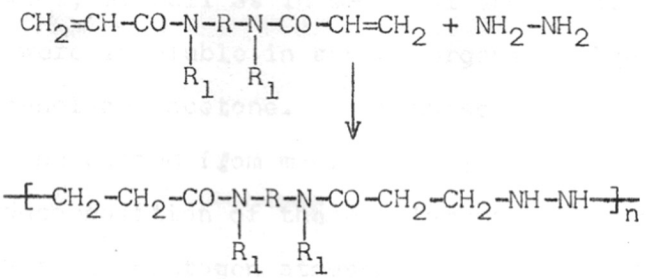
and Toda[12] also reported the polyaddition of piperazines to divinyl sulfone. However, the intrinsic viscosities of these poly(sulfone-amines) were less than 0.6 dl/g.

Imai et al[13] reinvestigated the reaction of divinyl sulfone with piperazine and obtained high molecular weight polymers.

Yoda et al[14] obtained transparent poly(amide-amines) from acrylates such as cyanomethyl acrylate, diphenoxymethyl acrylate with diamines.

Polymers from bisacrylamides and hydrazine

Ferruti et al[7,15] prepared linear poly(amide-hydrazines) from hydrazine (or 1,1-dimethylhydrazine) and bis-acrylamides. Since hydrazine has four mobile hydrogens, it must be considered to be a polyfunctional monomer in the polyaddition reaction. However, as in the polyaddition of bis(secondary) diamines to bisacrylamides, the steric bulkiness of the amino group exerts a dominant influence on the rate of polymerization. This may be the reason why hydrazine reacts with an equimolar amount of bisacrylamide according to the equation to give a linear polymer.

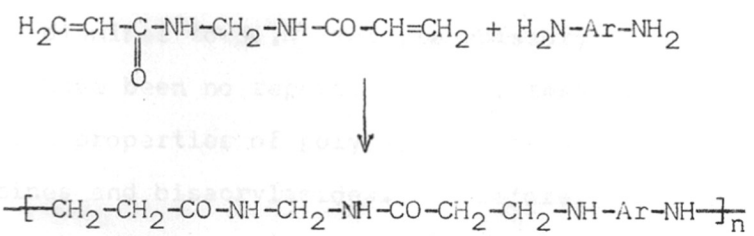


Poly(amide-hydrazine)

They confirmed the structure of this polymer by elemental and spectral analysis. They observed that linear polymers were obtained from equimolar amounts of hydrazine and bisacrylamide, whereas, cross-linked polymers were obtained with higher amounts of bisacrylamide.

Polymers from bisacrylamides and aromatic diamines

Imai et al[16] prepared poly(amideamines) with high molecular weights by the polyaddition of aromatic primary diamines with N,N'-methylenebisacrylamide.



Poly(amide-amine)

These poly(amide-amines) dissolved readily in polar aprotic solvents such as N,N -dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, as well as in m-cresol and dichloroacetic acid, but they were insoluble in common organic solvents such as benzene, methanol and acetone. From these polymers, the dark brown films can be casted from m-cresol which were somewhat brittle. The decomposition of these polymers occurs at around 270°C both in air and nitrogen atmospheres.

PRESENT INVESTIGATION, RESULTS AND DISCUSSION

Michael type polyaddition of primary and secondary diamines to various types of bisacrylamides has been extensively studied[7,16,17]. Imai et al[16] have studied the polyaddition of aromatic diamines such as 4,4'-oxydianiline (ODA) and 4,4'-methylenedianiline (MDA) with N,N'-methylenebisacrylamide. They have studied the effect of solvent and acidic catalyst on molecular weight of poly(amide-amines). They found that the weak acid like acetic acid have a marked catalytic effect on the polyaddition of aromatic diamines to N,N'-methylenebisacrylamide.

There have been no reports in the literature of the synthesis and properties of poly(amide-amines) from sulfone ether diamines and bisacrylamides. Therefore, the present investigation was undertaken with a view to prepare a series of poly(amide-amines) having a sulfone and ether linkages and to study the structure-property relationship of the poly(amide-amines).

The present study includes :

A] the synthesis of sulfone ether diamines

a) 4,4'-bis(4-aminophenoxy) diphenyl sulfone

b) 4,4'-bis(4-amino-3-methylphenoxy) diphenyl sulfone

c) 4,4'-bis(4-amino-2,5-dimethylphenoxy) diphenyl sulfone

d) 4,4'-bis(4-amino-3,5-dimethylphenoxy) diphenyl sulfone

B] the synthesis of bisacrylamides

a) N,N'-methylenebisacrylamide

b) N,N'-butylidenebisacrylamide and

c) N,N'-benzylidenebisacrylamide

C] the synthesis of poly(amide-amines) from these monomers.

The scheme for the synthesis of poly(amide-amines) is given in Fig.20.

Sulfone Ether Diamines

The scheme for the synthesis of aminophenols and diamines therefrom is given in Fig.21.

The appropriate aminophenols were prepared by using the procedure described by Nilsson et al[18].

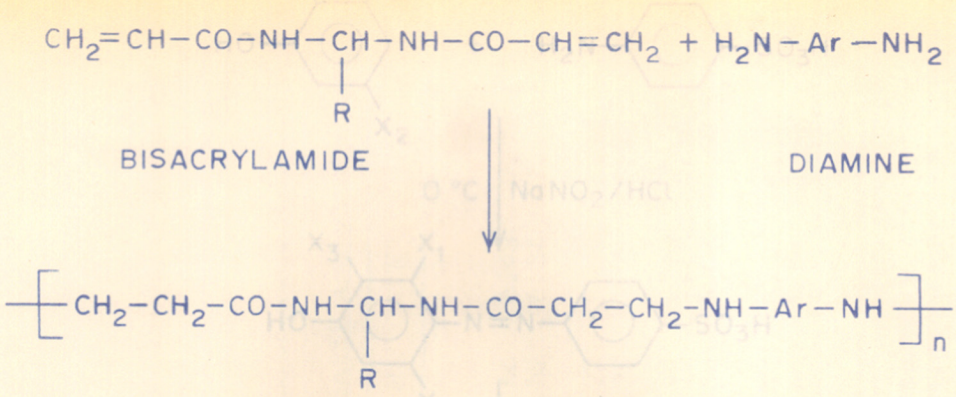
The sulfone ether diamines were prepared from sodium salt of appropriate p-aminophenol and 4,4'-dichlorodiphenyl sulfone in dimethyl sulfoxide at 160°C in nitrogen atmosphere using the method of Kawakami et al[19].

The diamines were purified by recrystallization from suitable solvent (Table-15). The structures of these diamines were confirmed by elemental and spectral analysis such as IR and NMR. The physical characteristics of these diamines are recorded in Table-15.

Infrared Spectra

The IR spectra are in good accordance with the structures assigned to them. As an illustration, the IR spectrum of 4,4'-bis(4-amino-3-methylphenoxy) diphenyl sulfone is given in Fig.22.

The infrared spectra of all the diamines showed the characteristic absorption bands in the N-H stretching region of the

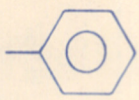


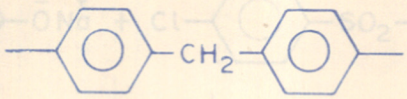
POLY (AMIDE – AMINE)

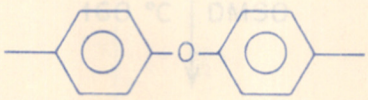
Where

R = –H

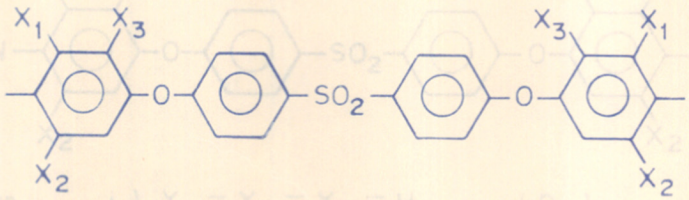
= $-CH_2-CH_2-CH_3$ and

= 

Ar = i) 

= ii) 

and

= iii) 

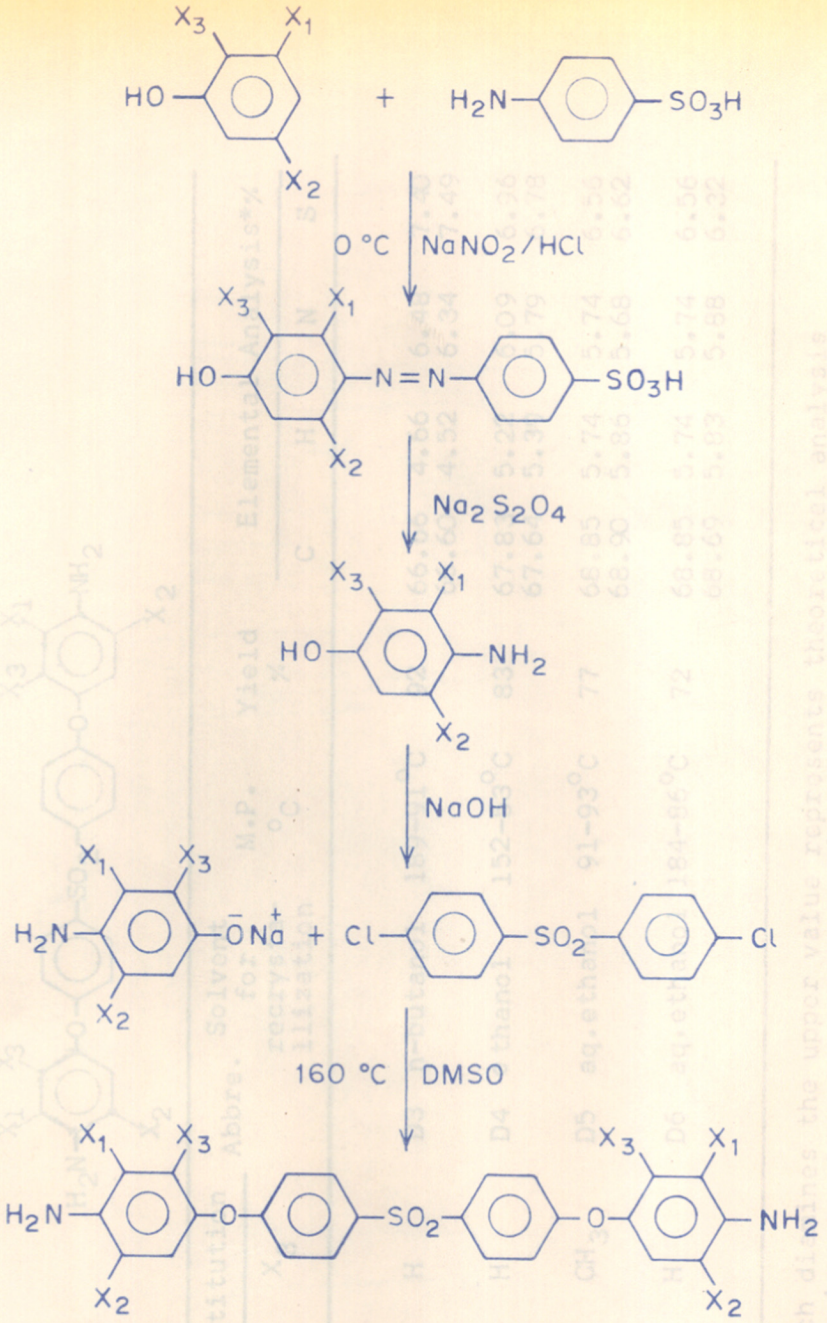
$X_1 = X_2 = X_3 = H$

$X_1 = CH_3, X_2 = X_3 = H$

$X_1 = H, X_2 = X_3 = CH_3$

$X_1 = X_2 = CH_3, X_3 = H$

FIG. 20. SCHEME FOR SYNTHESIS OF POLY (AMIDE-AMINES)



Where i) $X_1 = X_2 = X_3 = H$ (D_3)

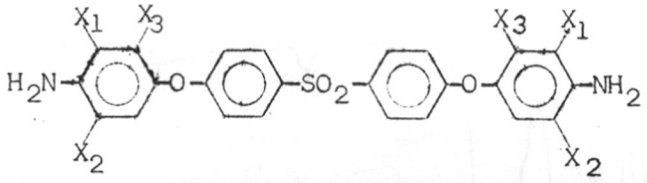
ii) $X_1 = CH_3$, $X_2 = X_3 = H$ (D_4)

iii) $X_1 = H$, $X_2 = X_3 = CH_3$ (D_5) and

iv) $X_1 = X_2 = CH_3$, $X_3 = H$ (D_6)

FIG. 21. SCHEME FOR SYNTHESIS OF SULFONE ETHER DIAMINES

Table-15 : Physical characteristics of sulfone ether diamines



No.	Methyl substitution			Abbre.	Solvent for recrystallization	M.P. °C	Yield %	Elemental Analysis*%			
	X_1	X_2	X_3					C	H	N	S
1.	H	H	H	D3	n-butanol	189-91°C	92	66.66 66.60	4.66 4.52	6.48 6.34	7.40 7.49
2.	CH_3	H	H	D4	ethanol	152-53°C	83	67.83 67.64	5.22 5.39	6.09 5.79	6.96 6.78
3.	H	CH_3	CH_3	D5	aq.ethanol	91-93°C	77	68.85 68.90	5.74 5.86	5.74 5.68	6.56 6.62
4.	CH_3	CH_3	H	D6	aq.ethanol	184-86°C	72	68.85 68.69	5.74 5.83	5.74 5.88	6.56 6.32

* For each diamines the upper value represents theoretical analysis and the lower value shows the results obtained experimentally.

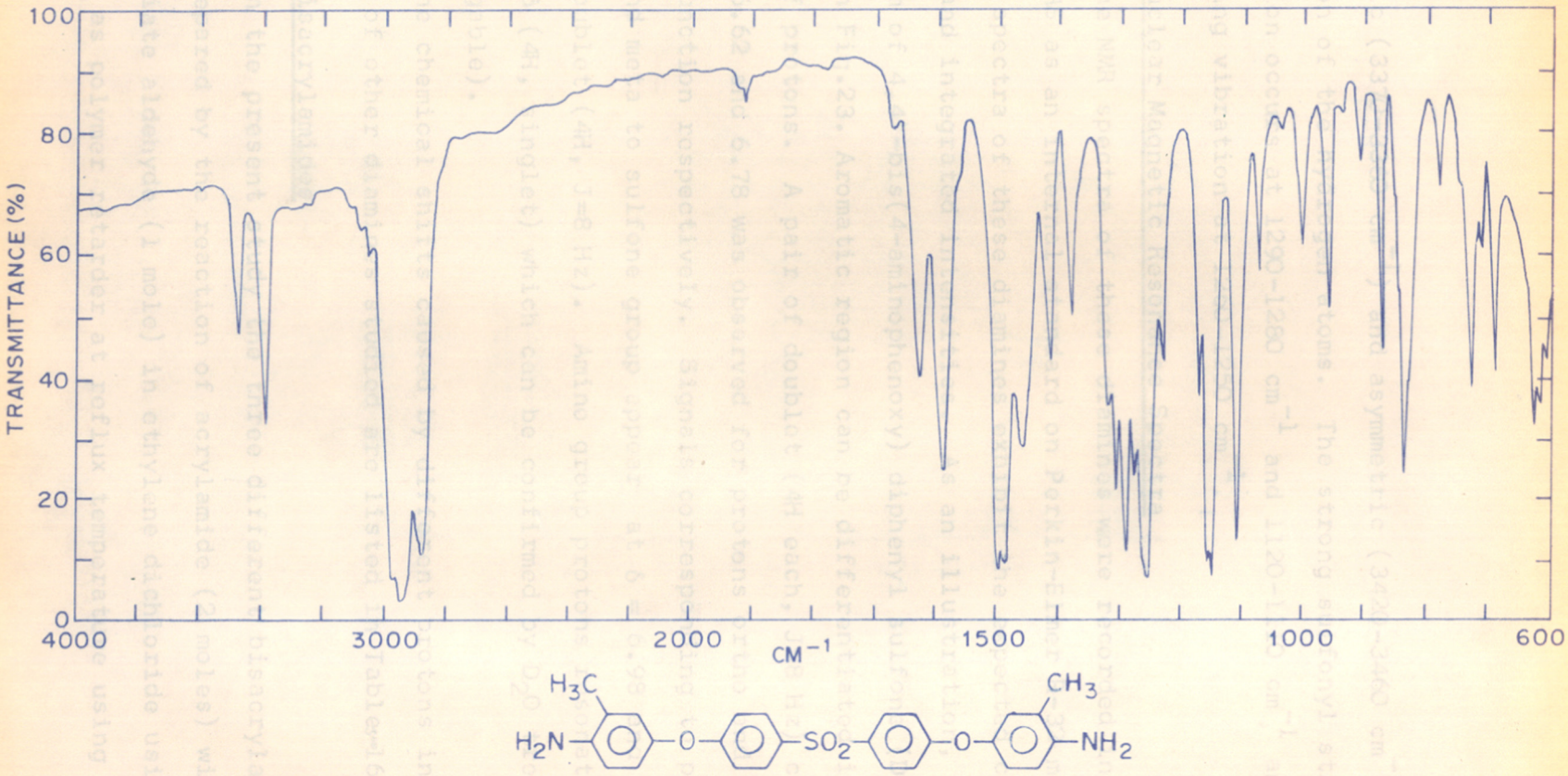


FIG. 22. IR SPECTRUM OF 4-4'-BIS(4-AMINO-3-METHYL PHENOXY) DIPHENYL SULFONE (D_4)

symmetric (3370-3360 cm^{-1}) and asymmetric (3420-3460 cm^{-1}) vibration of the hydrogen atoms. The strong sulfonyl stretching absorption occurs at 1290-1280 cm^{-1} and 1120-1110 cm^{-1} and ether stretching vibration at 1260-1250 cm^{-1}.

Nuclear Magnetic Resonance Spectra

The NMR spectra of these diamines were recorded in DMSO-d_6 using TMS as an internal standard on Perkin-Elmer R-32 model. The NMR spectra of these diamines exhibit the expected chemical shifts and integrated intensities. As an illustration, the NMR spectrum of 4,4'-bis(4-aminophenoxy) diphenyl sulfone (D3) is given in Fig.23. Aromatic region can be differentiated in four types of protons. A pair of doublet (4H each, J=8 Hz) centered at δ = 6.62 and 6.78 was observed for protons ortho and meta to amino function respectively. Signals corresponding to protons ortho and meta to sulfone group appear at δ = 6.98 and 7.82 each being doublet (4H, J=8 Hz). Amino group protons resonate at δ = 4.95 (4H, singlet) which can be confirmed by D_2O treatment (exchangable).

The chemical shifts caused by different protons in NMR spectra of other diamines studied are listed in Tables 16 to 18.

Bisacrylamides

In the present study the three different bisacrylamides were prepared by the reaction of acrylamide (2 moles) with the appropriate aldehyde (1 mole) in ethylene dichloride using hydroquinone as polymer retarder at reflux temperature using the

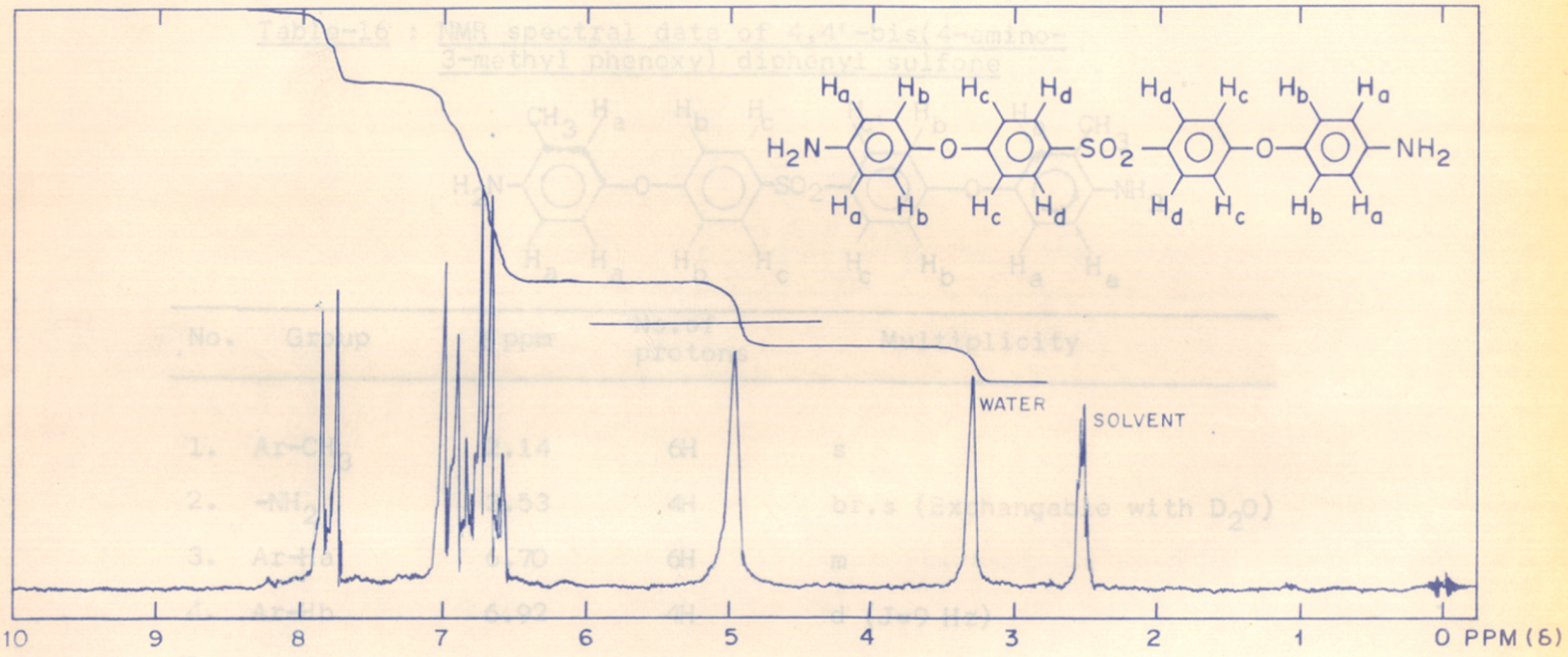
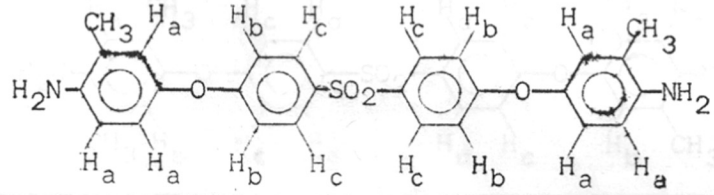


FIG. 23. NMR SPECTRUM OF 4,4'-BIS(4-AMINOPHENOXY) DIPHENYL SULFONE (D_3)

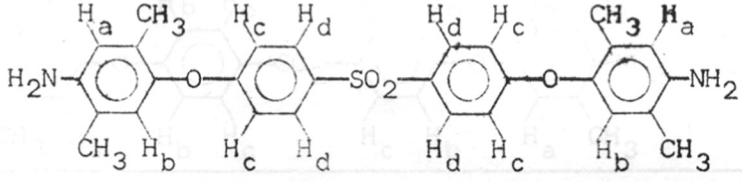
Table-16 : NMR spectral data of 4,4'-bis(4-amino-3-methyl phenoxy) diphenyl sulfone



No.	Group	δ ppm	No.of protons	Multiplicity
1.	Ar-CH_3	2.14	6H	s
2.	-NH_2	3.53	4H	br.s (Exchangable with D_2O)
3.	Ar-Ha	6.70	6H	m
4.	Ar-Hb	6.92	4H	d (J=9 Hz)
5.	Ar-Hc	7.78	4H	d (J=9 Hz)

s = singlet, d = doublet, m = multiplet, br = broad

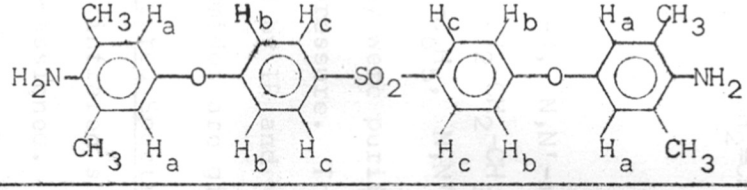
Table-17 : NMR spectral data of 4,4'-bis(4-amino-2,5-dimethylphenoxy) diphenyl sulfone



No.	Group	δppm	No.of protons	Multiplicity
1.	Ar-CH_3	1.98	6H	s
2.	Ar-CH_3	2.08	6H	s
3.	-NH_2	4.43	4H	br.s (Exchangable with D_2O)
4.	Ar-Ha	6.55	2H	s
	OR			
5.	Ar-Hb	6.59	2H	s
6.	Ar-Hc	6.88	4H	d (J=8.5 Hz)
7.	Ar-Hd	7.77	4H	d (J=8.5 Hz)

s = singlet, d = doublet, m = multiplet, br = broad

Table-18 : NMR spectral data of 4,4'-bis(4-amino-3,5-dimethylphenoxy) diphenyl sulfone



No.	Group	δppm	No.of protons	Multiplicity
1.	Ar-CH_3	2.10	12H	s
2.	-NH_2	4.50	4H	br.s (Exchangable with D_2O)
3.	Ar-Ha	6.59	4H	s
4.	Ar-Hb	6.92	4H	d (J=8 Hz)
5.	Ar-Hc	7.75	4H	d (J=8 Hz)

s = singlet, d = doublet, br = broad

method described by Feuer and Lynch[20] as shown.

$$2CH_2=CH-CONH_2 \quad + \quad R-CHO$$

Acrylamide ↓ Aldehyde

$$CH_2=CH-CO-NH-\underset{\displaystyle R}{\underset{|}{CH}}-NH-CO-CH=CH_2$$

Bisacrylamide

where R = -H, N,N'-methylenebisacrylamide (B1)

$=-CH_2-CH_2-CH_3$, N,N'-butylidenebisacrylamide (B2) and

$=-C_6H_5$, N,N'-benzylidenebisacrylamide (B3)

They were purified by recrystallization and dried under reduced pressure. The structures of these bisacrylamides were confirmed by IR and NMR. The physical characteristics of these bisacrylamides are given in Table-19.

Infrared Spectra

The infrared spectra are in good accordance with the structures assigned. The absorption bands of these bisacrylamides are recorded in Table-20. As an illustration, the IR spectrum of N,N'-methylenebisacrylamide is shown in Fig.24.

Nuclear Magnetic Resonance Spectra

The NMR spectra of these bisacrylamides were recorded in DMSO-d_6 using TMS as internal standard. The chemical shifts caused by different protons in NMR spectra are recorded in Table-21.

Table-19 : Physical characteristics of bisacrylamides

$H_2C=CH-CO-NH-\underset{R}{CH}-NH-CO-CH=CH_2$

No.	R	Abbre.	Solvent for recrystallization	M.P. °C	Yield %	Elemental Analysis* % C	H	N
1.	-H	B1	Aqueous acetone	182-84	90.0	54.55 54.63	6.50 6.62	18.19 17.92
2.	$-CH_2-CH_2-CH_3$	B2	Ethylene chloride	195-96	75.0	61.22 61.10	8.16 8.28	14.29 13.05
3.	$-C_6H_5$	B3	Ethanol	288-90	84.0	67.82 67.69	6.09 6.20	12.17 11.94

* The upper value represents the theoretical analysis and the lower value shows the results obtained experimentally.

Table-20 : Infrared frequencies for absorption bands of bisacrylamides

$CH_2=CH-CO-NH-\underset{\displaystyle R}{\underset{|}{CH}}-NH-CO-CH=CH_2$

Frequency (cm^{-1})			Assignment
R = -H (B1)	R = $-CH_2-CH_2-CH_3$ (B2)	R = $-C_6H_5$ (B3)	
-	-	700, 740	Aromatic C-H out-of-plane deformation (five adjacent H atoms)
915	930	930	CH_2 out-of-plane deformation (for $CH_2=CH-$)
990	995	985	C-H out-of-plane deformation (for $CH_2=CH-$)
1305	1310	1310	Amide III band; C-H in-plane deformation
1410	1415	1410	CH_2 in-plane deformation (for $CH_2=CH-$)
1540	1525	1560	Amide II band
1620	1630	1630	C=C stretching vibration
1660	1670	1670	Amide I band
3070, 3305	3120, 3290	3120, 3270	N-H stretching

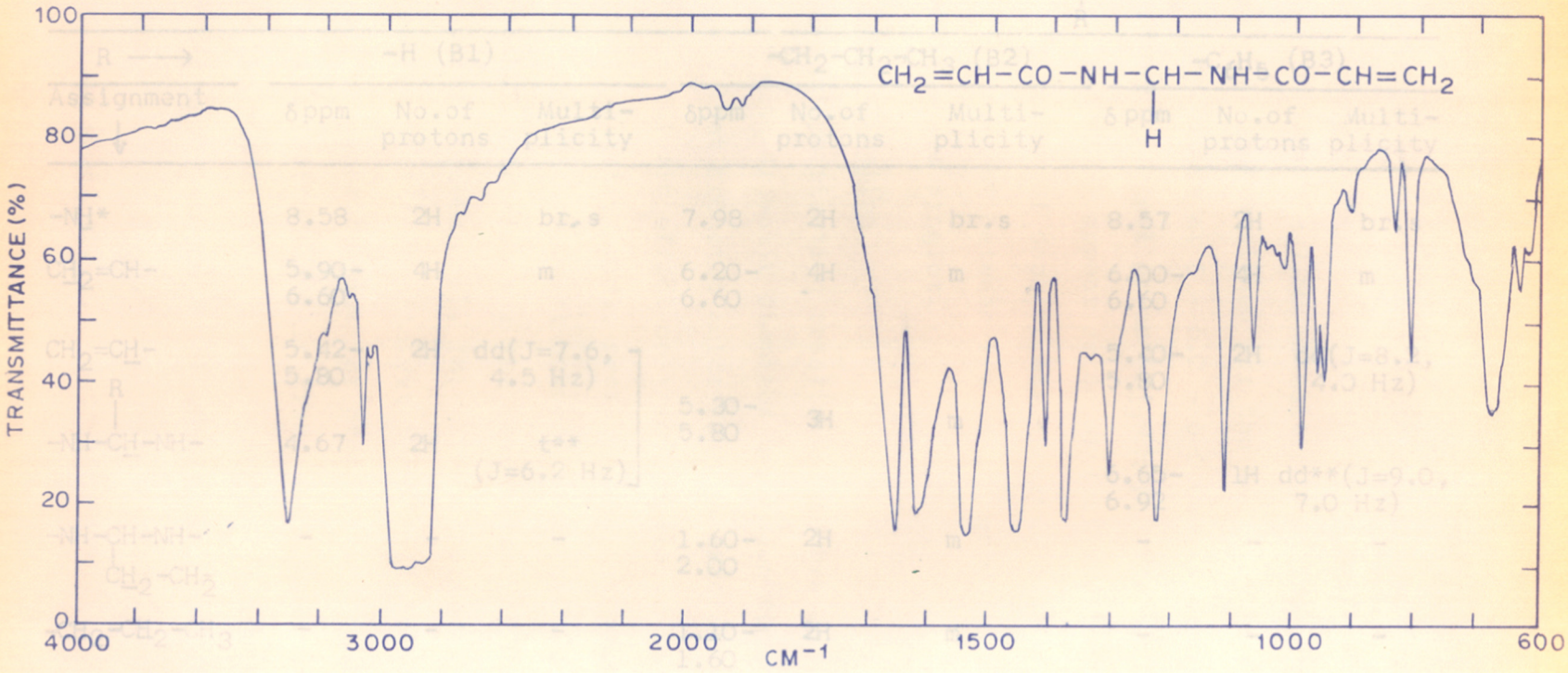


FIG. 24. IR SPECTRUM OF N, N'-METHYLENEBISACRYLAMIDE (B_1)

Table-21 : NMR spectral data of bisacrylamides $CH_2=CH-CO-NH-\underset{\underset{R}{|}}{CH}-NH-CO-CH=CH_2$

R ⟶ / Assignment ↓	-H (B1) δppm	No.of protons	Multiplicity	$-CH_2-CH_2-CH_3$ (B2) δppm	No.of protons	Multiplicity	$-C_6H_5$ (B3) δppm	No.of protons	Multiplicity
-NH*	8.58	2H	br.s	7.98	2H	br.s	8.57	2H	br.s
$CH_2=CH-$	5.90-6.60	4H	m	6.20-6.60	4H	m	6.00-6.60	4H	m
$CH_2=CH-$ R	5.42-5.80	2H	dd(J=7.6, 4.5 Hz)				5.40-5.80	2H	dd(J=8.2, 4.0 Hz)
-NH-CH-NH-	4.67	2H	t** (J=6.2 Hz)	5.30-5.80	3H	m			
							6.65-6.92	1H	dd**(J=9.0, 7.0 Hz)
-NH-CH-NH- CH_2-CH_2	-	-	-	1.60-2.00	2H	m	-	-	-
$-CH_2-CH_2-CH_3$	-	-	-	1.10-1.60	2H	m	-	-	-
$-CH_2-CH_2-CH_3$	-	-	-	0.92	3H	t (J=7.0 Hz)	--	-	-
Ar-H	-	-	-	-	-	-	7.18-7.50	5H	m

s = singlet, d = doublet, t = triplet, m = multiplet, * = Exchanges with D_2O

** = After D_2O exchange becomes singlet

The NMR spectrum of N,N'-benzylidenebisacrylamide is shown in Fig.25. Signals corresponding to five aromatic protons appear at δ = 7.18 - 7.50 as multiplet. The broad singlet at δ = 8.57 (2H) was assigned for the N-H protons (exchangable with D_2O). A multiplet at δ = 6.0 - 6.6 (4H) was observed for methylene protons of vinyl group ($C\underline{H}_2$=CH-). The protons adjacent to carbonyl (=C<u>H</u>-CO-) appear as doublet of doublet at δ = 5.4 - 5.8 (2H). A doublet of doublet was observed at δ = 6.65 - 6.92 for the proton present between two NH groups which after D_2O treatment became singlet.

Polymerization

The polymerization reaction of double bond of maleimide compounds with aromatic diamines have been reported by Crivello[21]. They found that Brönsted acids such as glacial acetic acid have a marked catalytic effect on this reaction. Imai et al[16] have found that slightly acidic m-cresol was the most suitable reaction medium than polar solvents such as dimethyl formamide and dimethyl sulfoxide for the preparation of high molecular weight poly(amide-amines). They also reported that acetic acid was the most efficient catalyst than trifluoroacetic acid or boric and phosphoric acids for preparation of high molecular weight polymer from aromatic diamine and N,N'-methylenebisacrylamide. Therefore, in this study the polymerization was carried out in m-cresol using glacial acetic acid as catalyst.

The reaction of N,N'-methylenebisacrylamide with 4,4'-oxydianiline (ODA) and 4,4'-methylenedianiline (MDA) as reported

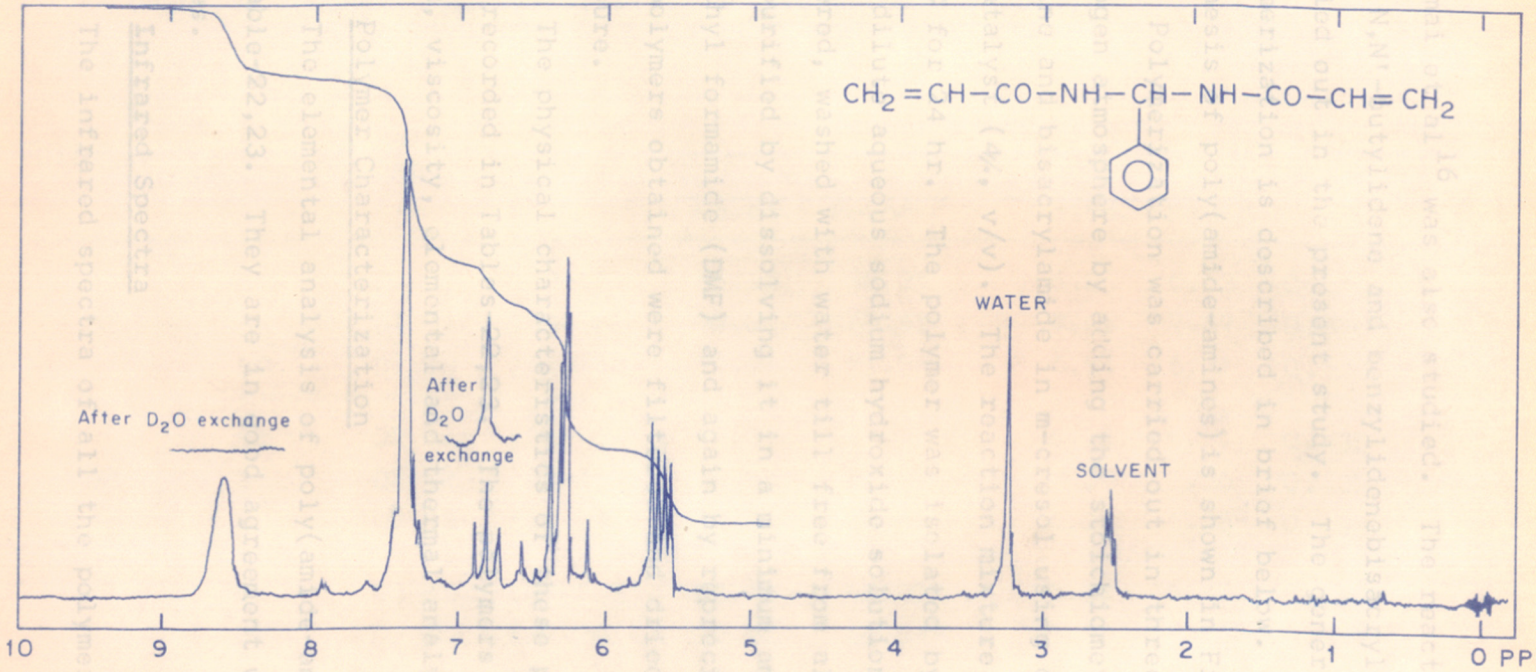


FIG. 25. NMR SPECTRUM OF N, N'-BENZYLIDENEBISACRYLAMIDE (B_3)

by Imai et al[16] was also studied. The reactions of ODA and MDA with N,N'-butylidene and benzylidenebisacrylamides were also carried out in the present study. The general procedure of the polymerization is described in brief below. The scheme for the synthesis of poly(amide-amines) is shown in Fig.20.

Polymerization was carried out in three neck flask in nitrogen atmosphere by adding the stoichiometric amount of diamine and bisacrylamide in m-cresol using glacial acetic acid as catalyst (4%, v/v). The reaction mixture was stirred at 100°C for 24 hr. The polymer was isolated by precipitation with dilute aqueous sodium hydroxide solution. The polymer was filtered, washed with water till free from alkali. The polymer was purified by dissolving it in a minimum amount of N,N-dimethyl formamide (DMF) and again by reprecipitation with water. The polymers obtained were filtered and dried under reduced pressure.

The physical characteristics of these polymers obtained are recorded in Tables-22,23. The polymers were characterized by IR, viscosity, elemental and thermal analysis.

Polymer Characterization

The elemental analysis of poly(amide-amines) are given in Table-22,23. They are in good agreement with the theoretical values.

Infrared Spectra

The infrared spectra of all the polymers exhibited a broad

Table-22 : Characteristics of poly(amide-amines)

Diamine	Bis-acrylamide	Polymer Abbre.	M.P. °C	Elemental Analysis %				η_{inh} dl/g*
				C		H		
				Calcd.	Found	Calcd.	Found	
D1	B1	D1 B1	153-157	68.16	68.25	6.86	6.62	0.512
	B2	D1 B2	159-162	70.04	69.91	7.61	7.67	0.506
	B3	D1 B3	161-165	72.91	71.58	6.54	6.31	0.509
D2	B1	D2 B1	150-154	64.39	64.08	6.26	6.31	0.435
	B2	D2 B2	164-167	66.58	66.32	7.08	7.36	0.430
	B3	D2 B3	169-175	59.76	69.49	6.05	6.25	0.438
D3	B1	D3 B1	132-135	63.48	63.40	5.12	5.42	0.390
	B2	D3 B2	158-160	64.97	64.64	5.73	5.50	0.382
	B3	D3 B3	160-165	67.67	67.72	5.34	5.62	0.393

* 0.5% solution in m-cresol.

Table-23 : Characteristics of poly(amide-amines)

Diamine	Bis-acrylamide	Polymer Abbre.	M.P. °C	Elemental Analysis %				η_{inh} dl/g*
				C		H		
				Calcd.	Found	Calcd.	Found	
D3	B1	D3 B1	132-135	63.48	63.40	5.12	5.42	0.390
	B2	D3 B2	158-160	64.97	64.64	5.73	5.50	0.382
	B3	D3 B3	160-165	67.67	67.72	5.34	6.52	0.393
D4	B1	D4 B1	120-125	64.47	64.37	5.54	5.69	0.362
	B2	D4 B2	142-145	65.86	65.48	6.10	6.25	0.358
	B3	D4 B3	128-132	67.82	67.68	5.51	5.71	0.355
D5	B1	D5 B1	113-116	65.42	65.26	5.91	5.82	0.349
	B2	D5 B2	135-140	66.62	66.71	6.42	6.36	0.340
	B3	D5 B3	124-127	68.52	68.41	5.85	5.76	0.343
D6	B1	D6 B1	108-110	65.42	65.31	5.91	5.98	0.335
	B2	D6 B2	132-135	66.62	66.52	6.42	6.29	0.323
	B3	D6 B3	120-125	68.52	68.40	5.58	5.64	0.330

* 0.5 solution in m-cresol.

N-H stretching band at 3380-3330 cm^{-1}, a amide carbonyl absorption at 1680-1650 cm^{-1}, ether absorption at 1260-1230 cm^{-1}, sulfonyl stretching absorption at 1290-1270 cm^{-1} and 1140-1120 cm^{-1} with the absence of vinyl absorption at 915-930 cm^{-1} and 990-980 cm^{-1}.

The IR spectra of the polymers D5 B1, D4 B2 and D3 B3 are given in Fig. 26-28.

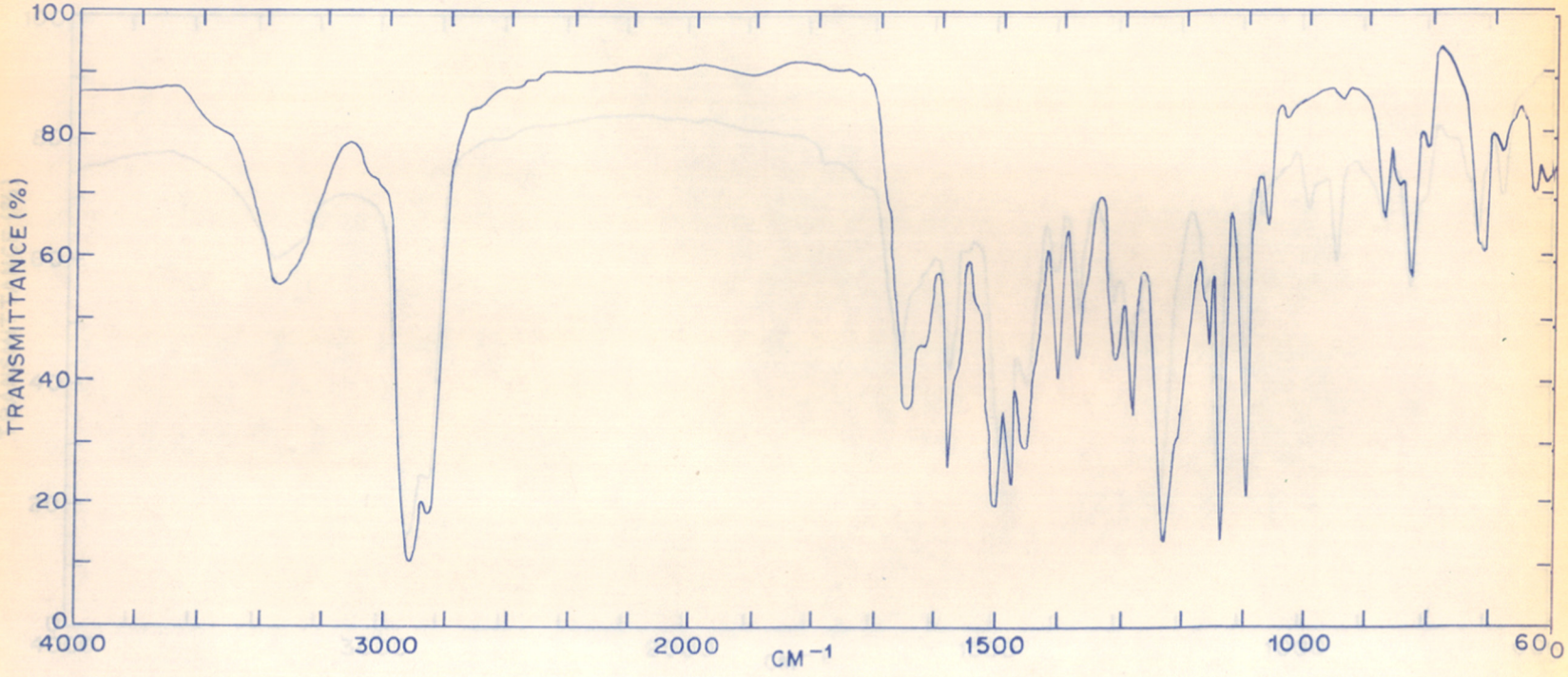
Viscosity

The inherent viscosities(η_{inh}) of these poly(amide-amines) were determined in m-cresol at 30°C with a modified Ubbelohde viscometer. The inherent viscosity value is defined as follows.

$$\eta_{inh} = \frac{2.303 \log t/to}{C}$$

where, to and t represents the viscometer flow period for m-cresol and the polymer solution respectively. The solution concentration C is 0.5 g/100 ml.

The inherent viscosities (Table-22) of the polymers obtained from N,N'-methylenebisacrylamide with ODA and MDA are the same as reported by Imai et al[16]. However, there was no any marked difference in viscosities of the polymers obtained from other substituted bisacrylamides (B2 and B3) with ODA and MDA. On comparing the inherent viscosities of the polymers from ODA and MDA, it was found that the viscosities of polymers obtained from MDA have higher values. This may be attributed to the reactivities of the amino groups.



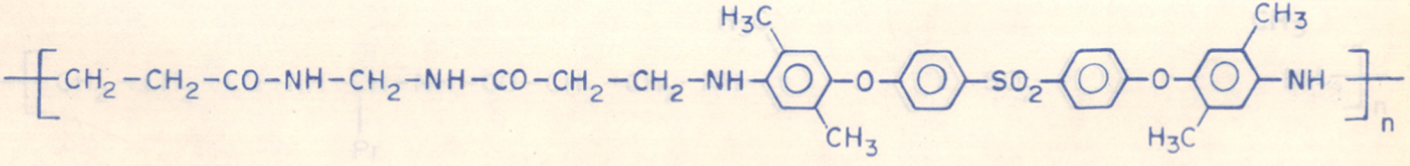
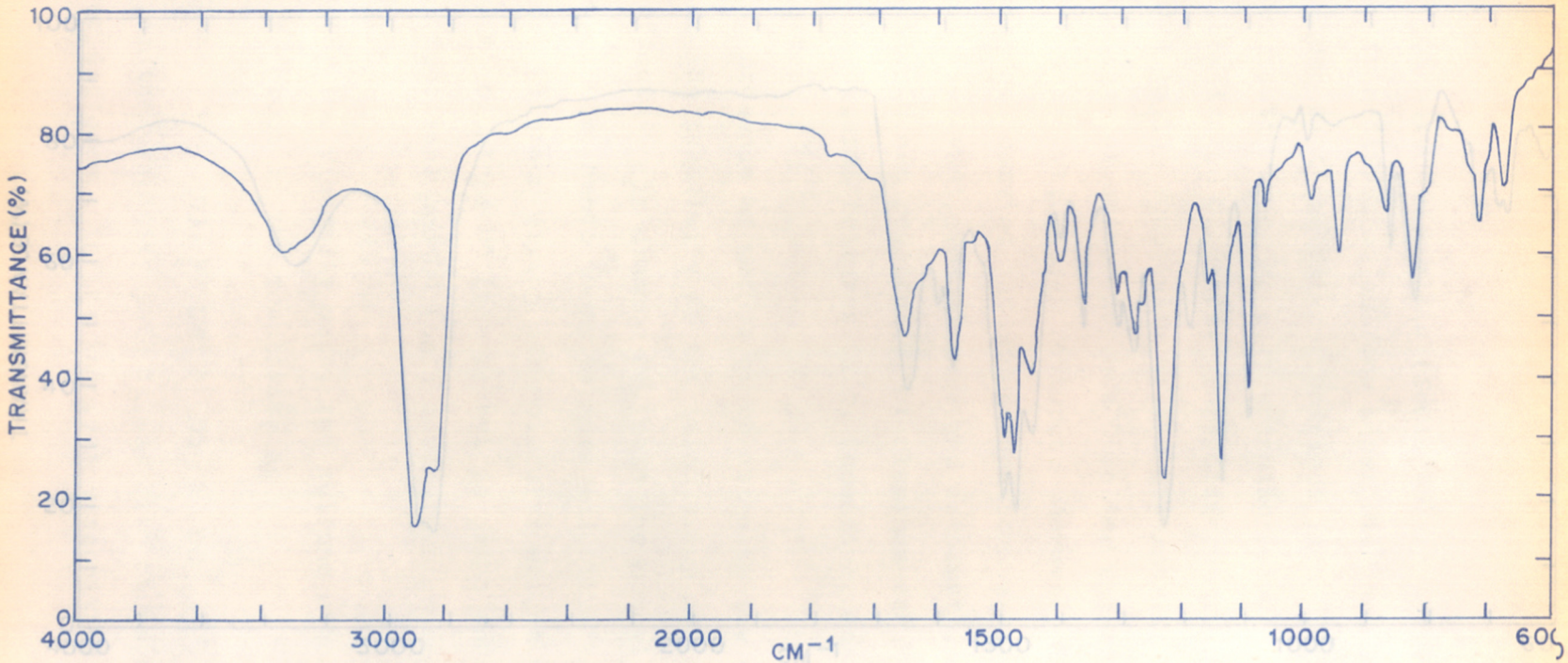


FIG. 26. IR SPECTRUM OF POLY (AMIDE-AMINE), $D_5 B_1$



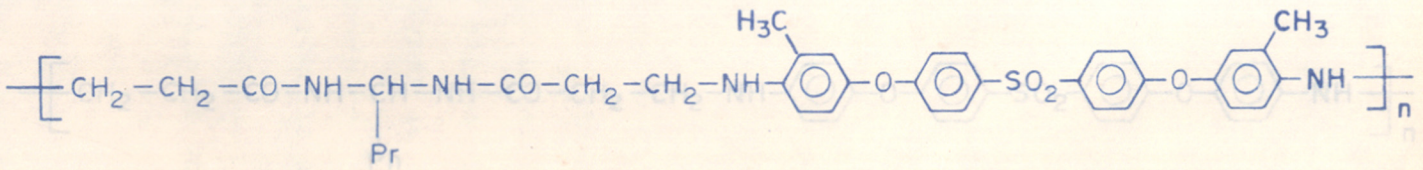
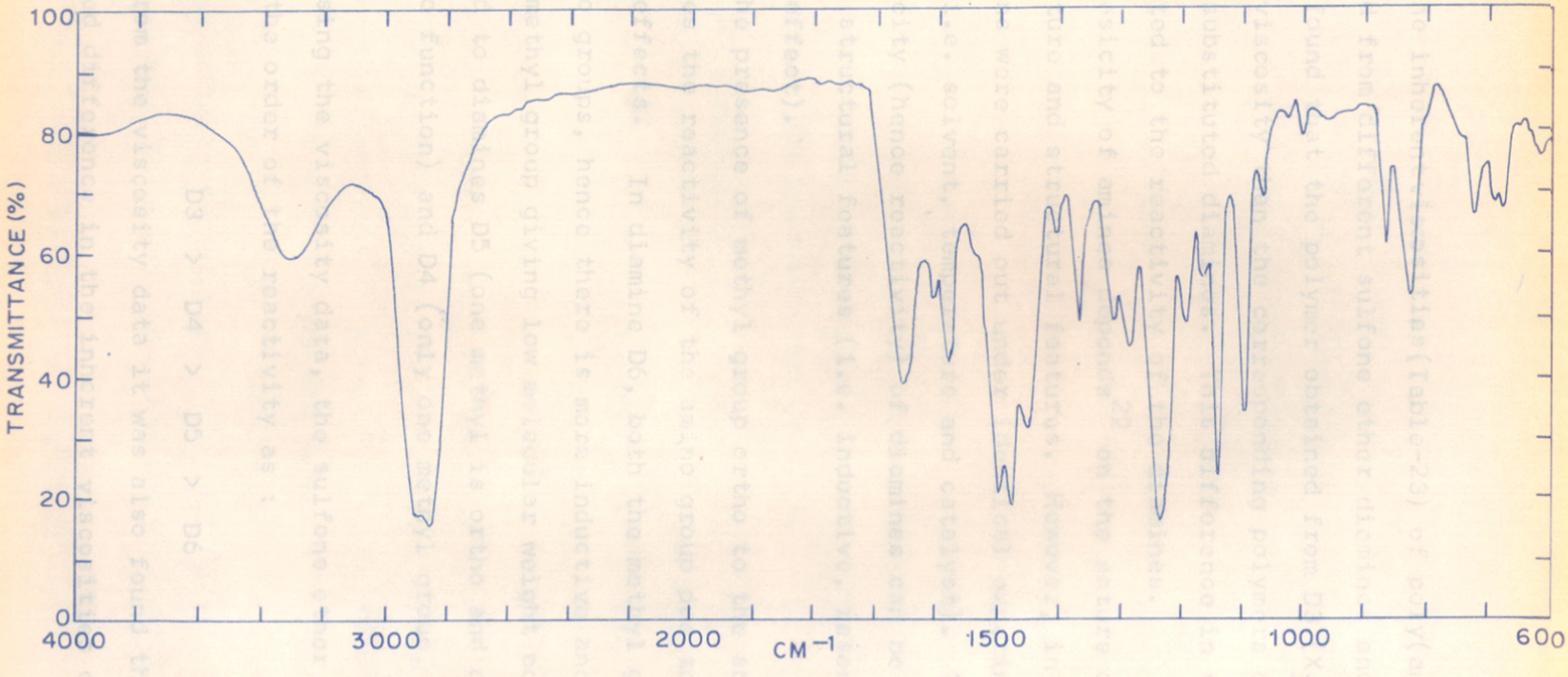


FIG. 27. IR SPECTRUM OF POLY (AMIDE-AMINE), $D_4 B_2$



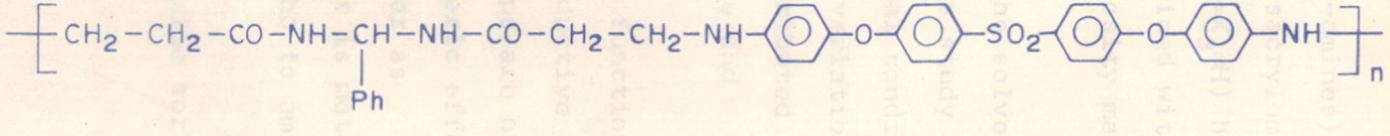


FIG. 28. IR SPECTRUM OF POLY (AMIDE-AMINE), D_3B_3

The inherent viscosities (Table-23) of poly(amide-amines) obtained from different sulfone ether diamines and bisacrylamides, it was found that the polymer obtained from D3 ($X_1=X_2=X_3=H$) has higher viscosity than the corresponding polymers obtained with methyl substituted diamines. This difference in viscosity may be related to the reactivity of the diamines.

Basicity of amines depends[22] on the nature of the solvent, temperature and structural features. However, in this study the reactions were carried out under identical experimental conditions (i.e. solvent, temperature and catalyst). The variation in basicity (hence reactivity) of diamines can be attributed only to structural features (i.e. inductive, resonance and steric effect).

The presence of methyl group ortho to the amino function decreases the reactivity of the amino group due to inductive and steric effects. In diamine D6, both the methyl groups are ortho to amino groups, hence there is more inductive and steric effect of the methyl group giving low molecular weight polymer as compared to diamines D5 (one methyl is ortho and other is meta to amino function) and D4 (only one methyl group ortho to amino group).

Using the viscosity data, the sulfone ether diamine series occupy the order of the reactivity as :

D3 > D4 > D5 > D6

From the viscosity data it was also found that there was no marked difference in the inherent viscosities of the polymers

obtained from the bisacrylamides (B1, B2 and B3) with each diamines. This indicates that the substituents ($-CH_2CH_2CH_3$ or $-C_6H_5$ instead of $-H$) in methylenebisacrylamide are far away from the reactive site and have no effect on the reactivity on vinyl double bonds.

Polymer Solubility

Solubility was determined at 3% concentration in various solvents. All the polymers readily dissolved in aprotic polar solvents such as N,N -dimethylformamide (DMF), dimethylsulfoxide (DMSO), N,N -dimethylacetamide (DMAC), N-methyl-2-pyrrolidone (NMP) as well as in m-cresol and dichloroacetic acid. However, they were insoluble in non-polar solvents such as benzene, pet. ether, carbon tetra chloride, toluene, etc.

Thermal Stability

In the present study, to evaluate the effect of sulfone ether diamine/bisacrylamide structure on the thermal stability of poly(amide-amines) the thermo-oxidative degradation of polymer was studied by TG method.

Thermogravimetric analysis (TG), differential thermal analysis (DTA) and derivative thermogravimetry (DTG) were performed simultaneously by heating polymers at a constant rate of $5^{\circ}C$/min in air with Netzsch STA 409. Temperature was measured by a platinum - platinum Rhodium (10%) thermocouple.

Temperatures for different weight loss of polymer were determined from TG curves and are presented in Table-24. The

Table-24 : Temperatures for different weight loss of poly(amide-amines)

No.	Weight loss %	Temperature °C					
		D6 B1	D5 B1	D4 B1	D3 B1	D3 B2	D3 B3
1.	5.0	275	290	295	285	250	250
2.	10.0	330	325	325	315	270	280
3.	15.0	405	370	390	365	295	310
4.	20.0	420	390	410	410	320	350
5.	25.0	430	400	420	415	375	395
6.	30.0	440	405	425	420	395	415
7.	35.0	445	415	440	430	415	425
8.	40.0	470	455	460	440	430	430
9.	45.0	565	530	535	505	480	470
10.	50.0	630	580	590	560	545	545
11.	55.0	685	640	635	610	605	605
12.	60.0	-	695	675	655	695	655
13.	65.0	-	-	-	705	-	-

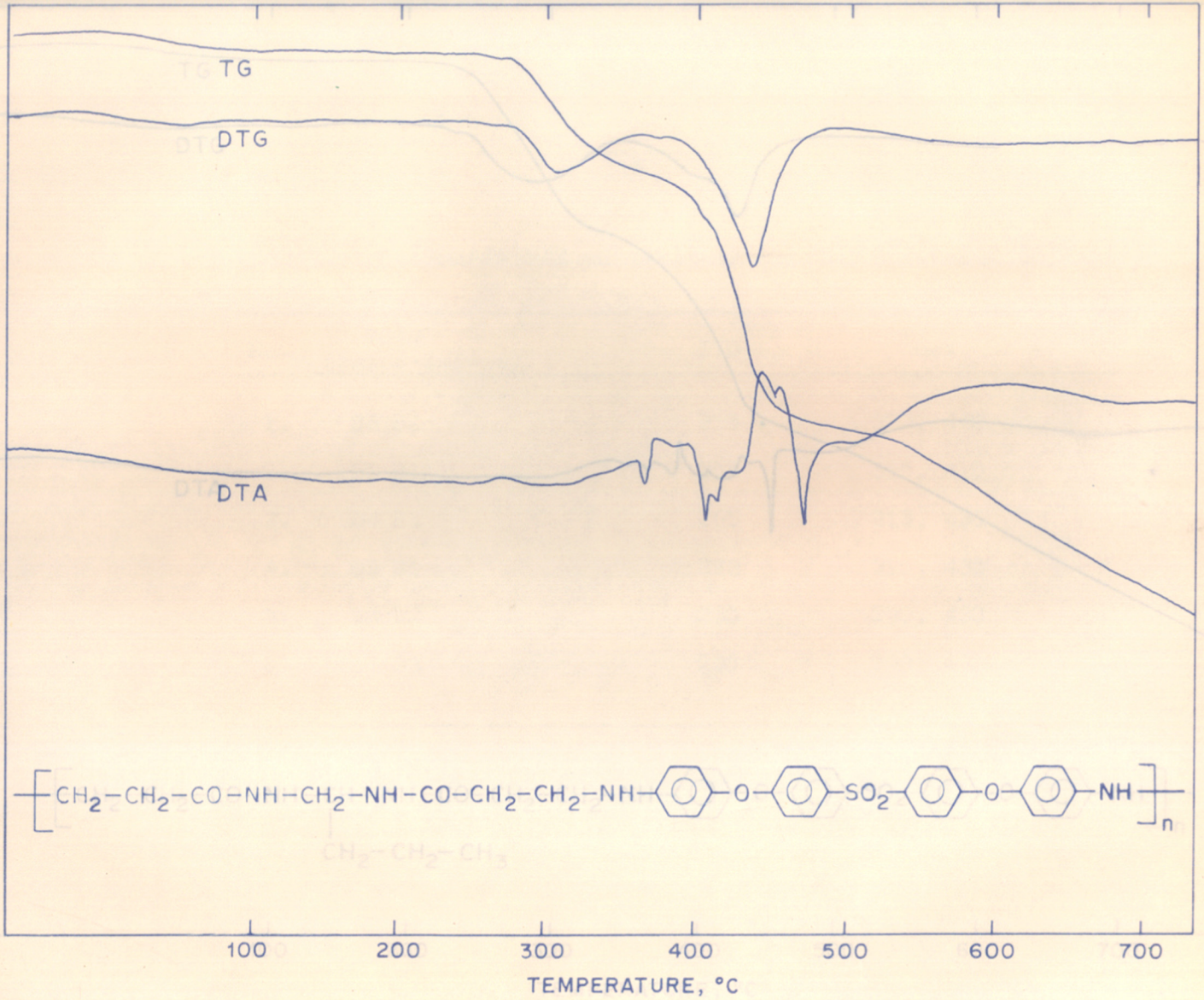
initial decomposition temperature (taking the sharp drop in the curves as marking the onset of decomposition reaction) and temperature for maximum decomposition (T_{max}) are given in Table-25. As an illustration, the TG curves for 4,4'-bis(4-aminophenoxy) diphenyl sulfone with N,N'-methylene bisacrylamide and N,N'-butylidene bisacrylamide are given in Fig.29 and 30 respectively.

The results show that the initial decomposition temperature (IDT) of these polymers vary between 230 to 275°C. Further increase in the temperature causes rapid decomposition of the polymer. The small weight loss (3±1%) can be attributed to removal of absorbed moisture from the polymers (since amide linkages are polar in nature).

A] Poly(amide-amines) from N,N'-methylene bisacrylamide and sulfone ether diamines

With dynamic heating, the initial temperature of decomposition (IDT) is one of the main criteria of the heat stability of polymer. Upto this temperature the polymer retains its fundamental chemical structure.

A comparison of IDT of poly(amide-amines) examined shows that the poly(amide-amine) D3 B1 have the highest thermal stability. Alkyl group substitution in diamine component has a marked effect on the thermal stability of polymers. Thus tabulated results (Table-25) show that IDT is highest for polymer D3 B1 and introduction of methyl group (Polymer D4 B1) reduces IDT by 10°C. The initial temperature of decomposition and therefore thermal stability decreases with further addition of



$$\left[CH_2-CH_2-CO-NH-CH_2-NH-CO-CH_2-CH_2-NH-\bigcirc-O-\bigcirc-SO_2-\bigcirc-O-\bigcirc-NH\right]_n$$

FIGURE 29. THERMOGRAM OF POLY (AMIDE–AMINE), D_3B_1

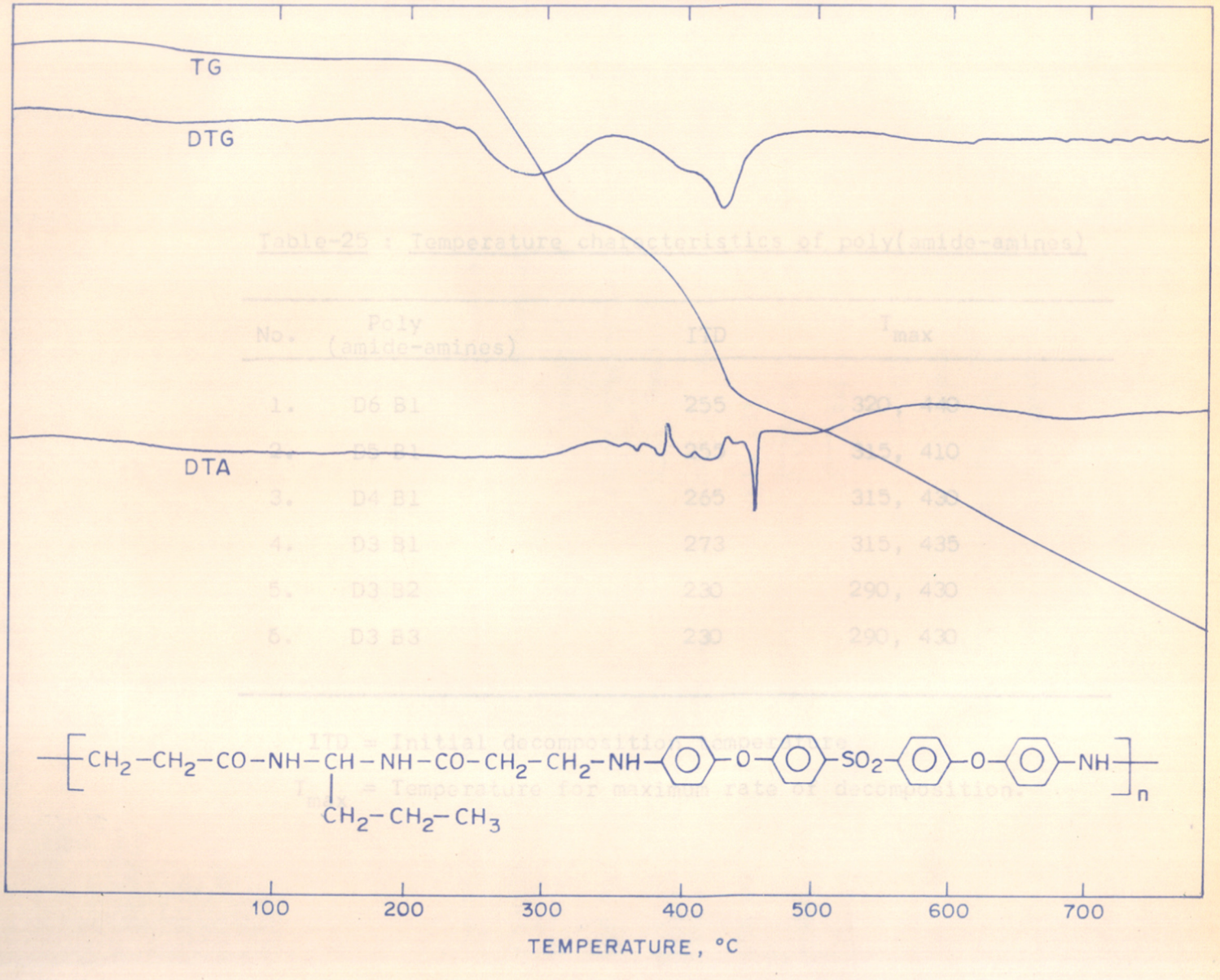


FIGURE 30. THERMOGRAM OF POLY (AMIDE-AMINE), D_3B_2

Table-25 : Temperature characteristics of poly(amide-amines)

No.	Poly (amide-amines)	ITD	T_{max}
1.	D6 B1	255	320, 440
2.	D5 B1	255	315, 410
3.	D4 B1	265	315, 430
4.	D3 B1	273	315, 435
5.	D3 B2	230	290, 430
6.	D3 B3	230	290, 430

ITD = Initial decomposition temperature

T_{max} = Temperature for maximum rate of decomposition.

alkyl groups. Thus IDT is lowest for polymer D5 B1 and D6 B1.

The DTG curves of all polymers showed T_{max} twice. This indicates that decomposition of poly(amide amines) occurs in two steps. The T_{max} at higher temperature was assigned to decomposition of aromatic structure, whereas T_{max} at lower temperature may be due to decomposition of amide linkage.

B] Poly(amide-amines) from 4,4'-bis(4-aminophenoxy) diphenyl sulfone and different bisacrylamides

A comparison of IDT (Table-25) shows that polymer D3 B1 has higher IDT than polymer D3 B2 and D3 B3. This indicates that the substituents ($-CH_2CH_2CH_3$ or $-C_6H_5$ instead of H) in methylene bisacrylamide lower the thermal stability. The DTG curves of these polymers also showed T_{max} twice (Table-25). The T_{max} at lower temperature was assigned to the decomposition of amide linkage and T_{max} at higher temperature for the decomposition of aromatic structure.

EXPERIMENTAL

Materials

[1] Acrylamide (Cyanamide, USA) was recrystallized twice from methanol and dried in vacuum.

[2] Paraformaldehyde (BDH, England) was used as received.

[3] n-Butyraldehyde (BDH) was distilled and then used.

[4] Benzaldehyde was obtained from local market and purified by distillation.

[5] 4,4'-Dichlorodiphenyl sulfone (EGA, Chemie, West Germany) was used as received.

[6] 4,4'-Methylenedianiline (Bayer, A.G., West Germany) was recrystallized from benzene.

[7] 4,4'-Oxydianiline (EGA,Chemie, West Germany) was recrystallized from tetrahydrofuran.

[8] p-Aminophenol was recrystallized from water.

[9] Hydroquinone was obtained from Sarabhai M.Chemicals Ltd. (India) and used as received.

[10] Glacial acetic acid (AR Grade) was distilled and then used.

[11] Ethylene dichloride and m-cresol of commercial grade were purified by distillation.

[12] The methyl substituted p-amino phenols were prepared by the reduction of the azo compound formed by a diazo coupling reaction of phenol with sulfanilic acid as reported by Nilsson et al[18].

Sulfone Ether Diamines

4,4'-bis(4-aminophenoxy) diphenyl sulfone (D3)

Into a 500 ml, three neck round bottom flask equipped with a mechanical stirrer, a reflux condenser, Dean-Stark trap, a thermometer and a nitrogen gas inlet were placed 21.8 g (0.2 mole) p-aminophenol, 100 ml dimethyl sulfoxide and 150 ml toluene. The solution was saturated with nitrogen, heated to 50°C and 8.0 g (0.2 mole) of 50% aqueous solution of sodium hydroxide was added. The temperature was increased to 110-120°C and water was removed via toluene/water azeotrope. After complete removal of water (which requires about 6 hr.), the remaining toluene was removed until the reaction temperature reached to 160°C.

The heating was discontinued and the reaction was cooled to 100°C, 28.7 (0.1 mole) of 4,4'-dichlorodiphenylsulfone in 100 ml toluene was slowly added to reaction mixture to control the resulting exotherm. After complete addition of chlorosulfone, the temperature was raised to 165°C and maintained for 2 hr. The toluene was removed by distillation. The reaction mixture was allowed to cool to room temperature and poured into 100 ml 2% sodium hydroxide. The solid obtained was filtered, washed several times with water and then further with 1% sodium sulfite solution and isopropanol. The crude diamine was recrystallized from butanol, dried under vacuum and stored in coloured bottle under nitrogen atmosphere.

Preparation of :

i) 4,4'-Bis(4-amino-3-methyl phenoxy) diphenyl sulfone (D4)

ii) 4,4'-Bis(4-amino-2,5-dimethylphenoxy) diphenyl sulfone (D5)

iii) 4,4'-Bis(4-amino-3,5-dimethylphenoxy) diphenyl sulfone (D6)

Similar experiments with 3-methyl 4-aminophenol, 2,5-dimethyl 4-aminophenol, 3 5-dimethyl 4-aminophenol and 4,4'-dichlorodiphenylsulfone lead to the synthesis of D4, D5 and D6 respectively.

Bisacrylamides

i) N,N'-Methylenebisacrylamide (B1)

Into a 100 ml round bottom flask equipped with a reflux condensor were placed 14.2 g acrylamide (0.2 mole), 3.0 g paraformaldehyde (0.1 mole), 0.2 g hydroquinone, 50 ml ethylene dichloride and 5-6 drops of concentrated hydrochloric acid. The reaction mixture was refluxed for 30 min. and cooled to room temperature. The product obtained was filtered at suction, washed with water. The crude bisacrylamide was recrystallized from aqueous acetone and dried under vacuum.

ii) N,N'-Butylidenebisacrylamide (B2)

iii) N,N'-Benzylidenebisacrylamide (B3)

The reaction conditions described for the preparation of N,N'-methylenebisacrylamide were followed to obtain B2 and B3 from acrylamide with n-butyraldehyde and benzaldehyde respectively.

Poly(amide-amine) from N,N'-methylenebisacrylamide and 4,4'-bis(4-aminophenoxy) diphenyl sulfone

Into a 50 ml, three neck round bottom flask, equipped with a thermometer, nitrogen gas inlet, a reflux condenser and a magnetic stirrer were placed 0.77 g (0.05 mole) N,N'-methylenebisacrylamide, 2.16 g (0.05 mole) 4,4'-bis(4-aminophenoxy) diphenyl sulfone, 0.4 ml glacial acetic acid and 10 ml m-cresol. The reaction mixture was stirred at 100°C for 24 hours. Nitrogen atmosphere was prevailed throughout the course of the reaction. The polymer was precipitated by pouring it into dilute aqueous sodium hydroxide, it was then filtered and washed with water.

The polymer was purified by reprecipitation from dimethyl formamide and dried at 50°C under reduced pressure.

Similar experimental conditions were followed to obtain other poly(amide-amines).

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SUMMARY

SUMMARY

of the thesis entitled 'Studies in Polymerization of Acrylamide; Modified Acrylamides and Polymers therefrom' submitted to the University of Poona for the degree of Doctor of Philosophy in Chemistry by S.M.Jagadale, Division of Polymer Chemistry, National Chemical Laboratory, Poona 411 008.

The present thesis describes :

I] Redox System - Acrylamide Polymers

II] Modified New Acrylamide Monomers and Polymers

III] New Poly(amide-amine) Polymers

Part-I : Redox System - Acrylamide Polymers

The reducing action of ascorbic acid has been described by earlier workers[1,2], in the titrimetric determination of several inorganic and organic substances. The kinetics of the redox system, ascorbic acid-peroxydisulfate was studied by Mushran and Mehrotra[3]. This redox system has been used for aqueous polymerization of methacrylamide[4] and methyl methacrylate[5]. The present study explains the work on aqueous polymerization of acrylamide with an ascorbic acid-peroxidisulfate system as redox initiator at 35±0.2°C in the presence of atmospheric oxygen. The concentrations studied were :

[Acrylamide] = $(2.0 - 15.0) \times 10^{-2}$ mole/litre

[Peroxydisulfate] = $(1.5 - 10.0) \times 10^{-3}$ mole/litre

[Ascorbic acid] = $(2.84 - 28.4) \times 10^{-4}$ mole/litre

temperatures were between 25-50°C.

Within these ranges the initial rate showed a half-order dependence on peroxydisulfate, a first-order dependence on a monomer concentration, and a first-order dependence on a low concentration of ascorbic acid [$(2.84 - 8.54) \times 10^{-4}$ mole/litre].

At higher concentrations of ascorbic acid the rate remained constant in the concentration range [(8.54 - 22.72) x 10^{-4} mole/litre], then varied as an inverse half-power at still higher concentrations of ascorbic acid [(22.72 - 28.4) x 10^{-4} mole/litre]. The initial rate increased with an increase in polymerization temperature. The overall energy of activation was 12.203 Kcal/mole in a temperature range of 25-50°C. Water-miscible organic solvents depressed the initial rate and the limiting conversion. The viscometric average molecular weight increased with an increase in temperature and initial monomer concentration but decreased with increasing concentration of peroxydisulfate and an additive, dimethyl formamide.

Part-II : Modified New Acrylamide Monomers and Polymers

Isocyanates, the esters of isocyanic acid, are very versatile compounds. The presence of high unsaturation in -N=C=O is responsible for the high reactivity of isocyanates. Isocyanates react with compounds containing 'active hydrogen'. The reaction can be described as the attack of a nucleophile on the electrophilic carbon atom in the isocyanate (-N=C=O) group. The hydrogen atom gets attached to the nitrogen of the isocyanate group, while remainder of reactant to the carbonyl carbon atom :

$$R\text{-}N{=}C{=}O \xrightarrow{H\text{-}X} R\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}X$$

It has been reported in the literature[6] that phenyl isocyanate reacts with the amide group of acrylamide to yield acryloylurea, which can be readily polymerized.

The present investigation was undertaken with a view to synthesize new isocyanato acryloylurea monomers and to polymerize them into new polymers.

Acrylamide was reacted with the following diisocyanates

in the presence of organic polymer retarder :

1) 2,4-Toluene diisocyanate (TDI)
2) 4,4'-Methylene bis(phenyl isocyanate)(MDI) and
3) 1,6-Hexamethylene diisocyanate (HDI)

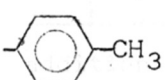
The scheme for the synthesis of isocyanato acryloylurea monomers is as shown below :

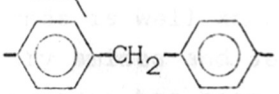
$$CH_2=CH-CONH_2 + OCN-R-NCO$$

Acrylamide ↓ Diisocyanate

$$CH_2=CH-CO-NH-CO-NH-R-NCO$$

Acryloylurea

where R =  [I]

=  [II]

= $-(CH_2)_6-$ [III]

These monomers were characterized by elemental and spectral analysis such as IR and NMR. They are in good agreement with the structures assigned.

The free -NCO group of the monomers I, II and III was further reacted with water, ethyl alcohol, glycol and glycerin to obtain the modified acryloylurea monomers. These monomers were characterized by elemental analysis and IR spectra.

The polymerization of all these monomers was carried out in N-methyl-2-pyrrolidone (NMP) in nitrogen atmosphere using 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The polymers were characterized by IR spectra and viscosities.

IR spectra of these polymers indicate that the polymerization occure through vinyl group. It was observed that the IR

spectra of the polymers obtained from monomers I, II and III (having free isocyanate group) showed no absorption at 2270 cm^{-1} corresponding to the isocyanate group. This may be due to the reaction of the free isocyanate group with the solvent (NMP)[7].

The viscosities of the polymers obtained from isocyanato acryloylurea monomers are in the following order :

II > I > III

Further modifications of the isocyanato acryloylurea monomers (I, II and III) with water, ethanol, glycol and glycerin gave the polymers with decreasing order of the viscosity in each series.

Part-III : New Poly(amide-amine) Polymers

The facile addition of nucleophiles to the double bonds of acrylamide compounds is well known and the Michael-type polyaddition of primary amines and secondary diamines to various types of bisacrylamides has been extensively studied[8,9]. It has been reported that weak acids like acetic acid have a marked catalytic effect on the polyaddition of aromatic diamines to bismaleimide compounds giving linear high molecular weight polymers[10].

The present investigation was undertaken with a view to prepare a series of poly(amide-amines) having a sulfone and ether linkages and to study the structure-property relationship of the poly(amide-amines).

The reaction of N,N'-methylenebisacrylamide with 4,4'-oxydianiline (ODA) and 4,4'-methylenedianiline (MDA) as reported by Imai et al[11] was also carried out. The reactions of ODA and MDA with N,N'-butylidene and benzylidenebisacrylamides were also carried out.

The poly(amide-amines) have been synthesized by the reaction of bisacrylamides and diamines in m-cresol using acetic

acid as a catalyst at 100°C in nitrogen atmosphere.

The scheme for the synthesis of poly(amide-amines) is given in Fig.1.

The sulfone ether diamines were synthesized using the method described by Kawakami et al[12] by condensation of sodium salt of unsubstituted and substituted p-aminophenols with 4,4'-dichlorodiphenyl sulfone in dimethyl sulfoxide at 160°C. The structures of these diamines were confirmed by elemental and spectral analysis such as IR and NMR.

Three different bisacrylamides were prepared by the reaction of acrylamide with appropriate aldehyde in ethylene dichloride using the method described by Feuer and Lynch[13] as shown below :

$$\underset{\text{Acrylamide}}{2CH_2=CH-CONH_2} + \underset{\text{Aldehyde}}{R-CHO}$$

$$\downarrow$$

$$CH_2=CH-CO-NH-\underset{\displaystyle R}{\underset{|}{CH}}-NH-CO-CH=CH_2$$

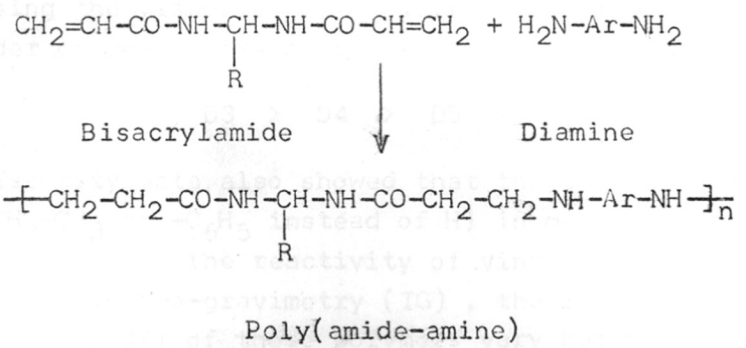
Bisacrylamide

where R = -H, N,N'-methylenebisacrylamide (B1)
= $-CH_2-CH_2-CH_3$, N,N'-butylidenebisacrylamide (B2) and
= $-C_6H_5$, N,N'-benzylidenebisacrylamide (B3)

The structures of the bisacrylamides were confirmed by elemental and spectral analysis such as IR and NMR.

The polymers obtained were characterized by IR spectra, viscosities, elemental and thermal analysis.

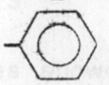
The elemental analysis and IR spectra are in good agreement with the structures of polymers. The inherent viscosities of poly(amide-amines) obtained from different sulfone ether diamines and bisacrylamides showed that the polymer obtained from D3 ($X_1=X_2=X_3=H$) has higher viscosity than the corresponding polymers

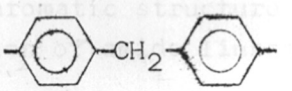


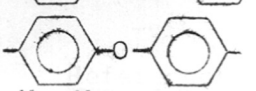
Poly(amide-amine)

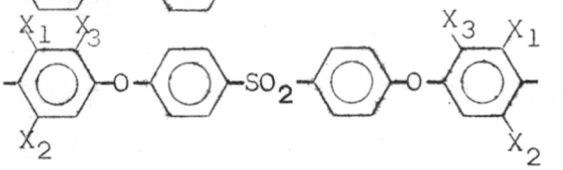
where R = -H [B1]

= $-CH_2-CH_2-CH_3$ and [B2]

=  [B3]

Ar =  [D1]

=  [D2]

= 

$X_1 = X_2 = X_3 = H$ [D3]

$X_1 = CH_3$, $X_2 = X_3 = H$ [D4]

$X_1 = H$, $X_2 = X_3 = CH_3$ [D5]

$X_1 = X_2 = CH_3$, $X_3 = H$ [D6]

Fig.1 - Scheme for synthesis of poly(amide-amines)

obtained with methyl substituted diamines.

Using the viscosity data, sulfone ether diamines occupy the order of reactivity as :

D3 > D4 > D5 > D6

Viscosity data also showed that the substituents ($-CH_2-CH_2-CH_3$ or $-C_6H_5$ instead of H) in methylenebisacrylamide have no effect on the reactivity of vinyl group.

In the thermo-gravimetry (TG) , the initial decomposition temperature (IDT) of these polymers vary between 230-275°C. A comparison of IDT showed that the alkyl group substitution in diamine component and the substitution in methylenebisacrylamide ($-CH_2-CH_2-CH_3$ or $-C_6H_5$ instead of H) decreases the thermal stability.

The DTG curves showed Tmax twice, corresponding to the decomposition of aromatic structure (at higher temperature) and to the decomposition of amide linkage (at lower temperature).

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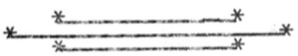

PUBLICATIONS

PUBLICATIONS

'Studies of Redox Polymerization. Aqueous Polymerization of Acrylamide by an Ascorbic Acid-Peroxydisulfate System'

H.Narain, S.M.Jagadale and N.D.Ghatge

J.Polym.Sci. Polym.Chem.Ed. 19, 1225-1238 (1981)